Facile Fabrication of MOF and Natural Polymer-derived Carbon-Aerogel with Multiscale Porosity for Persulfate Activation in Water Treatment

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Experimental

Materials

2-Methylimidazole (2-MIM), cobalt (II) acetate tetrahydrate ($Co(CH_3COO)_2$), methylene blue (MB), rhodamine 6G (Rh6G), crystal violet (CV), rhodamine B (RhB), peroxymonosulfate (PMS), p-benzoquinone (p-BQ), 2,4,6-trichlorophenol (2,4,6-TCP) were purchased from Sigma-Aldrich Korea. Ethanol (EtOH), tert-butyl alcohol (TBA), sodium hydroxide (NaOH), L-histidine (L-His), and hydrogen chloride (HCl) were obtained from SAMCHUN. Agarose (AG, type I, low EEO) with product number A6013 and CAS number 9012–36–6 was also purchased from Sigma Aldrich Korea. All reagents were used as received without further purification. Deionized water (DIW) was used in all experiments.

Fabrication of ZIF-67 nanoparticles

ZIF-67 nanoparticles were synthesized using a straightforward procedure. First, 0.5 M of 2-MIM was dissolved in 250 mL of DIW under stirring at 150 rpm. Separately, 0.05 M of $Co(CH_3COO)_2$ was dissolved in 125 mL of DIW and added to the prepared 2-MIM solution. The resulting mixture was aged for 24 h at room temperature. The synthesized ZIF-67 particles were then centrifuged at 10,000 rpm for 15 min, thoroughly washed several times with DIW, and dried at 80 ℃ for 12 h.

Fabrication of the CoNCAs

To fabricate CoNCAs, 0.66 g of ZIF-67 nanoparticles were sonicated in 30 mL of DIW until well dispersed. Subsequently, 0.33 g of AG powder, at a weight ratio of 2:1 (ZIF-67:AG), was added to the dispersion and stirred at 80 °C for 1 h. Additional samples with weight ratios of 1:1, 1:2, and 1:4 were prepared similarly, maintaining the total weight at approximately 1 g. The mixed solutions were cooled and transferred into 126.4 mm × 126.4 mm square dishes

or cylindrical molds to form hydrogel composites of desired shapes. The ZIF-67@AG (Z67@AG) hydrogels were then frozen using liquid nitrogen for 30 min and freeze-dried for 2 days. The resulting hybrid aerogels were pyrolyzed at 900 ℃ for 3 h under N_2 flow of 150 cc/min, with a heating rate of 2 ℃/min, to obtain CoNCAs.

Characterization

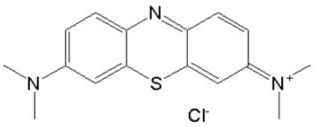
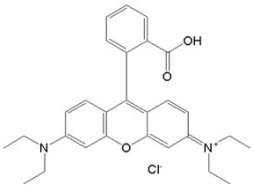
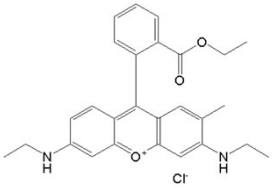
The structural surface and morphology of the samples were analyzed using field emission scanning electron microscopy (FESEM, JSM-7610F-Plus). The nanoporous structure was examined using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEM-F200). Pore size distribution and N_2 adsorption–desorption isotherms were determined using an ASAP-2020 instrument (Micromeritics Inc., USA). The chemical composition and crystal structure of the samples were characterized by X-ray diffraction (XRD) in the 5°–70° range with a step size of 2° min^{-1}, using Cu-Kα radiation (λ = 1.54 Å, 40 kV/40 mA). Raman spectroscopy (XPER RF, Nanobase, Sweden) was performed with a 532 nm excitation source. Dye concentration after catalytic reactions was measured using a UV-Vis spectrometer (SPECORD 210, Shimadzu, Germany). The leaching concentration of dissolved cobalt was measured using ICP-OES (inductively coupled plasma-optical emission spectrometer, Perkin Elmer, Optima 8300).

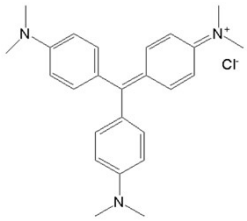
Evaluation of catalytic degradation performance

The catalytic decomposition performance of CoNCAs was evaluated using a consistent catalyst weight (0.2 g/L) to activate PMS (0.5 g/L) for the degradation of MB and 2,4,6-TCP. Additional organic dyes, including RhB, Rh6G, and CV, were used to further evaluate the decomposition efficiency of CoNCAs, as summarized in Table S1. Prior to degradation tests, CoNCA was immersed in 100 mL of 10 mg/L MB solution and stirred for 40 min to achieve adsorption-desorption equilibrium. PMS was then introduced to the solution to initiate catalytic

reactions. To study the influence of pH, 1 M HCl and NaOH were used to adjust the solution's pH. Samples of 2 mL were extracted every minute, with free radicals quenched using scavengers such as TBA and EtOH. The decomposition efficiency was calculated as C_t/C_0 (C_0: initial concentration of MB, C_t: remaining concentration of MB, t: certain time), and MB concentrations were quantified with a UV-Vis spectrometer. Cyclic tests were conducted under the same conditions to assess catalyst reusability, involving repeated degradation and recovery processes through pyrolysis. To evaluate the long-term stability of the catalyst, CoNCA was soaked in deionized water from 10 minutes to 7 days before the test, and the water was collected and measured for Co leaching test via ICP analysis. All experiments were performed at least three times to minimize experimental errors and ensure reproducibility.

Table S1. The information of several organic pollutants as catalyzed models

Organic pollutant	Structural formula	Chemical formula	Molecular weight (g/mol)
Methylene blue (MB)		$C_{16}H_{18}ClN_3S$	319.86
Rhodamine B (RhB)		$C_{28}H_{31}ClN_2O_3$	479.02
Rhodamine 6G (Rh6G)		$C_{28}H_{31}N_2O_3Cl$	479.02

Crystal violet (CV)		$C_{25}N_3H_{30}Cl$	407.97

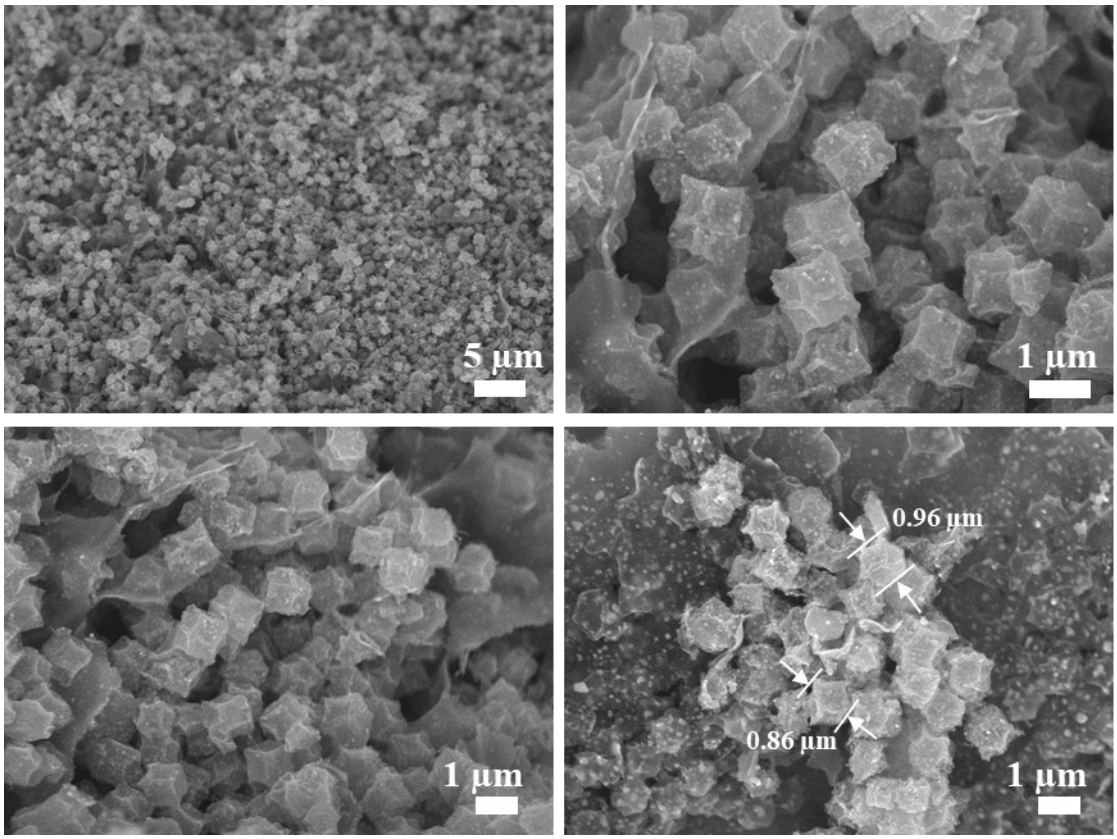


Fig. S1. SEM images of low magnification of CoNCA(2:1)

Table S2. The summary of BET surface areas, total pore volumes and average pore diameters of CoNCAs

Samples	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
CoNCA (2:1)	158.32	0.1963	4.9602
CoNCA (1:1)	168.08	0.2162	5.1442
CoNCA (1:2)	207.02	0.2037	3.9362
CoNCA (1:4)	276.55	0.1895	2.7406

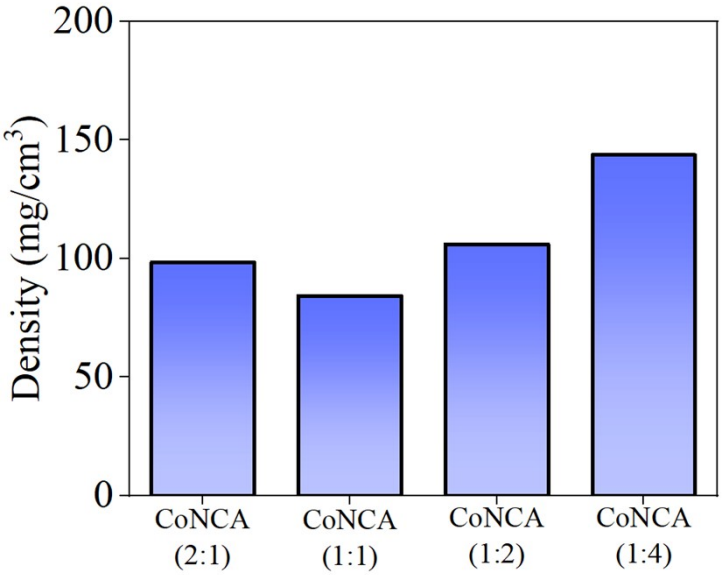


Fig. S2. Densities of CoNCA as a function of ZIF-67 and AG ratio.

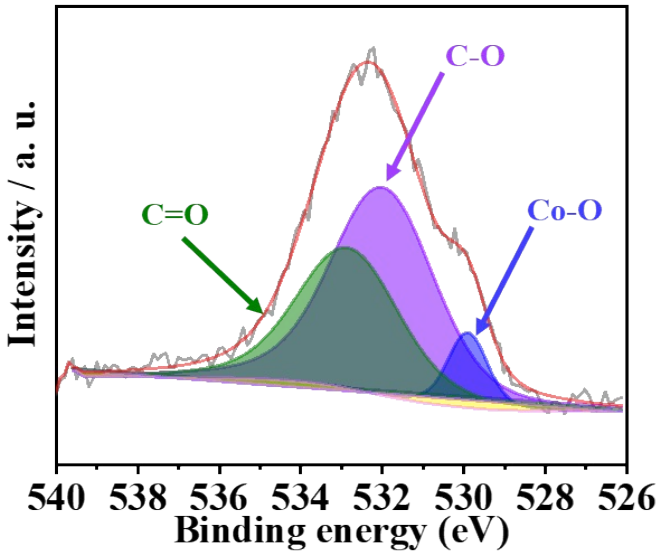


Fig. S3. The high resolution of O 1s spectra of CoNCA(2:1)

Table S3. Atomic percent of element obtained from XPS.

Samples	C 1s (%)	Co 2p (%)	N 1s (%)	O 1s (%)
CoNCA (2:1)	92.12	1.48	1.13	5.27
CoNCA (1:1)	92.82	1.2	1.26	4.72

CoNCA (1:2)	92.81	0.95	1	5.24
CoNCA (1:4)	95.66	0.46	1.06	2.82

Table S4. Comparison of different catalysts for the degradation of Methylene blue by PMS activation.

Catalyst	Pollutant	Reaction conditions	Degradation efficiency (%)	Time (min)	Refs.
Co@N-PC	MB (30 mg/L)	[Catalyst] = 0.01 g/L, [PMS] = 0.15 g/L, pH = 6.3, T = 25 ℃	100	30	[1]
FeCo-BDC	MB (30 mg/L)	[Catalyst] = 0.03 g/L, [PMS] = 0.31 g/L, pH = N.A., T = 25 ℃	100	15	[2]
$MnCo_2O_{4.5}$ NPs	MB (20 mg/L)	[Catalyst] = 0.2 g/L [PMS] = 0.5 g/L, pH = N.A., T = 25 ℃	96.7	20	[3]
Fe^0/Fe_3O_4/biochar	MB (20 mg/L)	[Catalyst] = 0.3 g/L, [PMS] = 0.4 g/L, pH = 7, T = 25 ℃	99.9	60	[4]
CaO	MB (20 mg/L)	[Catalyst] = 0.3 g/L, [PMS] = 0.9 g/L, pH = 7.0 T = 25 ℃	97.1	20	[5]
$CoMoO_4/CoFe_2O_4$	MB (20 mg/L)	[Catalyst] = 0.03 g/L, [PMS] = 0.3 g/L, pH = 9.4, T = 30 ℃	99.5	20	[6]
β-FeOOH@MnO_2	MB (20 mg/L)	[Catalyst] = 0.5 g/L, [PMS] = 0.03 g/L, pH = 7.0, T = 25 ℃.	99	20	[7]
CoNCA	MB (20 mg/L)	[Catalyst] = 0.2 g/L, [PMS] = 0.5 g/L, pH = 7.0, T = 25 ℃	97	8	This work

Table S5. Comparison of various catalysts for the degradation of methylene blue.

Catalyst	Methods	Pollutant	Degradation efficiency (%)	Time (min)	Refs.
Pd-doped TiO_2	Photocatalysis	MB (20 mg/L)	87.8	120	[8]
MIL-88A@TiO_2	Photocatalysis	MB (20 mg/L)	97	8	[9]

Activated carbon bead	Adsorption	MB (20 mg/L)	96.7	600	[10]
$MgFe_2O_4$	Adsorption	MB (10 mg/L)	98.0	30	[11]
TiO_2 nanotube array	Electrochemical oxidation	MB (20 mg/L)	100	90	[12]
Graphene oxide/alginate	Electro-adsorption	MB (50 mg/L)	90.37	30	[13]
CoNCA	SR-AOP	MB (20 mg/L)	97	8	This work

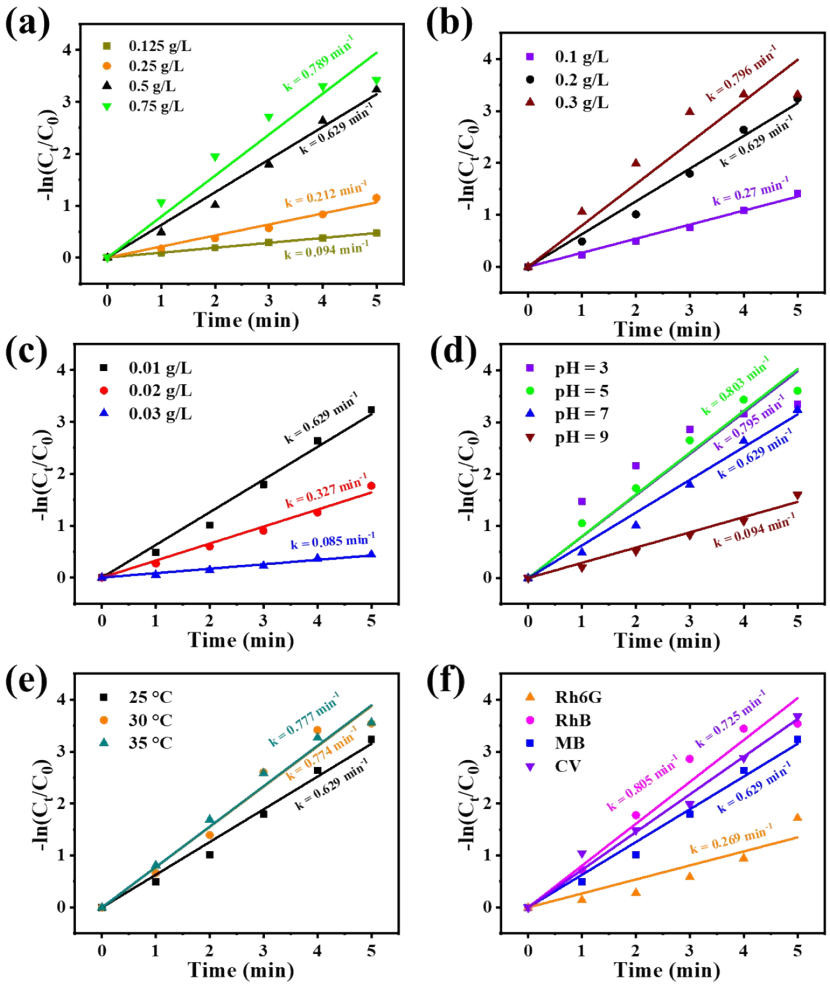


Fig. S4. The kinetic rate constants of (a) PMS dosage, (b) catalyst dosage, (c) MB concentration, (d) pH, (e) reaction temperature, and (f) various organic pollutants in the CoNCA/PMS system.

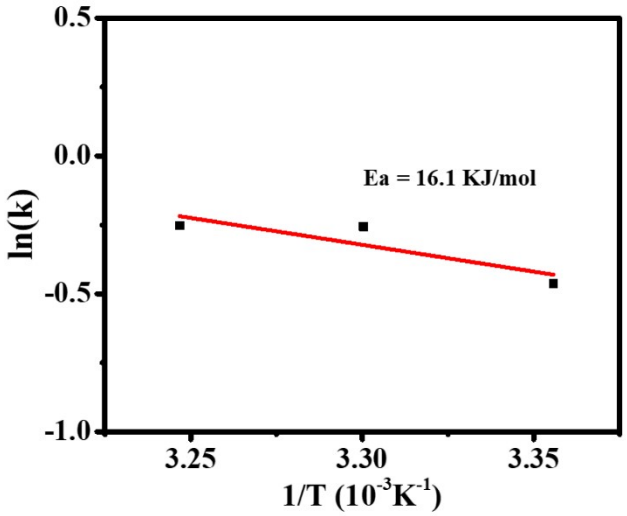


Fig. S5. Arrhenius plot of ln(k) vs. 1/(T×10^{-3}) in the CoNCA/PMS catalytic system.

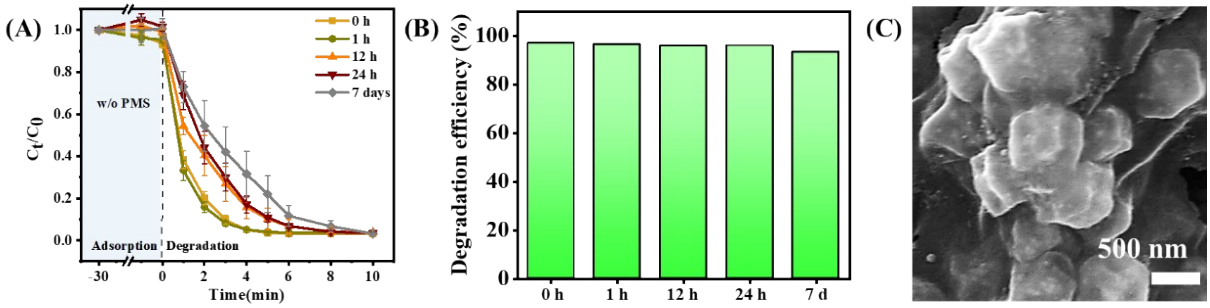


Fig. S6. Degradation (A) test and (B) efficiency of CoNCA (1:1) as a function of immersion time. (C) SEM image of CoNCA (1:1) after immersion in DIW for 7 days.

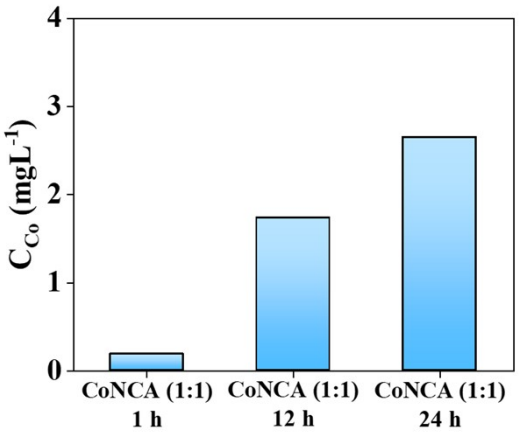


Fig. S7. Concentration of the leached Co ions of CoNCA (1:1) as a function of immersion time.

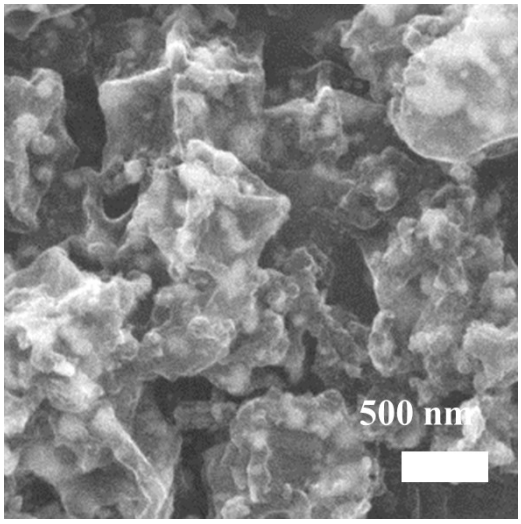


Fig. S8. SEM images of CoNCA (2:1) after grinding.

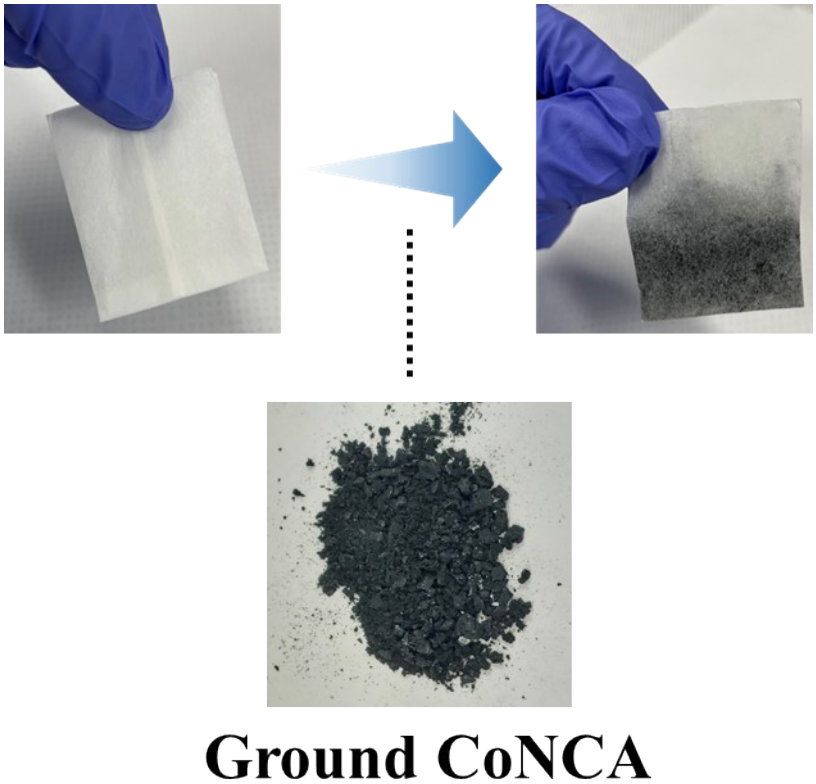


Fig. S9. Tea bag demo filter for practical application using CONCA.

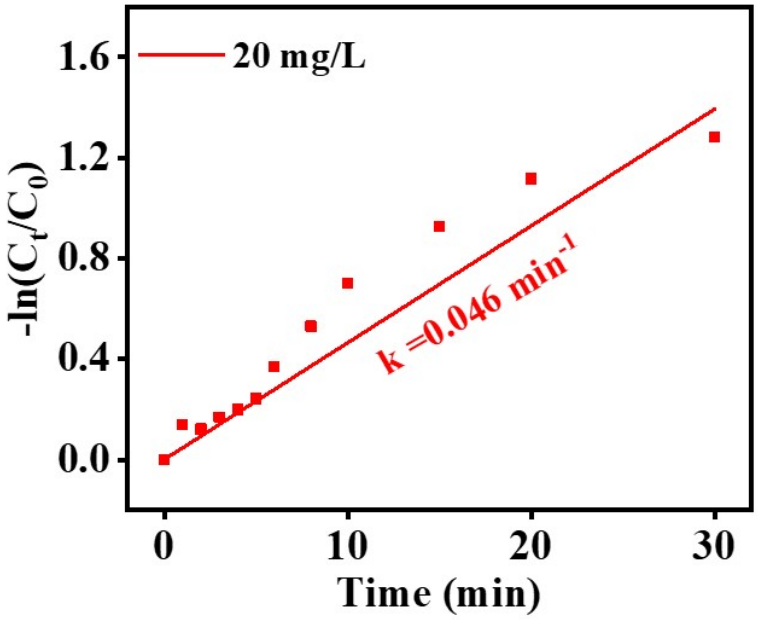


Fig. S10. Kinetic rates of 2,4,6-TCP degradation in CoNCA within 30 min. (Reaction condition: [Catalyst dosage] = 0.2 g/L, [2,4,6-TCP] = 20 mg/L, [PMS dosage] = 0.5 g/L, T = 25°C, and Initial pH = 7).

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