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Pyridyl-containing polymer blends stabilized iron phthalocyanine to degrade sulfonamides by enzyme-like process

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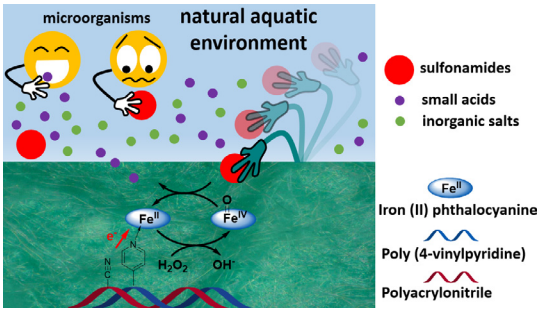
HIGHLIGHTS

- FePc-P4VP/PAN NFs were prepared as a biomimetic catalytic system by mimicking enzymes.
- The coordination structure of the FePc-pyridine was to mimic the active sites of the enzyme.
- The PAN molecular chain intertwined with P4VP to mimic the protein skeleton structure of the enzyme.
- FePc-P4VP/PAN NFs are efficient and stable for sulfonamides degradation.
- Transformation products of SQX were finally transformed to small molecule acids.

GRAPHICAL ABSTRACT



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ABSTRACT

Self-purification of an aquatic environment occurs through the enzymatic functioning of microorganisms; however, nowadays, pollutant release has exceeded the self-purification capacity in the aquatic environment, and some antibiotics, such as sulfonamides, can inhibit microorganism reproduction. Therefore, to enhance the self-purification capacity in an aquatic environment, we developed a biomimetic catalytic system by mimicking the catalytic mechanism of enzymes. This system is based on iron phthalocyanine coordinates on poly (4-vinylpyridine)/polyacrylonitrile nanofibers. The resulting coordination structure was characterized by digital microscopy, X-ray photoelectron spectroscopy etc. The catalytic system was highly active and stable for sulfonamide degradation, even in the presence of inorganic salts at neutral pH. Gas chromatography–mass spectroscopy and high-definition electrospray ionization mass spectrometry proved the heterolytic cleavage of the peroxide O—O bond to generate high-valency iron-oxo species instead of homolytic cleavage to generate ·OH in a catalytic system. Detailed density functional theory calculations, ultra-performance liquid chromatography and high-definition mass spectrometry showed that the aromatic compounds were degraded to small acids by the electrophilic attack of iron-oxo active species.

1. Introduction

Sulfonamide and its derivatives are used widely in the prevention and treatment of diseases in humans and in animal husbandry and aquaculture [1–5]. Large fractions of sulfonamides from wastewater of animal farms, aquafarms and hospitals that are excreted unaltered or as metabolites have been detected in aquatic and soil environments [6–9]. In an aquatic ecosystem, microorganisms utilize enzyme to decompose organic pollutants [10];

Abbreviations: OH, hydroxyl radicals; MPs, metalloporphyrins; MPcs, metallophthalocyanines; P4VP, poly (4-vinylpyridine); PAN, polyacrylonitrile; NFs, nanofibers; FePc, iron phthalocyanine; P4VP/PAN NFs, nanofibers of P4VP mix with PAN; FePc/PAN NFs, nanofibers of FePc mix with PAN; FePc-P4VP/PAN NFs, P4VP/PAN NFs-supported FePc; SQX, sulfaquinoxaline; DFT, density functional theory; EPR, electron paramagnetic resonance; UPLC, ultra-performance liquid chromatography; HDMS, high-definition mass spectrometry; XPS, X-ray photoelectron spectroscopy; ICP, inductively-coupled plasma.

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however, with an increase in sulfonamide emissions, the proliferation of microbial communities have been inhibited [11], which has resulted in a deteriorating water quality. Sulfonamide residuals can be accumulated in organisms through the food chain, and exhibit potential toxicity to human beings and aquatic organisms when present as components of complex mixtures [12,13]. In recent years, some physical-, chemical- and biological-treatment methods such as activated carbon adsorption, advanced oxidation technologies based on hydroxyl radicals (·OH) and enzyme biocatalysts, have been developed to play a significant role in wastewater treatment [14–20]. However, above methods face challenges for application in a natural aquatic environment because of disadvantages such as contaminants are enriched in and need to be treated further [21], a non-selectivity of ·OH in the presence of high background constituents in a natural aquatic environment [22] and the perishability of enzymes in a practical application [23]. Therefore, the development of a benign ecosystem and effective, cost-effective and environmentally sustainable catalytic systems is critical.

Biological enzymes, such as cytochrome P450 and horseradish peroxidase, generally exhibit high efficiency in some oxidation reactions in vivo because their metalloporphyrins (MPs) catalytic structures utilize O_2 or H_2O_2 to oxidize substrates under mild conditions [24–27]. Metallophthalocyanines (MPcs) have attraction as catalysts because they are similar in structure to MPs complexes, and they are cost effective, simple mass preparation and stable chemical structure [28]. However, MPcs and their derivatives in aqueous solution result in catalytically inactive dimers [29] and secondary pollution in environmental treatment [30]. To overcome the drawback of homogeneous MPcs catalysts, the supported catalytic systems have been proposed [28]. In previous studies, immobilization of MPs on various supports is an effective way to improve the catalytic activity and stability, such as carbon nanotubes [31–33], activated carbon fibers [34,35], mesoporous carbon [36], cellulose [37–39] and polymers [40,41]. Among the MPc-supported catalysts that activate H_2O_2, homolytic cleavage of the peroxide O—O bond occurs to generate ·OH as the dominant active species to eliminate organic contaminants. In competition with the homolytic cleavage process, heterolytic cleavage of the peroxide O—O bond to generate high-valence metal-oxo active species has been identified as an active species in key enzymatic processes [42,43]. Hence, some studies have imitated the essentials of natural enzymes (e.g., the active center of P450 coordinates the S atom of cysteine with the Fe atom of heme) to generate a high-valence metal-oxo active species by H_2O_2 or O_2 activation. This occurs, for example, in the extra introduction of hydrosoluble axial fifth ligands in MPc-covalently supported catalysts [39] or in the synthesis of N-bridged diiron phthalocyanine [44]. However, the covalent fixation approach often requires a preliminary modification of the support and/or the MPcs [28].

Poly (4-vinylpyridine) (P4VP) is applied extensively in the formation of metallic polymer compounds because metal atoms can be bonded to nitrogen atoms of pyridinyl moieties [45,46]. P4VP usually acts as a block polymer [47,48] or as a polymer coating on other materials [49]. In this study, the mixture of P4VP and polyacrylonitrile (PAN) as low-cost and easily available polymeric supports via electrospinning was used to prepare P4VP/PAN nanofibers (NFs). Iron phthalocyanine (FePc) molecules were immobilized on P4VP/PAN NFs by coordination between FePc and P4VP to obtain FePc-P4VP/PAN NFs. The fibrous grade of the polymer was confirmed and characterized by digital microscopy (DM), ultraviolet visible spectrophotometry (UV–vis) and UV–vis diffuse reflection spectre at the macro level and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) at the micro level, as an important factor for the catalysts based on P4VP. Sulfaquinoxaline (SQX) was used as a model sulfonamide to test the activity and stability of the catalyst system in the presence of inorganic salts at neutral pH. The generated active species were determined by electron paramagnetic resonance (EPR) tests, classical quenching tests, GC–MS, high-definition ESI-MS and density functional theory (DFT) calculation. The degradation pathway of SQX was studied through Ultra-performance liquid chromatography (UPLC) and high-definition mass spectrometry (HDMS).

2. Material and methods

2.1. Materials

Poly (4-vinylpyridine) (P4VP average molecular weight 60,000) was purchased from Sigma-Aldrich. Anhydrous tetrahydrofuran (THF) was purchased from Gaojing Fine Chemical Industry Co., Ltd., China. SQX, sulfadiazine, sulfamerazine, sulfametoxydiazine, sulfachlorpyridazine, sulfamethoxazole were purchased from Dr. Ehrenstorfer GmbH, Germany. Isonicotinic acid (INA) was purchased from Aladdin Industrial Corporation. Milli-Q water was used. All other chemicals were described in previous study [41].

2.2. Preparation of P4VP/PAN nanofibers (P4VP/PAN NFs)

P4VP (6 wt% P4VP vs. DMF) and PAN (6 wt% PAN vs. DMF) were dissolved in anhydrous DMF. Detailed method is referred to previous study [41].

2.3. Preparation of FePc /PAN nanofibers (FePc /PAN NFs)

FePc/PAN NFs were prepared as described previously [41].

2.4. Preparation of FePc-P4VP/PAN nanofibers (FePc-P4VP/PAN NFs)

FePc (10 wt% FePc vs. P4VP/PAN NFs) dissolved in anhydrous THF and P4VP/PAN NFs were added to a flask, and the flask was transferred to an oil bath with a magnetic stirrer and refluxed at 70 °C for 12 h. The reaction products were washed with THF and distilled water several times until the filtrate was colorless. The final FePc-P4VP/PAN NFs were obtained by freeze-drying. A schematic representation of the FePc-P4VP/PAN NFs evolution process is shown in Fig. S1. The content of FePc in FePc-P4VP/PAN NFs based on inductively-coupled plasma (ICP) results (Varian 720-ESICP-OES) (Fig. S2), which was 1.625×10^{-4} mol/g.

2.5. Characterization

The chemical structure of P4VP/PAN NFs, FePc-P4VP/PAN NFs and FePc powders was analyzed by ATR-FTIR spectroscopy (Nicolet 5700). The XPS parameters were describe in the literature [33]. A digital microscope (DM, VHX-2000, Keyence, Japan) and field emission scanning electronic microscope (ULTRA-55) were used to study the catalyst. UV–vis was performed using a UV-2550 spectrophotometer (Shimadzu, Japan) and UV–vis diffuse reflection spectra were recorded using a UV–vis spectrometer (1J1-0015, HITACHI).

2.6. Degradation experiments

All reactions were executed in a glass sample beaker that contained 1 g/L catalytic NFs with an initial substrate concentration of 0.02 mM with H_2O_2 (10 mM) as oxidant. The temperature and oscillation speed were controlled by using a water-bathing constant temperature vibrator (DSHZ 300A, Taicang, Jiangsu). Information for sample preparation and measurement using