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Surface-nucleated heterogeneous growth of zeolitic imidazolate framework-A
unique precursor towards catalytic ceramic membranes: synthesis,
characterization and organics degradation

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Abstract

A novel Co_3O_4 nanocatalyst functionalized Al_2O_3 ceramic membrane (CoFCM) with a honeycomb structure was prepared via an optimized surface-nucleated zeolitic imidazolate framework (ZIF-67) growth method. The Co_3O_4 hollow structure which was confirmed via chemical characterizations (XRD, FTIR, Raman and XPS), was formed on the membrane surface by direct one-step calcination of ZIF-67 membrane. The CoFCM was characterized by various techniques including the field emission scanning electron microscopy and atomic force microscopy. The results reveal the formation of well-defined Co_3O_4 layer on the porous Al_2O_3 ceramic membrane with 1.5 - 2 μm thickness. The growth mechanism of CoFCM was further proposed via XPS and the catalytic activity of CoFCM was investigated for the removal of sulfamethoxazole (SMX). The membrane performance was examined under a home-made dead-end mode. Results indicate that CoFCM has a rougher surface with an initial membrane resistance of $1.19 \times 10^{11} \text{ m}^{-1}$ and performs outstanding catalytic activities. The pure water permeability of CoFCM is $3024 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is comparable to that of the pristine ceramic membrane (< 10% difference). The SMX removal efficiency achieved to > 90% in 90 min with an Oxone addition of 0.1 g L^{-1} . Meanwhile, the membrane showed excellent durability by retaining > 95% of initial flux for at least 3 operational cycles with a low cobalt ion leaching via Oxone-assisted cleaning. Furthermore, the reaction mechanism of Oxone activation by CoFCM was proposed from the results of the electron paramagnetic resonance (EPR) and radical scavenger experiments.

Keywords: MOF-template; Heterogeneous growth; ZIF-67; Hybrid membrane; Peroxymonosulfate; sulfamethoxazole

1. Introduction

In recent years, ceramic membrane is gaining increasing acceptance for treatment of municipal and industrial wastewater streams because of its high stability and permeability in extreme environments [1,2]. In view of these properties, the ceramic membrane offers a potential novel application as a hybrid filtration and catalytic system. In this hybrid system, much faster conversion of reactants can be achieved due to the unlimited mass transfer process [3]. Over the recent decades, the coupling of ceramic membranes with oxidation has proven to be an effective technology to enhance pollutants treatment performance by generating reactive oxygen species and preventing membrane fouling [4–6]. Up to now, the oxidation-filtration coupling technologies are mainly limited to photocatalysis or ozonation to generate hydroxyl radicals for pollutant degradation [4,7–9].

Compared with hydroxyl radical-based advanced oxidation technologies, sulfate radical ($\text{SO}_4^{\cdot-}$)-based advanced oxidation processes (SR-AOPs) have gained increasing attention due to its properties of higher oxidation potential, wider pH range (2-8) and longer half-life time (30-40 μs) [10]. The $\text{SO}_4^{\cdot-}$ is generally produced from peroxymonosulfate (PMS, Oxone) and persulfate (PS) via transition metals or metal oxides [11–13]. Among them, cobalt-based nanoparticles exhibit excellent catalytic activity. To date, lots of work have been done to prepare high performance Co-based nanomaterials for PMS activation [14–17]. However, nanoparticles tend to aggregate, leading to loss of catalytic activity [18]. Furthermore, surfaces of the nanocatalysts could be covered by deposited solute species including pollutants and their degradation products, leading to deactivation of active sites on their surface [19]. To address these limitations, one possible way is to load nanocatalysts onto membrane surface to increase the surface area as well as decrease the aggregation.

To prepare a catalyst functionalized membrane, dip-coating and hydrothermal methods have been investigated [20,21]. However, these methods need multiple steps and the morphologies are very difficult to control. Herein, we present a facile and scalable method to synthesize a magnetic hollow cobalt oxide functionalized ceramic membrane (CoFCM) for sulfamethoxazole (SMX) degradation. SMX is one kind of widely used antibiotics and has been detected in various systems [22–25]. Meanwhile, it is hard to be removed by the traditional methods because of its resistance to natural biodegradation [26,27]. To address this problem, one potential strategy is the advanced oxidation processes owing to their non-selectivity to a wide variety of organic pollutants via generation of strong reactive species.

In this work, a Co-based zeolitic imidazolate framework, ZIF-67, was formed on the ceramic membrane surface via surface-nucleated growth. The hollow CoFCM structure could be achieved easily through direct calcination of ZIF-67 by taking advantages of its thermal behavior and chemical reactivity [16,28]. To our knowledge, this is the first report on synthesis of CoFCM via ZIF-67 template method and use it for PMS activation. The performance of the resulting CoFCM was examined in a home-made dead-end membrane filtration system. Also, the plausible PMS activation mechanism in CoFCM/Oxone system was evaluated via the radical trapping and electron paramagnetic resonance (EPR) experiments.

2. Experimental Section

2.1 Materials

All chemicals were of reagent grade or higher and were used without further purification. Sulfamethoxazole (SMX), Sodium hydroxide (NaOH), methanol (CH₄O), *tert*-butanol (C₄H₁₀O), powder Al₂O₃ (100 mesh, 99%), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) and 2-methylimidazole (2-MIM) were purchased from Sigma-Aldrich, Singapore. Oxone (PMS, 2KHSO₅·KHSO₄·K₂SO₄) was supplied by Alfa Aesar, Singapore. 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was provided by Aladdin, China. Porous Al₂O₃ ceramic membrane (CM) with a pore size of 500 nm and porosity of around 55% was provided by Nanjing Shuyihui Scientific Instruments CO., LTD (Nanjing, China). The diameter of the ceramic membrane is 22 mm and the thickness is 2 mm.

2.2 Preparation of Co₃O₄ functionalized ceramic membrane (CoFCM)

Before the CoFCM preparation, the synthesis of zeolitic imidazolate framework (ZIF-67) was optimized via changing the precursor concentrations (33 mM to 330 mM based on Co concentration). To prepare CoFCM, the ceramic membranes were firstly washed with 1 M NaOH to remove the impurities followed by washing with DI water to neutral pH and drying at 100 °C for 24 h for later use. Surface-nucleated heterogeneous growth method was used for the synthesis of porous hybrid CoFCM and the schematic illustration is shown in Fig 1. First, the ceramic disc was immersed in the 2-MIM (2-methylimidazole) solution (Solution A, 0.66 g of 2-MIM in 15 mL methanol) for 30 min, after washing several times with methanol to remove the redundant solution, the disc was placed into the metal precursor solution (Solution B, 0.291 g of Co(NO₃)₂·6H₂O in 15 mL methanol) for another 30 min. After

washing with methanol, the disc was positioned into the mixture of two solutions (Solution A and Solution B) which was settled at room temperature in the quiescent solution. After aging for 24 h, the purple disc was washed with methanol to remove the reductant solution followed by washing with DI water and dried overnight at 105°C. The remaining purple ZIF-67 powders were collected from the mother solution and washed with methanol and DI water several times with the assistance of centrifuge for later test. To confirm the formation of covalent bonds between ceramic disc and ZIF-67, a control experiment in which the disc was replaced by Al₂O₃ powder was conducted in the same condition. In the surface-nucleated heterogeneous growth process, Al could be linked with 2-MIM via Al-N bond followed by the formation of ZIF-67 on the membrane surface, which would minimize the infiltration of ZIF-67 particles into the internal pores. The infiltration of ZIF-67 particles into the internal pores will result in undesirable pore plugging and decreased water permeability.

The CoFCM was then prepared through a one-step calcination of ZIF-67 functionalized membrane in a furnace with the temperature raising from room temperature to the desired temperature at a ramping rate of 5°C min⁻¹, and then stabilized for 3 h. The resulted CoFCM was denoted as M-temp while the pristine membrane without Co₃O₄ was referred as M0. In addition, Co₃O₄ powder was also prepared under the same condition using ZIF-67 as the precursor and was denoted as ZIF-67@temp in the following sections. After the calcination process, all membranes were washed with DI water followed by drying in an oven at 60°C overnight for later use.

Fig 1. Schematic illustration of the fabrication of CoFCM via a surface-nucleated ZIF-67 growth method (Solution A, 0.66 g of 2-MIM in 15 mL methanol; Solution B, 0.291 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 15 mL methanol)

2.3 Characterization techniques

The thermo-transformation of ZIF-67 was investigated by thermogravimetric analysis (TGA) (SDT-Q600, TA instrument, USA) in the temperature range of 100-900°C under air atmosphere (heating rate of $10^\circ\text{C min}^{-1}$ and air flow of 100 mL min^{-1}). Nitrogen adsorption-desorption analyses were conducted on a Quantachrome Autosorb -1 Analyzer at liquid N_2 temperature of 77 K. The resulting specific surface areas as well as porosities were calculated from N_2 adsorption data by the multipoint Brunauer-Emmett-Teller (BET) and DFT methods.

The surface morphologies as well as elements distribution were acquired by a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL). Meanwhile, atomic force microscopy (AFM, Cypher S, Asylum Research) was employed to characterize the membrane surface roughness.

X-rays diffractometer (XRD, Bruker D8 Advance) was used to analyze the crystal structures of the material. The 2θ range was scanned from $5-75^\circ$ at a step size of 0.02 and the crystallite sizes of as-synthesized particles were calculated using Scherrer's equation:

$$D = R \lambda / \beta \cos \theta \quad (1)$$

where D is the estimated diameter of the particles (nm), R is 0.89 (Scherrer's constant), λ means the incident wavelength, which is 0.154 nm in this study, β (rad) is the peak width at half height and θ ($^\circ$) is the diffraction angle.

The vibrational absorbance of as-synthesized particles was investigated by Fourier transformed infra-red spectrometer (FTIR, Perkin Elmer) and Raman spectrometer (HORIBA Scientific). Meanwhile, X-ray photoelectron spectroscopy (XPS) analysis (Kratos Axis Supra, Shimadzu) was conducted on to detect the elements' chemical states in ZIF-67 and Co_3O_4 .

Electron paramagnetic resonance (EPR) experiments were employed on a Biospin ELEXSYS II E500 EPR spectrometer (Bruker) using DMPO as spin trapping agent to probe the free reactive oxygen species (ROS) and the information was analyzed by Xeon software (Bruker). Furthermore, chemical quenching experiments were conducted by adding methanol and *tert*-butanol as the scavengers due to their different reaction rates to hydroxyl radical and sulfate radical.

2.4 SMX degradation experiments with CoFCM

SMX degradation with CoFCM was evaluated in a dead-end filtration mode, which was operated under a constant flux (Fig S1). The initial pH of feed solution (50 mL) is 5 with a SMX concentration of 10 mg L^{-1} . A high-pressure metering pump (5979 Optos Pump 2HM, Eldex) was used to feed the solution into the membrane cell module (SS316 stainless steel), in which the membrane was secured tightly. The constant flow mode (flow rate was set at 1 mL min^{-1}) was used and trans-membrane pressure (TMP) was recorded as 0.07 bar in a dead-end system and the permeate was then re-circulated back to the feed tank. A control experiment with the pristine Al_2O_3 membrane (M0) was also performed to quantify the performance of membrane. The membranes (M0 and CoFCMs) were compacted to a steady state for 5 min before filtration experiment.

2.5 Analytical methods

The SMX concentration was quantified using LC-2030C-3D liquid chromatography system (Shimadzu) with a reversed phase column (Inertsil ODS-3, $5 \mu\text{m}$, $4.6 \times 150 \text{ mm}$). The

detection wavelength was set at 264 nm and the mobile phases are 60% methanol and 40% water (0.1% acetic acid). The flow rate was 0.8 mL min⁻¹ and the injection volume was 10 µL. For Oxone quantification, 1 mL of the samples was initially mixed with 0.02 g of KI for the oxidation of I⁻ by HSO₅⁻ (Eqs.2-3)

The concentration of I₃⁻ was then determined by a UV-1800 spectrophotometer (Shimadzu, Japan) at λ_{max} = 352 nm (Fig S2). Inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer) was conducted to measure the mass of cobalt leached from membranes.

3. Results and discussion

3.1 Study of the ZIF-67-template method

In this study, the effect of different precursor concentrations on ZIF-67 synthesis was investigated and the results are shown in Fig 2. The optimum mole ratio of Co²⁺ to 2-MIM, which is 1:8, is important for the successful synthesis of ZIF-67 [29]. The concentrations of precursors would affect both morphology and yield of ZIF-67. With increasing precursor concentration, the well-defined ZIF-67 particle size increased with a higher yield and subsequently became more irregular due to the presence of excessive precursors in solution. In this work, the Co(NO₃)₂·6H₂O concentration of 33 mM was chosen because it shows the most uniform particle distribution (Fig 2b).

Fig 2. SEM images of ZIF-67 prepared with different $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentrations (mole ratio of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 2-MIM was fixed at 1/8)

To examine the calcination temperature effect on the formation of Co_3O_4 , different temperatures (350, 450 and 550°C) were used in the calcination process. The sizes and morphologies of as-synthesized ZIF-67 and Co_3O_4 calcined at different temperatures were observed by FESEM (Fig 3). **The results show that all particles perform good uniformity in this study** (Figs 3a-c). However, when the temperature increased to 550°C, the ZIF-67 crystals aggregated and the structural backbone of the metal-organic framework disappeared (Fig 3d). A magnified FESEM image in Fig 3a depicts the very smooth surface over the whole particle, indicating the single-crystal-like feature of the ZIF-67. It displays a uniform rhombic dodecahedra structure due to the combination of Co ions and 2-methylimidazole through coordination bonds and shows a uniform particle size of approximately 200 nm with sodalite topology. After calcination at 350°C for 3 h, the pristine polyhedral morphology is retained well, but the size of polyhedral crystals shrinks slightly (Fig 3b). When the calcination temperature increased to 450°C, part of the pristine polyhedral morphology is still retained and the size of polyhedral shrinks a bit more (Fig 3c). Meanwhile, the surface of ZIF-67@450 becomes rougher after calcination, indicating the formation of inter-particle pores during the calcination process, leading to the increase in average pore radius (Table 1) [30]. Once ZIF-67 was calcined to form Co_3O_4 , its original sodalite structure deformed through concaving and shrinking due to the heat treatment. However, some edges of ZIF-67, even though skewed, can still be discerned. The morphology changes during calcination should be caused by the different rates of crystallization and specific plane growth under different calcination temperatures (Fig S3a). The particle sizes observed in FESEM were slightly larger than that of those estimated from Scherrer's equation (Table 1).

Fig 3 FESEM images of ZIF-67 (a) and Co_3O_4 calcined at different temperatures (b-350, c-450 and d-550)

Fig 4 shows ZIF-67 exhibits a gradual weight loss step of 4.5% up to 350°C, corresponding to the removal of guest molecule from the cavities and some unreacted reagents. A drastic weight loss of 65.7% is located in the temperature range of 350-400°C, indicating the decomposition of organic ligands in ZIF-67. Meanwhile, the sample calcined at 350°C still contains some carbon (Fig S3b), showing the incomplete transformation. The presence of carbon in the sample is undesirable as it can compete with the pollutant for reaction with ROS during catalytic oxidation process. As the temperature further increased, a long plateau was obtained at the temperature range of 400-900°C with a residual weight of 34.3%, due to the formation of Co_3O_4 . The results are **consistent** with the calculated weight loss from $\text{Co}(\text{C}_4\text{H}_5\text{N}_2)_2$ (molecular weight of 220) to $\text{CoO}_{4/3}$ (molecular weight of 80). To ensure complete transformation from ZIF-67 to Co_3O_4 as well as to conserve the pristine polyhedral morphology, 450°C was chosen as the calcination temperature for the following studies and the Co_3O_4 prepared at this condition was denoted as ZIF-67@450.

Fig 4. TGA curve of ZIF-67 showing weight change at heating under air atmosphere.

3.2 Characterization of ZIF-67 and ZIF-67@450

Fig 5. N₂ adsorption-desorption isotherms of ZIF-67 and ZIF-67@450

To explore the textural property of ZIF-67@450, N₂ adsorption-desorption isotherms of the ZIF-67 crystal and ZIF-67@450 particles were recorded at 77 K (Fig 5). The specific surface areas and total pore volumes were calculated and summarized in Table 1. The original ZIF-67 crystals showed typical microporous characters with a high surface area and

large total pore volume. After calcination at 450°C for 3 h, notable reduction of the BET specific surface areas from 1463.0 to 20.4 m² g⁻¹ and total pore volumes from 0.64 to 0.02 cm³ g⁻¹ were observed in the ZIF-67@450 because of the folding of ZIF-67 structure (Table 1).

Table 1 The physical properties of ZIF-67 and ZIF-67@450

Parameters	ZIF-67	ZIF-67@450
BET specific surface area ^a (m ² g ⁻¹)	1463.0	20.4
DFT cumulative surface area ^b (m ² g ⁻¹)	2131.0	13.6
Pore volume ^b (cc g ⁻¹)	0.64	0.02
Pore radius ^b (nm)	0.92	1.39
DFT cumulative porosity ^c (%)	60.0	12.1
XRD crystallite size ^d (nm)	55.8	52.8

^a Calculated from multi-point BET method

^b Calculated from DFT method

^c Determined by assuming uniform densities of ZIF-67 and Co₃O₄ as 0.89 and 6.057 g cm⁻³

^d Calculated using Scherrer's equation

Fig 6a presents the X-ray diffraction (XRD) pattern of ZIF-67 and ZIF-67@450. All the diffraction peaks of ZIF-67 **agree** well with the simulated patterns [31]. The XRD pattern of the product after the one-step calcination of ZIF-67 confirms that a pure Co₃O₄ spinel phase with a face-centred cubic lattice (04-016-4508) is obtained. The peaks at 19.0, 31.3, 36.9, 44.8, 59.4 and 65.2 can be indexed to the (111), (220), (311), (400), (511) and (440) planes of Co₃O₄ (04-016-4508) (Fig S4). The XRD patterns shown in Fig 4a indicate that ZIF-67 had been completely converted to Co₃O₄ with the disappearance of original pattern of ZIF-67. **While the broad diffraction peaks could be caused by the nano-sized effects of Co₃O₄.**

Fig 6. The chemical characterization of ZIF-67 and ZIF-67@450 (a-XRD, b-FTIR, c-Raman spectra and d-XPS)

The existence of Co_3O_4 was also verified by spectroscopic analyses. As reported previously, the Co_3O_4 with Co^{2+} ($3d^7$) and Co^{3+} ($3d^6$) located at tetrahedral and octahedral sites respectively [32]. The active modes for spinal crystallizes can be predicted via the space group theory:

$$\Gamma = A_{1g}(\text{R}) + E_g(\text{R}) + F_{1g}(\text{IN}) + 3F_{2g}(\text{R}) + 2A_{2u}(\text{IN}) + 2E_u(\text{IN}) + 4F_{1u}(\text{IR}) + 2F_{2u}(\text{IN}) \quad (4)$$

where (R) is Raman active vibrations, (IR) means infrared-active vibrations and (IN) represents inactive modes.

Fig 6c shows the Raman spectra of the ZIF-67 and ZIF-67@450. Four active Raman modes with the location at ~ 470 , 510 , 608 and 680 cm^{-1} could be distinguished, corresponding to E_g , F_{2g}^1 , F_{2g}^2 and A_{1g} modes of Co_3O_4 . All peaks are in agreement with the values of pure Co_3O_4 spinel structure yet with an average shift of $\Delta V < 5 \text{ cm}^{-1}$, which could be caused by the size effects and surface stress/strain. After calcination, the peak positions shift to low wavenumbers which is attributed to the optical phonon confinement effect in nanostructures that can cause uncertainty in the phonon wave vectors and then a downshift of Raman peaks [33].

In addition, the FTIR spectrum (Fig 6b) shows two main relatively sharp absorptions centered at ~ 580 and 660 cm^{-1} in ZIF-67@450, which originate from the fingerprint

stretching vibrations of the Co-O bond of the Co_3O_4 spinel oxides. More precisely, the observed 580 cm^{-1} band is characteristic of Co-O with Co denoting the Co^{3+} in the octahedral site while the 660 cm^{-1} band is attributable to the Co^{2+} in the tetrahedral site vibration in the spinel lattice [34]. Meanwhile, the FTIR spectrum shows no residual organic compounds after calcination process. In the original ZIF-67 sample, the absorption bands at 425 and 1580 cm^{-1} are assigned to the stretching vibration of Co-N and C-N, respectively. The bands at $1380\text{--}1450\text{ cm}^{-1}$ are associated with the entire imidazole ring stretching and the bands in the region of $800\text{--}1350\text{ cm}^{-1}$ are for the in-plane bending of the ring while those below 800 cm^{-1} are related to the out-of-plane bending [35].

XPS investigations were carried out to characterize the elemental composition of the surface of the particles as well as the chemical environment of the cobalt and oxygen atoms. It is reasonably surmised that N atoms would disappear along with the calcination process with oxygen (Fig 6d). In original ZIF-67, the N1s region spectra are deconvoluted into two components N1 (pyridinic-N, 398.2 eV) and N2 (Co-N, 399.1 eV) while the Co 2p core-level spectra are deconvoluted to display peaks of Co-N_x at 780.5 eV (Fig S5). In this structure, appropriately arranged N1 (pyridinic N) moieties with electron-donating properties are able to trap plentiful transitional metals to serve as outstanding metal-coordination (Co-N_x) active sites. Furthermore, free N1 atoms have excellent electronic storage ability to activate molecular oxygen under mild conditions [36]. After calcination, N1s peak disappears due to 2-methylimidazole ligands ring opening and conversion of ZIF-67 to Co_3O_4 (Figs 6d and Fig S5). The Co2p peaks show a slight broadening and shifting to lower binding energy, which could be deconvoluted to peaks related to the formed cobalt oxides (Fig 7a).

In the Co2p core-level spectrum of ZIF-67@450, two major peaks with binding energies of 780 and 795 eV are observed, corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ respectively (Fig 7a). The 15 eV energy difference between the Co 2p peaks is indicative of spinel Co_3O_4 [37]. It is well known that both Co^{2+} and Co^{3+} exhibit similar binding energy peaks, however, the energy splitting (ΔE) between the two levels due to spin-orbit coupling should be different for the Co^{2+} and Co^{3+} configurations with $\Delta E = 15.0\text{ eV}$ for Co^{3+} and $\Delta E = 15.7\text{ eV}$ for Co^{2+} [38]. The XPS data (Fig 7a) for the spinel Co_3O_4 , which contains both Co^{2+} and Co^{3+} ions distributed on the A and the B sites as $[\text{Co}^{2+}]_A[\text{Co}^{3+}]_B\text{O}_4$, clearly show the presence of doublet at $D1 = 779.2\text{ eV}$ and $D2 = 780.8\text{ eV}$ for the Co $2p_{3/2}$ level and a doublet for the Co $2p_{1/2}$ level centered at $D3 = 794.1\text{ eV}$ and $D4 = 796.5\text{ eV}$. The separations between the doublet peaks are $\Delta E_{D3-D1} = 14.9\text{ eV}$ and $\Delta E_{D4-D2} = 15.7\text{ eV}$, which are close to the above-mentioned values for Co^{3+} and Co^{2+} , respectively, thus confirming the presence of Co^{3+} and

Co²⁺ in Co₃O₄. The peaks at 789.3 and 804.9 eV are considered shake-up satellite peaks, which further confirms the well-defined Co₃O₄ structure [39]. Other small peaks at 783 and 795 eV may result from a chemical shift of the main spin-orbit components because of the chemical interaction between cobalt and hydroxide [40].

Similar to that of Co 2p, the O 1s of ZIF-67@450 exhibits broadening and shifting to lower binding energy due to the formation of typical metal-oxygen bond (529.6 eV) (Fig 7b). The peak at 531.4 eV could be assigned to hydroxyl group because of the possible water on or between the Co₃O₄ nanocrystals [41] and a multiplicity of defect sites [38]. These results confirm that Co=N coordination bonds in ZIF-67 were broken and the Co species were oxidized to form Co₃O₄ by calcination in the air atmosphere.

Fig 7 High resolution of Co2p (a) and O1s (b) XPS spectra of ZIF-67@450

3.3 Characterization of CoFCMs

The effect of calcination temperature on the morphologies of CoFCMs is shown in Fig S6. Results indicate that M350 and M450 can form a porous network structure while M550 shows the aggregation of Co₃O₄, which is in accordance with the powder characterization (Fig 3). Figs 8a and b show the morphologies of pristine ceramic membrane (M0) and CoFCM (M450), respectively. The membrane surface changes significantly and becomes rougher after ZIF-67-derived Co₃O₄ modification. It exhibits that Co₃O₄ particles are deposited on the surface of membrane, forming a porous network of connected polygons (Fig 8b). The CoFCM increases the complexity of pore structure which would result in a great enhancement in pollutants retention ability. EDX microanalysis was performed on the surface of M450 (Fig 8c). The element mapping images shows the Co₃O₄ has been deposited on Al₂O₃ (Fig S7). Fig 8d shows a two-layer structure image of Co₃O₄ particle immobilized on the Al₂O₃ ceramic membrane. The top layer is the Co₃O₄ particle with an estimated

thickness of 1.5-2 μm . AFM was used to characterize topography of M0 and M450. The two-dimensional amplitude retraces surface images (Figs 8 e and f) show that M450 ($R_m = 86.9$ nm) was slightly rougher compared with M0 ($R_m = 79.5$ nm), which could be caused by the formation of Co_3O_4 on membrane surface.

Fig 8. Physical properties of M0 (control) and M450 (a-FESEM of M0 surface, b-FESEM of M450 surface, c-EDX analysis of M450 surface, d-FESEM of M450 cross section, e-AFM of M0 surface, f-AFM of M450 surface)

To analyze the bonding mechanism of CoFCM, XPS tests were carried out by investigating the various elemental chemical oxidation states and the spectra are presented in

Fig 9. According to the high resolution of Al 2p peak for Al₂O₃, (Fig 9a), only Al-O bonding for Al₂O₃ is present. However, in ZIF-67@450/Al₂O₃ (Fig 9b), both Al-O for Al₂O₃ and Al-O-Co bonding are detected, showing the chemical interaction between powder Al₂O₃ and ZIF-67@450. On the other hand, the characteristic peak of O 1s in Fig 9 d was found to consists of both Al-O and Co-O. The N1s spectra in ZIF-67/Al₂O₃ shows the existence of Al-N bonding (Fig S8), which further confirmed the chemical interaction between Al₂O₃ and ZIF-67. The chemical bonding between catalyst and membrane surface can avoid catalyst aggregation as well as detachment effectively, improving the stability of CoFCM for catalytic oxidation reactions.

Fig 9. High resolution of Al 2p (a,b) and O1s (c,d) XPS spectra of Al₂O₃ and ZIF-67@450/Al₂O₃

Table 2 shows the membrane properties of M0 and CoFCMs, the weight change could be ignored because of the low amount of Co₃O₄. The pure water permeability of M450 (3024 LMHB) was slightly lower (<10% difference) than that of M0 (3323 LMHB). This shows that Co₃O₄ particle formed a very thin porous layer which only induced a minimal effect on the membrane filtration resistance (Fig 8d). **Meanwhile, M450 shows a more hydrophobic surface which might be caused by the honeycomb structure on the membrane surface (Table 2). For M550, due to the highly hydrophilicity of Co₃O₄, the contact angle of M550**

decreased, resulting a higher pure water flux (Table 2). The effect of the Co_3O_4 on the pure water permeability can be evaluated by the intrinsic membrane resistance [9], R_m (m^{-1}), which are defined as:

$$R_m = (\Delta P) A t / \mu V \quad (5)$$

where ΔP is the trans-membrane pressure (Pa), A is the effective surface area of the membrane (m^2), t is the filtration time (s), μ is the kinematic viscosity of water ($1 \times 10^{-3} \text{ Pa}\cdot\text{s}$) and V is the volume of water flowing through the membrane. Before the modification, the R_m for M0 is calculated as $1.08 \times 10^{11} \text{ m}^{-1}$, while the R_m for M450 is $1.19 \times 10^{11} \text{ m}^{-1}$.

Table 2 Membrane properties of M0 and CoFCMs

Parameters	M0	M350	M450	M550
Weight (g)	1.97±0.05	1.97±0.04	1.97±0.03	1.97±0.07
LMHB ^a	3323	3121	3024	3420
R_m (m^{-1})	1.08×10^{11}	1.14×10^{11}	1.19×10^{11}	1.11×10^{11}
V ^b (cm^3)	0.2874	0.2859	0.2835	0.2839
P ^c (%)	56.5	56.2	55.7	55.8
Contact Angle ^d (°)	68.5	70.5	80.8	67.8

^a Pure water permeability ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)

^b Pore volume (cm^3)

^c Porosity (%)

^d Tested at 0.3 s

3.4 Catalytic performance of CoFCMs

Figs 10a and b show the effect of Oxone dosage on removal of SMX over M0 and M450 in the membrane filtration system. During the filtration and catalytic oxidation processes, SMX can be retained on the membrane surface, which consists of high density of Co_3O_4 particle. When Oxone is introduced into the system, the Co_3O_4 particle acts as active sites for Oxone activation, generating ROS for SMX degradation. Once degraded, the smaller SMX intermediates can be constantly removed from the reaction zone on the membrane surface. This promotes more efficient SMX degradation. For the pristine membrane (M0), **due to inactivity of Al_2O_3 , even** when Oxone dosage was increased to 0.1 g L^{-1} , the SMX removal in 90 min is insignificant (less than 15%, Fig 10 a), **which confirmed the negligible effect of Oxone oxidation in this process.** However, with the M450 membrane, it shows

significantly increased removal efficiency with increase of Oxone dosage (Fig 10 b) **because of the presence of Co_3O_4 on the membrane, which works as the catalyst to activate Oxone for radicals' generation.** The enhancement of SMX degradation with increasing Oxone dosage means the active sites on membrane surface were not totally occupied by Oxone. When Oxone dosage was set as 0.01 g L^{-1} , the removal efficiency reached a plateau after 40 min, indicating that Oxone is exhausted in this system. When the Oxone dosage was increased to 0.05 g L^{-1} , the SMX removal follows a first order removal kinetics (Fig S9) and Oxone is consumed at 90 min, since no redundant Oxone was detected in the solution (Fig 10 c). The increase of reaction rate could be caused by the higher density of catalytic sites as well as the higher reactant concentrations. If Oxone dosage was further increased to 0.1 g L^{-1} , there is no significant change in the rate constant, indicating that active sites on membrane surface became the rate limited factor when Oxone dosage is in excess (i.e. more than 0.05 g L^{-1}) and the flow rate is fixed (1 mL min^{-1}). Under a certain catalyst active sites for membranes, limited Oxone-surface contact was achieved. After reaction, the residual Oxone was detected and the maximum consumption rate was calculated as $0.56 \text{ mg L}^{-1} \text{ min}^{-1}$ in this system. Other CoFCMs (M350 and M550) shows the similar kinetics of SMX degradation (Fig S10). However, the M350 is not stable considering the TGA result indicates incomplete conversion of precursor to Co_3O_4 .

Fig 10. Catalytic performance of M0 and M450 (a,b-Effect of Oxone dosage; c- Oxone consumption ratios, d-durability of M450. Flow rate: [1 mL min⁻¹], TMP: [0.07 bar], SMX initial concentration: [10 mg L⁻¹])

To evaluate the membrane durability, it was used for 3 operational cycles (the initial concentration of SMX was 10 mg L⁻¹ and the Oxone dosage was 0.05 g L⁻¹ based on the Oxone consumption result (Fig 10c)). Fig 10d shows a slight decrease (<10%) in the SMX removal rate with increasing operational cycles, which could be caused by the accumulative adsorption of SMX and its degradation products onto the surface of the membrane that reduced the density of active reaction sites. The detected leached cobalt ion was 0.084 mg L⁻¹ after the 3rd run, which would not cause the acute toxic effects to aquatic life [42]. After cleaning with Oxone solution (0.1 g L⁻¹) without adding SMX, more than 95% of the SMX removal efficiency could be reclaimed in the subsequent experimental run. This indicates the durability could be achieved via Oxone assisted cleaning. Meanwhile, during the filtration test, TMP was monitored at 0.07 bar with a constant flow rate of 1 mL min⁻¹, which shows the insignificant fouling property of the membrane.

Three ROS including HO·, SO₄·⁻ and SO₅·⁻ have been reported in a Co-Oxone catalytic system [43]. To verify the ROS in the CoFCM, EPR experiments were performed

using DMPO as the spin trapping agent. As shown in Fig 11a, when only Oxone solution was tested with the addition of DMPO, no peaks were detected, suggesting that no significant ROS was formed. However, in the presence of ZIF-67@450, the characteristic signals of 5,5-dimethyl-2-pyrrolidone-N-oxyl (DMPOX) with heptet were detected, which was formed from the oxidation of DMPO with strong ROS ($\text{HO}\cdot$ and $\text{SO}_4^{\cdot-}$) [44,45].

Fig 11. a) EPR spectra with DMPO as the spinning agent (Reaction condition: [Oxone] = 0.10 g L⁻¹, [SMX] = 10 mg L⁻¹, [catalyst] = 0 or 2 g L⁻¹ and [DMPO] = 100 mM) and b) The effect of scavengers towards the SMX degradation

To further validate the primary ROS in the system, quenching experiments were conducted by adding methanol and *tert*-butanol (TBA) as the scavengers. It is widely accepted that methanol with an α -hydrogen ensures the quenching of both $\text{SO}_4^{\cdot-}$ ($2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{HO}\cdot$ ($9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [46,47], while TBA without α -hydrogen reacts more easily with $\text{HO}\cdot$ ($3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), but in a slower reaction rate with $\text{SO}_4^{\cdot-}$ ($4.0 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [11]. Meanwhile, $\text{SO}_5^{\cdot-}$ is relatively inert to both methanol and TBA due to its low rate constant with alcohols ($\leq 10^3 \text{ M}^{-1} \text{ s}^{-1}$) [48]. Fig 11b depicts the inhibition effects of different scavengers on the SMX degradation in the CoFCM/Oxone system. The degradation of SMX was inhibited entirely by addition of 1 M methanol, which indicated that the ROS generated in the system were mostly quenched. The results also confirmed the insignificant contribution of $\text{SO}_5^{\cdot-}$ on the SMX decomposition. Meanwhile, 1 M of TBA has little influence on the degradation of SMX in this system, implying that $\text{HO}\cdot$ plays a smaller role in the SMX decomposition compared with $\text{SO}_4^{\cdot-}$. In the SMX degradation process, several intermediate products were detected via LC-MS-MS. The detailed analysis method is shown in Text S1 and the products are listed in Table S1. The main degradation pathway is accompanied with the cleavage of sulfonamide bond as well as the formation of nitro-SMX molecule via the electron transfer reaction, which is in accordance with the previous study [49].

Based on the above observation, the proposed reaction mechanism in CoFCM is illustrated in Fig 12. In this system, $\text{SO}_4^{\cdot-}$ is the dominant ROS responsible for the SMX decomposition and the major reactions are as follows:

Fig 12. Illustration of the proposed reaction mechanism on SMX degradation in CoFCM

4. Conclusions

A novel cobalt oxide functionalized ceramic membrane (CoFCM) was successfully prepared by a facile surface-nucleated zeolitic imidazolate framework (ZIF-67) growth method to activate Oxone for SMX degradation in a dead-end membrane filtration mode. The method to synthesize ZIF-67 as well as Co_3O_4 was optimized. The porous Co_3O_4 hollow structure was produced after one-step calcination of ZIF-67 precursor at 450°C and was distributed as a honeycomb structure on the membrane surface. The CoFCM shows a high performance on the removal of SMX as well as a high durability via Oxone-assisted cleaning. Overall, the CoFCM shows a new prospect for plentiful catalytic applications. Meanwhile,

the MOF-directed surface-nucleated growth followed by one-step calcination is a promising method for fabrication of nanocatalysts functionalized ceramic membranes.

Abbreviations

ZIF	zeolitic imidazolate framework
CoFCM	Co ₃ O ₄ nanocatalyst functionalized Al ₂ O ₃ ceramic membrane
MOF	metal organic framework
SMX	sulfamethoxazole
2-MIM	2-methylimidazole
ZIF-67@450	Co ₃ O ₄ prepared via calcination of ZIF-67 at 450°C
M0	pristine Al ₂ O ₃ ceramic membrane
M450	CoFCM prepared at 450°C

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Surface-nucleated heterogeneous growth of zeolitic imidazolate framework-A
unique precursor towards catalytic ceramic membranes: synthesis,
characterization and organics degradation

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Abstract

A novel Co₃O₄ nanocatalyst functionalized Al₂O₃ ceramic membrane (CoFCM) with a honeycomb structure was prepared via an optimized surface-nucleated zeolitic imidazolate framework (ZIF-67) growth method. The Co₃O₄ hollow structure which was confirmed via chemical characterizations (XRD, FTIR, Raman and XPS), was formed on the membrane surface by direct one-step calcination of ZIF-67 membrane. The CoFCM was characterized by various techniques including the field emission scanning electron microscopy and atomic force microscopy. The results reveal the formation of well-defined Co₃O₄ layer on the porous Al₂O₃ ceramic membrane with 1.5 - 2 μm thickness. The growth mechanism of CoFCM was further proposed via XPS and the catalytic activity of CoFCM was investigated for the removal of sulfamethoxazole (SMX). The membrane performance was examined under a home-made dead-end mode. Results indicate that CoFCM has a rougher surface with an initial membrane resistance of $1.19 \times 10^{11} \text{ m}^{-1}$ and performs outstanding catalytic activities. The pure water permeability of CoFCM is $3024 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is comparable to that of the pristine ceramic membrane (< 10% difference). The SMX removal efficiency achieved to > 90% in 90 min with an Oxone addition of 0.1 g L^{-1} . Meanwhile, the membrane showed excellent durability by retaining > 95% of initial flux for at least 3 operational cycles with a low cobalt ion leaching via Oxone-assisted cleaning. Furthermore, the reaction mechanism of Oxone activation by CoFCM was proposed from the results of the electron paramagnetic resonance (EPR) and radical scavenger experiments.

Keywords: MOF-template; Heterogeneous growth; ZIF-67; Hybrid membrane; Peroxymonosulfate; sulfamethoxazole

1. Introduction

In recent years, ceramic membrane is gaining increasing acceptance for treatment of municipal and industrial wastewater streams because of its high stability and permeability in extreme environments [1,2]. In view of these properties, the ceramic membrane offers a potential novel application as a hybrid filtration and catalytic system. In this hybrid system, much faster conversion of reactants can be achieved due to the unlimited mass transfer process [3]. Over the recent decades, the coupling of ceramic membranes with oxidation has proven to be an effective technology to enhance pollutants treatment performance by generating reactive oxygen species and preventing membrane fouling [4–6]. Up to now, the oxidation-filtration coupling technologies are mainly limited to photocatalysis or ozonation to generate hydroxyl radicals for pollutant degradation [4,7–9].

Compared with hydroxyl radical-based advanced oxidation technologies, sulfate radical ($\text{SO}_4^{\cdot-}$)-based advanced oxidation processes (SR-AOPs) have gained increasing attention due to its properties of higher oxidation potential, wider pH range (2-8) and longer half-life time (30-40 μs) [10]. The $\text{SO}_4^{\cdot-}$ is generally produced from peroxymonosulfate (PMS, Oxone) and persulfate (PS) via transition metals or metal oxides [11–13]. Among them, cobalt-based nanoparticles exhibit excellent catalytic activity. To date, lots of work have been done to prepare high performance Co-based nanomaterials for PMS activation [14–17]. However, nanoparticles tend to aggregate, leading to loss of catalytic activity [18]. Furthermore, surfaces of the nanocatalysts could be covered by deposited solute species including pollutants and their degradation products, leading to deactivation of active sites on their surface [19]. To address these limitations, one possible way is to load nanocatalysts onto membrane surface to increase the surface area as well as decrease the aggregation.

To prepare a catalyst functionalized membrane, dip-coating and hydrothermal methods have been investigated [20,21]. However, these methods need multiple steps and the morphologies are very difficult to control. Herein, we present a facile and scalable method to synthesize a magnetic hollow cobalt oxide functionalized ceramic membrane (CoFCM) for sulfamethoxazole (SMX) degradation. SMX is one kind of widely used antibiotics and has been detected in various systems [22–25]. Meanwhile, it is hard to be removed by the traditional methods because of its resistance to natural biodegradation [26,27]. To address this problem, one potential strategy is the advanced oxidation processes owing to their non-selectivity to a wide variety of organic pollutants via generation of strong reactive species.

In this work, a Co-based zeolitic imidazolate framework, ZIF-67, was formed on the ceramic membrane surface via surface-nucleated growth. The hollow CoFCM structure could be achieved easily through direct calcination of ZIF-67 by taking advantages of its thermal behavior and chemical reactivity [16,28]. To our knowledge, this is the first report on synthesis of CoFCM via ZIF-67 template method and use it for PMS activation. The performance of the resulting CoFCM was examined in a home-made dead-end membrane filtration system. Also, the plausible PMS activation mechanism in CoFCM/Oxone system was evaluated via the radical trapping and electron paramagnetic resonance (EPR) experiments.

2. Experimental Section

2.1 Materials

All chemicals were of reagent grade or higher and were used without further purification. Sulfamethoxazole (SMX), Sodium hydroxide (NaOH), methanol (CH_4O), *tert*-butanol ($\text{C}_4\text{H}_{10}\text{O}$), powder Al_2O_3 (100 mesh, 99%), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methylimidazole (2-MIM) were purchased from Sigma-Aldrich, Singapore. Oxone (PMS, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) was supplied by Alfa Aesar, Singapore. 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was provided by Aladdin, China. Porous Al_2O_3 ceramic membrane (CM) with a pore size of 500 nm and porosity of around 55% was provided by Nanjing Shuyihui Scientific Instruments CO., LTD (Nanjing, China). The diameter of the ceramic membrane is 22 mm and the thickness is 2 mm.

2.2 Preparation of Co_3O_4 functionalized ceramic membrane (CoFCM)

Before the CoFCM preparation, the synthesis of zeolitic imidazolate framework (ZIF-67) was optimized via changing the precursor concentrations (33 mM to 330 mM based on Co concentration). To prepare CoFCM, the ceramic membranes were firstly washed with 1 M NaOH to remove the impurities followed by washing with DI water to neutral pH and drying at 100 °C for 24 h for later use. Surface-nucleated heterogeneous growth method was used for the synthesis of porous hybrid CoFCM and the schematic illustration is shown in Fig 1. First, the ceramic disc was immersed in the 2-MIM (2-methylimidazole) solution (Solution A, 0.66 g of 2-MIM in 15 mL methanol) for 30 min, after washing several times with methanol to remove the redundant solution, the disc was placed into the metal precursor solution (Solution B, 0.291 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 15 mL methanol) for another 30 min. After

washing with methanol, the disc was positioned into the mixture of two solutions (Solution A and Solution B) which was settled at room temperature in the quiescent solution. After aging for 24 h, the purple disc was washed with methanol to remove the reductant solution followed by washing with DI water and dried overnight at 105°C. The remaining purple ZIF-67 powders were collected from the mother solution and washed with methanol and DI water several times with the assistance of centrifuge for later test. To confirm the formation of covalent bonds between ceramic disc and ZIF-67, a control experiment in which the disc was replaced by Al₂O₃ powder was conducted in the same condition. In the surface-nucleated heterogeneous growth process, Al could be linked with 2-MIM via Al-N bond followed by the formation of ZIF-67 on the membrane surface, which would minimize the infiltration of ZIF-67 particles into the internal pores. The infiltration of ZIF-67 particles into the internal pores will result in undesirable pore plugging and decreased water permeability.

The CoFCM was then prepared through a one-step calcination of ZIF-67 functionalized membrane in a furnace with the temperature raising from room temperature to the desired temperature at a ramping rate of 5°C min⁻¹, and then stabilized for 3 h. The resulted CoFCM was denoted as M-temp while the pristine membrane without Co₃O₄ was referred as M0. In addition, Co₃O₄ powder was also prepared under the same condition using ZIF-67 as the precursor and was denoted as ZIF-67@temp in the following sections. After the calcination process, all membranes were washed with DI water followed by drying in an oven at 60°C overnight for later use.

Fig 1. Schematic illustration of the fabrication of CoFCM via a surface-nucleated ZIF-67 growth method (Solution A, 0.66 g of 2-MIM in 15 mL methanol; Solution B, 0.291 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 15 mL methanol)

2.3 Characterization techniques

The thermo-transformation of ZIF-67 was investigated by thermogravimetric analysis (TGA) (SDT-Q600, TA instrument, USA) in the temperature range of 100-900°C under air atmosphere (heating rate of $10^\circ\text{C min}^{-1}$ and air flow of 100 mL min^{-1}). Nitrogen adsorption-desorption analyses were conducted on a Quantachrome Autosorb -1 Analyzer at liquid N_2 temperature of 77 K. The resulting specific surface areas as well as porosities were calculated from N_2 adsorption data by the multipoint Brunauer-Emmett-Teller (BET) and DFT methods.

The surface morphologies as well as elements distribution were acquired by a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL). Meanwhile, atomic force microscopy (AFM, Cypher S, Asylum Research) was employed to characterize the membrane surface roughness.

X-rays diffractometer (XRD, Bruker D8 Advance) was used to analyze the crystal structures of the material. The 2θ range was scanned from $5-75^\circ$ at a step size of 0.02 and the crystallite sizes of as-synthesized particles were calculated using Scherrer's equation:

$$D = R \lambda / \beta \cos \theta \quad (1)$$

where D is the estimated diameter of the particles (nm), R is 0.89 (Scherrer's constant), λ means the incident wavelength, which is 0.154 nm in this study, β (rad) is the peak width at half height and θ ($^\circ$) is the diffraction angle.

The vibrational absorbance of as-synthesized particles was investigated by Fourier transformed infra-red spectrometer (FTIR, Perkin Elmer) and Raman spectrometer (HORIBA Scientific). Meanwhile, X-ray photoelectron spectroscopy (XPS) analysis (Kratos Axis Supra, Shimadzu) was conducted on to detect the elements' chemical states in ZIF-67 and Co_3O_4 .

Electron paramagnetic resonance (EPR) experiments were employed on a Biospin ELEXSYS II E500 EPR spectrometer (Bruker) using DMPO as spin trapping agent to probe the free reactive oxygen species (ROS) and the information was analyzed by Xeon software (Bruker). Furthermore, chemical quenching experiments were conducted by adding methanol and *tert*-butanol as the scavengers due to their different reaction rates to hydroxyl radical and sulfate radical.

2.4 SMX degradation experiments with CoFCM

SMX degradation with CoFCM was evaluated in a dead-end filtration mode, which was operated under a constant flux (Fig S1). The initial pH of feed solution (50 mL) is 5 with a SMX concentration of 10 mg L^{-1} . A high-pressure metering pump (5979 Optos Pump 2HM, Eldex) was used to feed the solution into the membrane cell module (SS316 stainless steel), in which the membrane was secured tightly. The constant flow mode (flow rate was set at 1 mL min^{-1}) was used and trans-membrane pressure (TMP) was recorded as 0.07 bar in a dead-end system and the permeate was then re-circulated back to the feed tank. A control experiment with the pristine Al_2O_3 membrane (M0) was also performed to quantify the performance of membrane. The membranes (M0 and CoFCMs) were compacted to a steady state for 5 min before filtration experiment.

2.5 Analytical methods

The SMX concentration was quantified using LC-2030C-3D liquid chromatography system (Shimadzu) with a reversed phase column (Inertsil ODS-3, $5 \mu\text{m}$, $4.6 \times 150 \text{ mm}$). The

detection wavelength was set at 264 nm and the mobile phases are 60% methanol and 40% water (0.1% acetic acid). The flow rate was 0.8 mL min⁻¹ and the injection volume was 10 µL. For Oxone quantification, 1 mL of the samples was initially mixed with 0.02 g of KI for the oxidation of I⁻ by HSO₅⁻ (Eqs.2-3)

The concentration of I₃⁻ was then determined by a UV-1800 spectrophotometer (Shimadzu, Japan) at λ_{max} = 352 nm (Fig S2). Inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000, Perkin Elmer) was conducted to measure the mass of cobalt leached from membranes.

3. Results and discussion

3.1 Study of the ZIF-67-template method

In this study, the effect of different precursor concentrations on ZIF-67 synthesis was investigated and the results are shown in Fig 2. The optimum mole ratio of Co²⁺ to 2-MIM, which is 1:8, is important for the successful synthesis of ZIF-67 [29]. The concentrations of precursors would affect both morphology and yield of ZIF-67. With increasing precursor concentration, the well-defined ZIF-67 particle size increased with a higher yield and subsequently became more irregular due to the presence of excessive precursors in solution. In this work, the Co(NO₃)₂·6H₂O concentration of 33 mM was chosen because it shows the most uniform particle distribution (Fig 2b).

Fig 2. SEM images of ZIF-67 prepared with different $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentrations
(mole ratio of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 2-MIM was fixed at 1/8)

To examine the calcination temperature effect on the formation of Co_3O_4 , different temperatures (350, 450 and 550°C) were used in the calcination process. The sizes and morphologies of as-synthesized ZIF-67 and Co_3O_4 calcined at different temperatures were observed by FESEM (Fig 3). The results show that all particles perform good uniformity in this study (Figs 3a-c). However, when the temperature increased to 550°C, the ZIF-67 crystals aggregated and the structural backbone of the metal-organic framework disappeared (Fig 3d). A magnified FESEM image in Fig 3a depicts the very smooth surface over the whole particle, indicating the single-crystal-like feature of the ZIF-67. It displays a uniform rhombic dodecahedra structure due to the combination of Co ions and 2-methylimidazole through coordination bonds and shows a uniform particle size of approximately 200 nm with sodalite topology. After calcination at 350°C for 3 h, the pristine polyhedral morphology is retained well, but the size of polyhedral crystals shrinks slightly (Fig 3b). When the calcination temperature increased to 450°C, part of the pristine polyhedral morphology is still retained and the size of polyhedral shrinks a bit more (Fig 3c). Meanwhile, the surface of ZIF-67@450 becomes rougher after calcination, indicating the formation of inter-particle pores during the calcination process, leading to the increase in average pore radius (Table 1) [30]. Once ZIF-67 was calcined to form Co_3O_4 , its original sodalite structure deformed through concaving and shrinking due to the heat treatment. However, some edges of ZIF-67, even though skewed, can still be discerned. The morphology changes during calcination should be caused by the different rates of crystallization and specific plane growth under different calcination temperatures (Fig S3a). The particle sizes observed in FESEM were slightly larger than that of those estimated from Scherrer's equation (Table 1).

Fig 3 FESEM images of ZIF-67 (a) and Co_3O_4 calcined at different temperatures (b-350, c-450 and d-550)

Fig 4 shows ZIF-67 exhibits a gradual weight loss step of 4.5% up to 350°C, corresponding to the removal of guest molecule from the cavities and some unreacted reagents. A drastic weight loss of 65.7% is located in the temperature range of 350-400°C, indicating the decomposition of organic ligands in ZIF-67. Meanwhile, the sample calcined at 350°C still contains some carbon (Fig S3b), showing the incomplete transformation. The presence of carbon in the sample is undesirable as it can compete with the pollutant for reaction with ROS during catalytic oxidation process. As the temperature further increased, a long plateau was obtained at the temperature range of 400-900°C with a residual weight of 34.3%, due to the formation of Co_3O_4 . The results are consistent with the calculated weight loss from $\text{Co}(\text{C}_4\text{H}_5\text{N}_2)_2$ (molecular weight of 220) to $\text{CoO}_{4/3}$ (molecular weight of 80). To ensure complete transformation from ZIF-67 to Co_3O_4 as well as to conserve the pristine polyhedral morphology, 450°C was chosen as the calcination temperature for the following studies and the Co_3O_4 prepared at this condition was denoted as ZIF-67@450.

Fig 4. TGA curve of ZIF-67 showing weight change at heating under air atmosphere.

3.2 Characterization of ZIF-67 and ZIF-67@450

Fig 5. N₂ adsorption-desorption isotherms of ZIF-67 and ZIF-67@450

To explore the textural property of ZIF-67@450, N₂ adsorption-desorption isotherms of the ZIF-67 crystal and ZIF-67@450 particles were recorded at 77 K (Fig 5). The specific surface areas and total pore volumes were calculated and summarized in Table 1. The original ZIF-67 crystals showed typical microporous characters with a high surface area and

large total pore volume. After calcination at 450°C for 3 h, notable reduction of the BET specific surface areas from 1463.0 to 20.4 m² g⁻¹ and total pore volumes from 0.64 to 0.02 cm³ g⁻¹ were observed in the ZIF-67@450 because of the folding of ZIF-67 structure (Table 1).

Table 1 The physical properties of ZIF-67 and ZIF-67@450

Parameters	ZIF-67	ZIF-67@450
BET specific surface area ^a (m ² g ⁻¹)	1463.0	20.4
DFT cumulative surface area ^b (m ² g ⁻¹)	2131.0	13.6
Pore volume ^b (cc g ⁻¹)	0.64	0.02
Pore radius ^b (nm)	0.92	1.39
DFT cumulative porosity ^c (%)	60.0	12.1
XRD crystallite size ^d (nm)	55.8	52.8

^a Calculated from multi-point BET method

^b Calculated from DFT method

^c Determined by assuming uniform densities of ZIF-67 and Co₃O₄ as 0.89 and 6.057 g cm⁻³

^d Calculated using Scherrer's equation

Fig 6a presents the X-ray diffraction (XRD) pattern of ZIF-67 and ZIF-67@450. All the diffraction peaks of ZIF-67 agree well with the simulated patterns [31]. The XRD pattern of the product after the one-step calcination of ZIF-67 confirms that a pure Co₃O₄ spinel phase with a face-centred cubic lattice (04-016-4508) is obtained. The peaks at 19.0, 31.3, 36.9, 44.8, 59.4 and 65.2 can be indexed to the (111), (220), (311), (400), (511) and (440) planes of Co₃O₄ (04-016-4508) (Fig S4). The XRD patterns shown in Fig 4a indicate that ZIF-67 had been completely converted to Co₃O₄ with the disappearance of original pattern of ZIF-67. While the broad diffraction peaks could be caused by the nano-sized effects of Co₃O₄.

Fig 6. The chemical characterization of ZIF-67 and ZIF-67@450 (a-XRD, b-FTIR, c-Raman spectra and d-XPS)

The existence of Co_3O_4 was also verified by spectroscopic analyses. As reported previously, the Co_3O_4 with Co^{2+} ($3d^7$) and Co^{3+} ($3d^6$) located at tetrahedral and octahedral sites respectively [32]. The active modes for spinal crystallizes can be predicted via the space group theory:

$$\Gamma = A_{1g}(\text{R}) + E_g(\text{R}) + F_{1g}(\text{IN}) + 3F_{2g}(\text{R}) + 2A_{2u}(\text{IN}) + 2E_u(\text{IN}) + 4F_{1u}(\text{IR}) + 2F_{2u}(\text{IN}) \quad (4)$$

where (R) is Raman active vibrations, (IR) means infrared-active vibrations and (IN) represents inactive modes.

Fig 6c shows the Raman spectra of the ZIF-67 and ZIF-67@450. Four active Raman modes with the location at ~ 470 , 510 , 608 and 680 cm^{-1} could be distinguished, corresponding to E_g , F_{2g}^1 , F_{2g}^2 and A_{1g} modes of Co_3O_4 . All peaks are in agreement with the values of pure Co_3O_4 spinel structure yet with an average shift of $\Delta V < 5 \text{ cm}^{-1}$, which could be caused by the size effects and surface stress/strain. After calcination, the peak positions shift to low wavenumbers which is attributed to the optical phonon confinement effect in nanostructures that can cause uncertainty in the phonon wave vectors and then a downshift of Raman peaks [33].

In addition, the FTIR spectrum (Fig 6b) shows two main relatively sharp absorptions centered at ~ 580 and 660 cm^{-1} in ZIF-67@450, which originate from the fingerprint

stretching vibrations of the Co-O bond of the Co_3O_4 spinel oxides. More precisely, the observed 580 cm^{-1} band is characteristic of Co-O with Co denoting the Co^{3+} in the octahedral site while the 660 cm^{-1} band is attributable to the Co^{2+} in the tetrahedral site vibration in the spinel lattice [34]. Meanwhile, the FTIR spectrum shows no residual organic compounds after calcination process. In the original ZIF-67 sample, the absorption bands at 425 and 1580 cm^{-1} are assigned to the stretching vibration of Co-N and C-N, respectively. The bands at $1380\text{--}1450\text{ cm}^{-1}$ are associated with the entire imidazole ring stretching and the bands in the region of $800\text{--}1350\text{ cm}^{-1}$ are for the in-plane bending of the ring while those below 800 cm^{-1} are related to the out-of-plane bending [35].

XPS investigations were carried out to characterize the elemental composition of the surface of the particles as well as the chemical environment of the cobalt and oxygen atoms. It is reasonably surmised that N atoms would disappear along with the calcination process with oxygen (Fig 6d). In original ZIF-67, the N1s region spectra are deconvoluted into two components N1 (pyridinic-N, 398.2 eV) and N2 (Co-N, 399.1 eV) while the Co 2p core-level spectra are deconvoluted to display peaks of Co-N_x at 780.5 eV (Fig S5). In this structure, appropriately arranged N1 (pyridinic N) moieties with electron-donating properties are able to trap plentiful transitional metals to serve as outstanding metal-coordination (Co-N_x) active sites. Furthermore, free N1 atoms have excellent electronic storage ability to activate molecular oxygen under mild conditions [36]. After calcination, N1s peak disappears due to 2-methylimidazole ligands ring opening and conversion of ZIF-67 to Co_3O_4 (Figs 6d and Fig S5). The Co2p peaks show a slight broadening and shifting to lower binding energy, which could be deconvoluted to peaks related to the formed cobalt oxides (Fig 7a).

In the Co2p core-level spectrum of ZIF-67@450, two major peaks with binding energies of 780 and 795 eV are observed, corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ respectively (Fig 7a). The 15 eV energy difference between the Co 2p peaks is indicative of spinel Co_3O_4 [37]. It is well known that both Co^{2+} and Co^{3+} exhibit similar binding energy peaks, however, the energy splitting (ΔE) between the two levels due to spin-orbit coupling should be different for the Co^{2+} and Co^{3+} configurations with $\Delta E = 15.0\text{ eV}$ for Co^{3+} and $\Delta E = 15.7\text{ eV}$ for Co^{2+} [38]. The XPS data (Fig 7a) for the spinel Co_3O_4 , which contains both Co^{2+} and Co^{3+} ions distributed on the A and the B sites as $[\text{Co}^{2+}]_A[\text{Co}^{3+}]_B\text{O}_4$, clearly show the presence of doublet at $D1 = 779.2\text{ eV}$ and $D2 = 780.8\text{ eV}$ for the Co $2p_{3/2}$ level and a doublet for the Co $2p_{1/2}$ level centered at $D3 = 794.1\text{ eV}$ and $D4 = 796.5\text{ eV}$. The separations between the doublet peaks are $\Delta E_{D3-D1} = 14.9\text{ eV}$ and $\Delta E_{D4-D2} = 15.7\text{ eV}$, which are close to the above-mentioned values for Co^{3+} and Co^{2+} , respectively, thus confirming the presence of Co^{3+} and

Co²⁺ in Co₃O₄. The peaks at 789.3 and 804.9 eV are considered shake-up satellite peaks, which further confirms the well-defined Co₃O₄ structure [39]. Other small peaks at 783 and 795 eV may result from a chemical shift of the main spin-orbit components because of the chemical interaction between cobalt and hydroxide [40].

Similar to that of Co 2p, the O 1s of ZIF-67@450 exhibits broadening and shifting to lower binding energy due to the formation of typical metal-oxygen bond (529.6 eV) (Fig 7b). The peak at 531.4 eV could be assigned to hydroxyl group because of the possible water on or between the Co₃O₄ nanocrystals [41] and a multiplicity of defect sites [38]. These results confirm that Co=N coordination bonds in ZIF-67 were broken and the Co species were oxidized to form Co₃O₄ by calcination in the air atmosphere.

Fig 7 High resolution of Co2p (a) and O1s (b) XPS spectra of ZIF-67@450

3.3 Characterization of CoFCMs

The effect of calcination temperature on the morphologies of CoFCMs is shown in Fig S6. Results indicate that M350 and M450 can form a porous network structure while M550 shows the aggregation of Co₃O₄, which is in accordance with the powder characterization (Fig 3). Figs 8a and b show the morphologies of pristine ceramic membrane (M0) and CoFCM (M450), respectively. The membrane surface changes significantly and becomes rougher after ZIF-67-derived Co₃O₄ modification. It exhibits that Co₃O₄ particles are deposited on the surface of membrane, forming a porous network of connected polygons (Fig 8b). The CoFCM increases the complexity of pore structure which would result in a great enhancement in pollutants retention ability. EDX microanalysis was performed on the surface of M450 (Fig 8c). The element mapping images shows the Co₃O₄ has been deposited on Al₂O₃ (Fig S7). Fig 8d shows a two-layer structure image of Co₃O₄ particle immobilized on the Al₂O₃ ceramic membrane. The top layer is the Co₃O₄ particle with an estimated

thickness of 1.5-2 μm . AFM was used to characterize topography of M0 and M450. The two-dimensional amplitude retraces surface images (Figs 8 e and f) show that M450 ($R_m = 86.9$ nm) was slightly rougher compared with M0 ($R_m = 79.5$ nm), which could be caused by the formation of Co_3O_4 on membrane surface.

Fig 8. Physical properties of M0 (control) and M450 (a-FESEM of M0 surface, b-FESEM of M450 surface, c-EDX analysis of M450 surface, d-FESEM of M450 cross section, e-AFM of M0 surface, f-AFM of M450 surface)

To analyze the bonding mechanism of CoFCM, XPS tests were carried out by investigating the various elemental chemical oxidation states and the spectra are presented in

Fig 9. According to the high resolution of Al 2p peak for Al₂O₃, (Fig 9a), only Al-O bonding for Al₂O₃ is present. However, in ZIF-67@450/Al₂O₃ (Fig 9b), both Al-O for Al₂O₃ and Al-O-Co bonding are detected, showing the chemical interaction between powder Al₂O₃ and ZIF-67@450. On the other hand, the characteristic peak of O 1s in Fig 9 d was found to consists of both Al-O and Co-O. The N1s spectra in ZIF-67/Al₂O₃ shows the existence of Al-N bonding (Fig S8), which further confirmed the chemical interaction between Al₂O₃ and ZIF-67. The chemical bonding between catalyst and membrane surface can avoid catalyst aggregation as well as detachment effectively, improving the stability of CoFCM for catalytic oxidation reactions.

Fig 9. High resolution of Al 2p (a,b) and O1s (c,d) XPS spectra of Al₂O₃ and ZIF-67@450/Al₂O₃

Table 2 shows the membrane properties of M0 and CoFCMs, the weight change could be ignored because of the low amount of Co₃O₄. The pure water permeability of M450 (3024 LMHB) was slightly lower (<10% difference) than that of M0 (3323 LMHB). This shows that Co₃O₄ particle formed a very thin porous layer which only induced a minimal effect on the membrane filtration resistance (Fig 8d). Meanwhile, M450 shows a more hydrophobic surface which might be caused by the honeycomb structure on the membrane surface (Table 2). For M550, due to the highly hydrophilicity of Co₃O₄, the contact angle of M550 decreased,

resulting a higher pure water flux (Table 2). The effect of the Co_3O_4 on the pure water permeability can be evaluated by the intrinsic membrane resistance [9], R_m (m^{-1}), which are defined as:

$$R_m = (\Delta P) A t / \mu V \quad (5)$$

where ΔP is the trans-membrane pressure (Pa), A is the effective surface area of the membrane (m^2), t is the filtration time (s), μ is the kinematic viscosity of water ($1 \times 10^{-3} \text{ Pa}\cdot\text{s}$) and V is the volume of water flowing through the membrane. Before the modification, the R_m for M0 is calculated as $1.08 \times 10^{11} \text{ m}^{-1}$, while the R_m for M450 is $1.19 \times 10^{11} \text{ m}^{-1}$.

Table 2 Membrane properties of M0 and CoFCMs

Parameters	M0	M350	M450	M550
Weight (g)	1.97±0.05	1.97±0.04	1.97±0.03	1.97±0.07
LMHB ^a	3323	3121	3024	3420
R_m (m^{-1})	1.08×10^{11}	1.14×10^{11}	1.19×10^{11}	1.11×10^{11}
V ^b (cm^3)	0.2874	0.2859	0.2835	0.2839
P ^c (%)	56.5	56.2	55.7	55.8
Contact Angle ^d ($^\circ$)	68.5	70.5	80.8	67.8

^a Pure water permeability ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)

^b Pore volume (cm^3)

^c Porosity (%)

^d Tested at 0.3 s

3.4 Catalytic performance of CoFCMs

Figs 10a and b show the effect of Oxone dosage on removal of SMX over M0 and M450 in the membrane filtration system. During the filtration and catalytic oxidation processes, SMX can be retained on the membrane surface, which consists of high density of Co_3O_4 particle. When Oxone is introduced into the system, the Co_3O_4 particle acts as active sites for Oxone activation, generating ROS for SMX degradation. Once degraded, the smaller SMX intermediates can be constantly removed from the reaction zone on the membrane surface. This promotes more efficient SMX degradation. For the pristine membrane (M0), due to inactivity of Al_2O_3 , even when Oxone dosage was increased to 0.1 g L^{-1} , the SMX removal in 90 min is insignificant (less than 15%, Fig 10 a), which confirmed the negligible effect of Oxone oxidation in this process. However, with the M450 membrane, it shows

significantly increased removal efficiency with increase of Oxone dosage (Fig 10 b) because of the presence of Co_3O_4 on the membrane, which works as the catalyst to activate Oxone for radicals' generation. The enhancement of SMX degradation with increasing Oxone dosage means the active sites on membrane surface were not totally occupied by Oxone. When Oxone dosage was set as 0.01 g L^{-1} , the removal efficiency reached a plateau after 40 min, indicating that Oxone is exhausted in this system. When the Oxone dosage was increased to 0.05 g L^{-1} , the SMX removal follows a first order removal kinetics (Fig S9) and Oxone is consumed at 90 min, since no redundant Oxone was detected in the solution (Fig 10 c). The increase of reaction rate could be caused by the higher density of catalytic sites as well as the higher reactant concentrations. If Oxone dosage was further increased to 0.1 g L^{-1} , there is no significant change in the rate constant, indicating that active sites on membrane surface became the rate limited factor when Oxone dosage is in excess (i.e. more than 0.05 g L^{-1}) and the flow rate is fixed (1 mL min^{-1}). Under a certain catalyst active sites for membranes, limited Oxone-surface contact was achieved. After reaction, the residual Oxone was detected and the maximum consumption rate was calculated as $0.56 \text{ mg L}^{-1} \text{ min}^{-1}$ in this system. Other CoFCMs (M350 and M550) shows the similar kinetics of SMX degradation (Fig S10). However, the M350 is not stable considering the TGA result indicates incomplete conversion of precursor to Co_3O_4 .

Fig 10. Catalytic performance of M0 and M450 (a,b-Effect of Oxone dosage; c-

Oxone consumption ratios, d-durability of M450. Flow rate: [1 mL min⁻¹], TMP: [0.07 bar],

SMX initial concentration: [10 mg L⁻¹])

To evaluate the membrane durability, it was used for 3 operational cycles (the initial concentration of SMX was 10 mg L⁻¹ and the Oxone dosage was 0.05 g L⁻¹ based on the Oxone consumption result (Fig 10c)). Fig 10d shows a slight decrease (<10%) in the SMX removal rate with increasing operational cycles, which could be caused by the accumulative adsorption of SMX and its degradation products onto the surface of the membrane that reduced the density of active reaction sites. The detected leached cobalt ion was 0.084 mg L⁻¹ after the 3rd run, which would not cause the acute toxic effects to aquatic life [42]. After cleaning with Oxone solution (0.1 g L⁻¹) without adding SMX, more than 95% of the SMX removal efficiency could be reclaimed in the subsequent experimental run. This indicates the durability could be achieved via Oxone assisted cleaning. Meanwhile, during the filtration test, TMP was monitored at 0.07 bar with a constant flow rate of 1 mL min⁻¹, which shows the insignificant fouling property of the membrane.

Three ROS including HO·, SO₄·⁻ and SO₅·⁻ have been reported in a Co-Oxone catalytic system [43]. To verify the ROS in the CoFCM, EPR experiments were performed

using DMPO as the spin trapping agent. As shown in Fig 11a, when only Oxone solution was tested with the addition of DMPO, no peaks were detected, suggesting that no significant ROS was formed. However, in the presence of ZIF-67@450, the characteristic signals of 5,5-dimethyl-2-pyrrolidone-N-oxyl (DMPOX) with heptet were detected, which was formed from the oxidation of DMPO with strong ROS ($\text{HO}\cdot$ and $\text{SO}_4^{\cdot-}$) [44,45].

Fig 11. a) EPR spectra with DMPO as the spinning agent (Reaction condition: [Oxone] = 0.10 g L⁻¹, [SMX] = 10 mg L⁻¹, [catalyst] = 0 or 2 g L⁻¹ and [DMPO] = 100 mM) and b) The effect of scavengers towards the SMX degradation

To further validate the primary ROS in the system, quenching experiments were conducted by adding methanol and *tert*-butanol (TBA) as the scavengers. It is widely accepted that methanol with an α -hydrogen ensures the quenching of both $\text{SO}_4^{\cdot-}$ ($2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{HO}\cdot$ ($9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [46,47], while TBA without α -hydrogen reacts more easily with $\text{HO}\cdot$ ($3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), but in a slower reaction rate with $\text{SO}_4^{\cdot-}$ ($4.0 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [11]. Meanwhile, $\text{SO}_5^{\cdot-}$ is relatively inert to both methanol and TBA due to its low rate constant with alcohols ($\leq 10^3 \text{ M}^{-1} \text{ s}^{-1}$) [48]. Fig 11b depicts the inhibition effects of different scavengers on the SMX degradation in the CoFCM/Oxone system. The degradation of SMX was inhibited entirely by addition of 1 M methanol, which indicated that the ROS generated in the system were mostly quenched. The results also confirmed the insignificant contribution of $\text{SO}_5^{\cdot-}$ on the SMX decomposition. Meanwhile, 1 M of TBA has little influence on the degradation of SMX in this system, implying that $\text{HO}\cdot$ plays a smaller role in the SMX decomposition compared with $\text{SO}_4^{\cdot-}$. In the SMX degradation process, several intermediate products were detected via LC-MS-MS. The detailed analysis method is shown in Text S1 and the products are listed in Table S1. The main degradation pathway is accompanied with the cleavage of sulfonamide bond as well as the formation of nitro-SMX molecule via the electron transfer reaction, which is in accordance with the previous study [49].

Based on the above observation, the proposed reaction mechanism in CoFCM is illustrated in Fig 12. In this system, $\text{SO}_4^{\cdot-}$ is the dominant ROS responsible for the SMX decomposition and the major reactions are as follows:

Fig 12. Illustration of the proposed reaction mechanism on SMX degradation in CoFCM

4. Conclusions

A novel cobalt oxide functionalized ceramic membrane (CoFCM) was successfully prepared by a facile surface-nucleated zeolitic imidazolate framework (ZIF-67) growth method to activate Oxone for SMX degradation in a dead-end membrane filtration mode. The method to synthesize ZIF-67 as well as Co_3O_4 was optimized. The porous Co_3O_4 hollow structure was produced after one-step calcination of ZIF-67 precursor at 450°C and was distributed as a honeycomb structure on the membrane surface. The CoFCM shows a high performance on the removal of SMX as well as a high durability via Oxone-assisted cleaning. Overall, the CoFCM shows a new prospect for plentiful catalytic applications. Meanwhile,

the MOF-directed surface-nucleated growth followed by one-step calcination is a promising method for fabrication of nanocatalysts functionalized ceramic membranes.

Abbreviations

ZIF	zeolitic imidazolate framework
CoFCM	Co ₃ O ₄ nanocatalyst functionalized Al ₂ O ₃ ceramic membrane
MOF	metal organic framework
SMX	sulfamethoxazole
2-MIM	2-methylimidazole
ZIF-67@450	Co ₃ O ₄ prepared via calcination of ZIF-67 at 450°C
M0	pristine Al ₂ O ₃ ceramic membrane
M450	CoFCM prepared at 450°C

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