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Binuclear metallophthalocyanine supported on treated silk fibres as a novel air-purifying material

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Abstract

Two kinds of water-soluble metallophthalocyanines, binuclear phthalocyaninecobalt(II) (Co_2Pc_2) and binuclear phthalocyanineiron(III) (Fe_2Pc_2), have been investigated as catalysts for the oxidation of 2-mercaptoethanol (MEA). In aqueous solution, Co_2Pc_2 exhibited higher catalytic activity than Fe_2Pc_2 at pH 11 and 25 °C. Furthermore, synergistic effect had been found when two catalysts were mixed at molar ratio of 1:1, which was deeply discussed. To make best use of such perfect catalytic oxidation performance, a new supporting method was introduced to prepare the novel air-purifying material, binuclear metallophthalocyanine fibres (Mt_2Pc_2F). Mt_2Pc_2F could be used to eliminate efficiently the malodors of methanthiol and hydrogen sulfide by catalytic oxidation reaction.

Keywords: Binuclear metallophthalocyanine; Catalytic oxidation; Synergistic effect; Silk fibres; Air-purifying material; Malodors

1. Introduction

Indoor air quality has become one of the most serious environmental concerns since a person spends about 22 h indoors on a daily basis [1,2]. Indoor air contains different types of air pollutants, including Volatile Organic Compounds (VOC) emitted from various sources, e.g. building materials, paints and other consumable products [3]. These pernicious gases have resulted in various diseases in humans, such as headache, nausea, eye irritation, sore throats, dizziness and fatigue [4,5]. Therefore, various treatment methods for eliminating indoor air pollutants have been extensively studied, including physical, chemical, biological and photocatalytic methods [6–8]. Traditional physical adsorbents such as charcoal and filtering materials have successfully reduced the concentration of pernicious indoor gases in some cases. However, the effectiveness of these removal materials is limited for a short period due to their removal capacities, and even they could not remove these pernicious indoor gases completely.

Environmental and safety regulations have become the strong driving force for the development of green technologies that avoid the use of toxic chemicals and minimize the generation of waste. Biotreatment is a promising technology for the abatement of pernicious indoor gases. Natural enzymes as biological catalysts are characteristic of high speed, specificity, sensitivity and mild reaction conditions, but they have no high temperature resistance and cannot be used in organic solvent. Therefore, an exploration for mimic enzyme has evoked a great deal of interests. Till date, the mimesis of cytochrome P-450 has mainly been focused on metalloporphyrin compounds since heme is the active center of P-450 [9,10]. However, synthetic metalloporphyrins often degrade during the catalytic process. One way of circumventing this problem has been to create a more resistant porphyrin ring through ring substitution using electron withdrawing axial ligands [11,12].

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As an analogue to porphyrin, phthalocyanine compounds have also been widely used as an oxidase-like enzyme, mainly due to their chemical, optical and thermal stability [13,14]. What's more, metallophthalocyanine complexes are often more easily prepared than metalloporphyrins. In principle, metallophthalocyanines have shown great catalytic activity under ambient conditions and high oxidants, acids, and alkalis resistance [15].

Natural enzymes are macromolecules. The macromolecules offer ideal frames for construction of versatile and robust catalytic sites. In comparison with natural enzymes, most artificial enzymes are small molecules. Therefore, one limitation of these catalysts is that they are inconvenient to be used in some fields because they are generally available only as powder or in solution. An efficient strategy for their practical use might be to attach them to a suitable support material.

Several types of supports have been used for this purpose, such as charcoal, organic polymers silica, zeolites, etc. [16–18]. Comparing to these materials, fibres may be the ideal candidates because they are easy to handle and provide a large contacting surface for harmful gases. China is very rich in silk, and there is a large quantity of waste silk that can be exploited. Silk fibres (SF) composed of 18 kinds of amino can be treated structurally by many chemical and physical methods. In this paper, two kinds of water-soluble binuclear metallophthanines (Mt_2Pc_2), binuclear phthalocyanineiron(III) (Fe_2Pc_2) and binuclear phthalocyaninecobalt(II) (Co_2Pc_2), were prepared, and both of them had perfect catalytic activity on 2-mercaptoethanol (MEA). Higher catalytic activity can be obtained when Fe_2Pc_2 and Co_2Pc_2 were mixed in equal molar quantity in aqueous solution. To take advantage of such excellent properties in practical way, Mt_2Pc_2 was supported on cationic silk fibres (CSF) to obtain air-purifying materials (Mt_2Pc_2CSF). Such materials showed high performance to eliminate CH_3SH and H_2S by catalytic oxidation reaction.

2. Experimental

2.1. Reagents and instruments

Pyromellitic anhydride and ammonium molybdenum were purchased from Shanghai Pharmaceutical Co., Ltd. (Shanghai, China). SF, marseilles soap, cationic agent MA (Scheme 2) and levelling agent Peregalo were donated by Dying and Finishing Lab in Zhejiang Sci-Tech University. Methanthiol (20%, w/w) was obtained from the Shanghai Research Institute of Flavour and Fragrance Industry. Hydrogen sulphide was prepared by reaction of sodium sulphide solution (20%, w/w) with phosphoric acid (10%, w/w). All the other solvents and reagents were of analytical grade and used without further purification.

PHS-3C precise pH meters (Shanghai REX instrument factory), U-3010 UV–vis Spectrometer (Hitachi), FT-IR Spectrometer (Perkin Elmer Spectrum one) and elemental analysis apparatus (Carlo-Erba 1106) were used to confirm the structure of Mt_2Pc_2. Precise gas detector tubes (Gastec Company in Japan) were directly used to test the concentrations of the odors.

2.2. Synthesis of binuclear metallophthalocyanine derivatives

According to the literatures [19], two kinds of planar binuclear metallophthalocyanines were synthesized by phenylanhydride–urea route, and their reactive processes are shown in Scheme 1. The products were purified to obtain Co_2Pc_2 and Fe_2Pc_2 [20], and their final yields were 24.59% and 19.12%, respectively.

2.3. Measuring the catalytic ability of binuclear metallophthalocyanine on MEA

The catalytic rate of the oxidation on MEA in aqueous solution was evaluated on the basis of the consumption of oxygen, measured using a self-made gas burette. The whole process was carried out at constant temperature.

2.4. Preparation of Mt_2Pc_2F

Two grams of SF was treated in the aqueous solution of MA ($50\ g\ L^{-1}$), Na_2OH ($15\ g\ L^{-1}$) and Permeater JFC ($2\ g\ L^{-1}$), with bath ratio 1:50, at 60 °C for 60 min. The SF was then washed with hot water, acetic acid solution ($2\ g\ L^{-1}$) and cool water, respectively, obtained cationic silk fibres (CSF). SF or CSF was put into the solution of Mt_2Pc_2 and levelling agent Peregalo (pH 4.5), supported 0.8% (w/w) Mt_2Pc_2 by controlling reaction conditions, washed with distilled water and dried in oven at 60 °C to obtain Mt_2Pc_2SF and Mt_2Pc_2CSF.

It was mentioned above that the carboxyl, hydroxyl and amino, etc. on SF could react with MA. Taking carboxyl for example, the reaction process was illustrated in Scheme 2. SF was initially treated with MA in order to provide a bridge group for the Mt_2Pc_2. The cationic tetra-alkylammonium (MA) on CSF had a strong electrostatic attraction to the dissociated carboxyl groups on Mt_2Pc_2 molecule. Thus, Mt_2Pc_2 can become bound to CSF to provide the deodorant package. The whole process of treatment and dyeing for SF is given in Scheme 2.

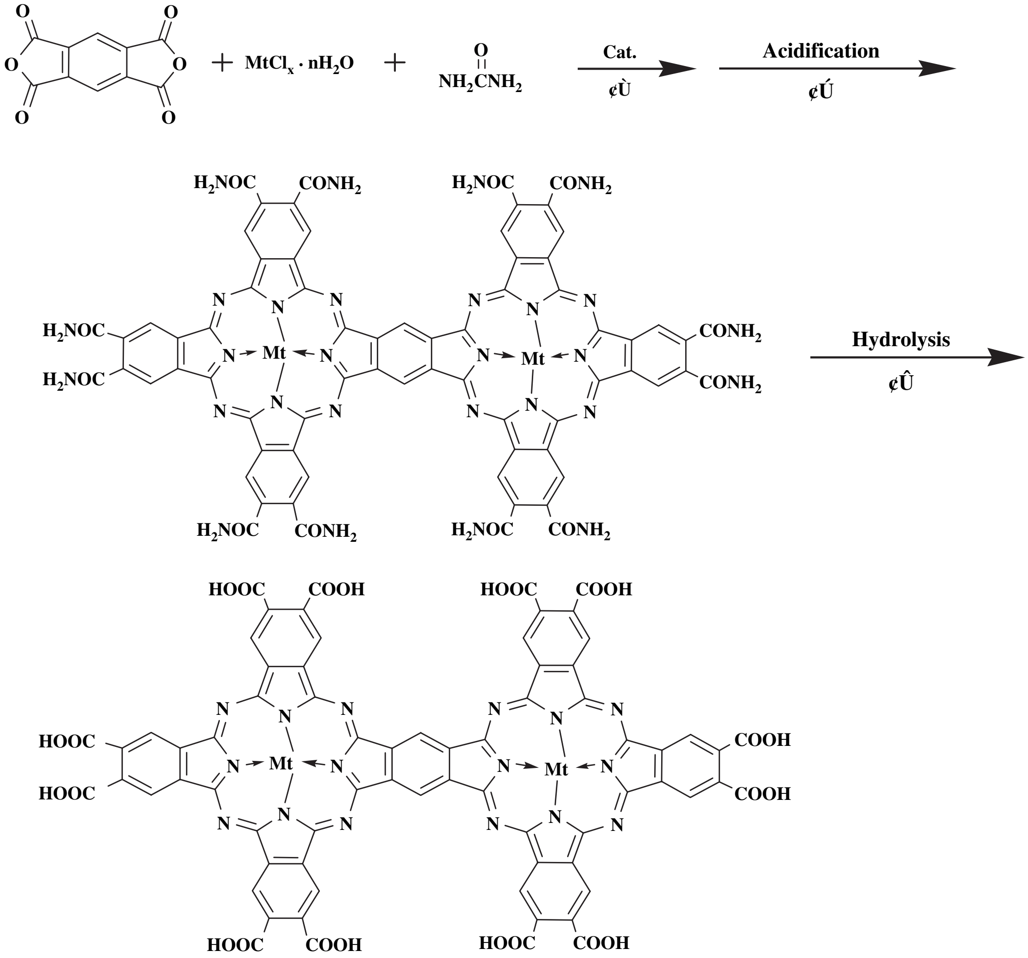
2.5. Measuring the deodorant performance of Mt_2Pc_2F

Two grams of Mt_2Pc_2F was suspended in a 5 L flask, in which quantitative malodors were injected, and then the concentrations of malodors were measured by corresponding gas detector tubes. The deodorant ability of Mt_2Pc_2F on malodors was determined by the concentration change.

3. Results and discussion

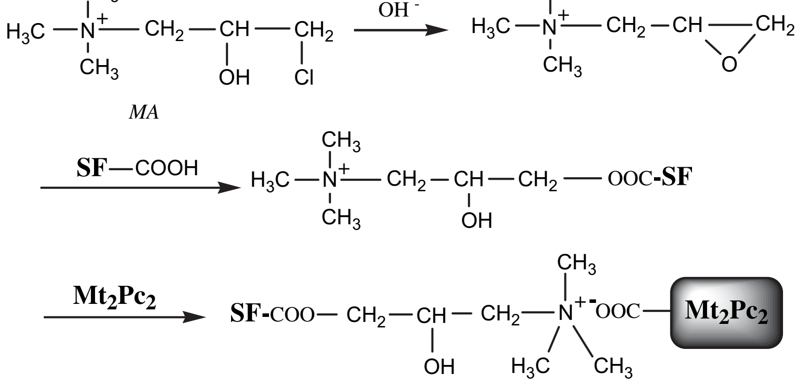
3.1. Characterization of binuclear metallophthalocyanine

The results of the purified Co_2Pc_2 and Fe_2Pc_2 for elemental analysis are given as follows: Calcd. for Co_2Pc_2, $C_{70}H_{26}O_{24}N_{16}Co_2\cdot 4H_2O$: C, 50.49%; H, 2.06%; N, 13.46%.



Scheme 1. The reactive scheme for preparing binuclear metallophthalocyanine [Mt = Co(II), Fe(III)].

Found: C, 50.12%; H, 2.10%; N, 13.49%. Calcd. for Fe_2Pc_2, $C_{70}H_{26}O_{24}N_{16}Fe_2 \cdot 4H_2O$: C, 50.68%; H, 2.07%; N, 13.51%. Found: C, 50.32%; H, 2.11%; N, 13.56%. The IR spectra of synthetic Co_2Pc_2 and Fe_2Pc_2 were shown in Fig. 1. The absorption peaks at 1261, 1066, 796, and 746 cm^{-1} in Fe_2Pc_2 were assigned to phthalocyanine, and the strong absorption peak at 1704 cm^{-1} was due to the carboxylic acid groups in Fe_2Pc_2. The absorption peaks at 1134, 1093, 771, and 745 cm^{-1} in Co_2Pc_2 were assigned to phthalocyanine, and the strong absorption peak at 1704 cm^{-1} was due to the carboxylic acid groups in Co_2Pc_2. Synthesized products were further confirmed according to the literatures [21].



Scheme 2. Mt_2Pc_2 supporting on SF treated by MA.

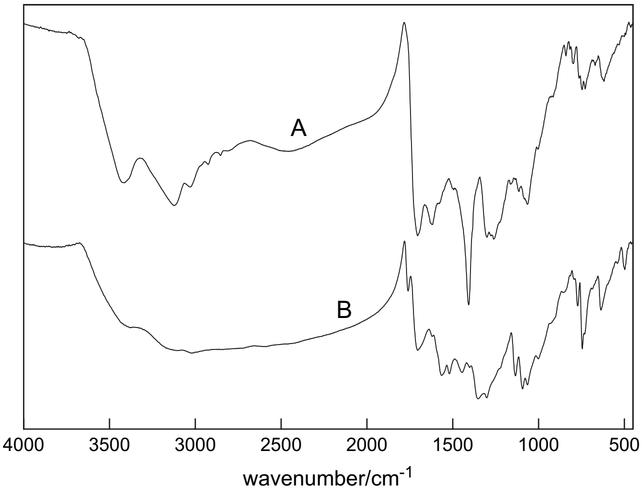


Fig. 1. IR spectra of Mt_2Pc_2 (A, Fe_2Pc_2; B, Co_2Pc_2).

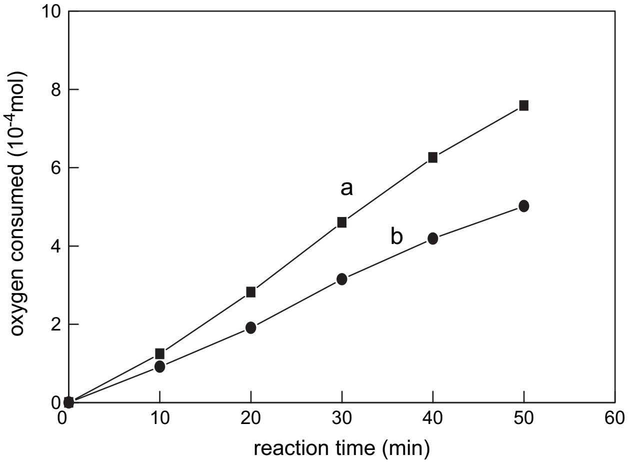


Fig. 3. Comparison of catalytic oxidation activity between Co_2Pc_2 and Fe_2Pc_2 on MEA ($T = 25$ °C, pH = 11, $[O_2]_0 = 8.59 \times 10^{-3}$ mol L^{-1}, a: Co_2Pc_2 and b: Fe_2Pc_2).

3.2. Catalytic activity of binuclear metallophthalocyanine in aqueous solution

Mt_2Pc_2 (150 mL, 1.0×10^{-5} mol L^{-1}) aqueous solution was placed in the airtight system, and then 10 mL MEA (20%, w/w) was added. The initial reaction velocity, $V_o = -d[O_2]/dt$ (mol^{-1} s^{-1}), was taken from the slope of the oxygen consumption in the reaction system. The dependence of V_o on pH in oxidation reaction is shown in Fig. 2. V_o increased as pH rose from 5 to 11 and reached the maximum at pH 11, but it drastically decreased above pH 11. This behavior was considered to be attributable to the dissociation of RSH, and RS^- was easy to coordinate with the central metal ion in phthalocyanine below pH 11. The excess OH^- above pH 11 hindered the coordination of RS^- with the central metal ion in phthalocyanine, leading to a fall in catalytic ability. In addition, it could be observed that Co_2Pc_2 had higher catalytic ability than Fe_2Pc_2 from Fig. 2. To further verify the phenomenon, the catalytic ability of Fe_2Pc_2 and Co_2Pc_2 was measured at pH 11 and 25 °C, as shown in Fig. 3. The results showed that the catalytic ability of Co_2Pc_2 was higher than that of Fe_2Pc_2, which agreed well with the results in Fig. 2.

An interesting phenomenon was observed that Co_2Pc_2 and Fe_2Pc_2 mixture ($CoFePc_2$) showed higher catalytic ability on MEA than individual Co_2Pc_2 and Fe_2Pc_2 under the same conditions, i.e. pH 11 and 25 °C, in aqueous solution (Fig. 4), and even the catalytic ability was the best at the molar ratio 1:1 of Co_2Pc_2 and Fe_2Pc_2. The reason for higher catalytic ability of the mixture attributed to their synergistic effect. The mechanism [22,23] of catalytic oxidation on mercaptan (RSH) by metallophthalocyanine is shown in Fig. 5. The central metal ion in phthalocyanine coordinates with RS^- given by RSH, which then combines with O_2 molecule to form ternary complex, and the single-electron transfers from RS^- to O_2 through a central metal in phthalocyanine ring, forming the radicals $RS^{\bullet}$ and $O_2^{\bullet -}$. The single-electron transfer process is the rate-determining step in the oxidation reaction [24]. Following

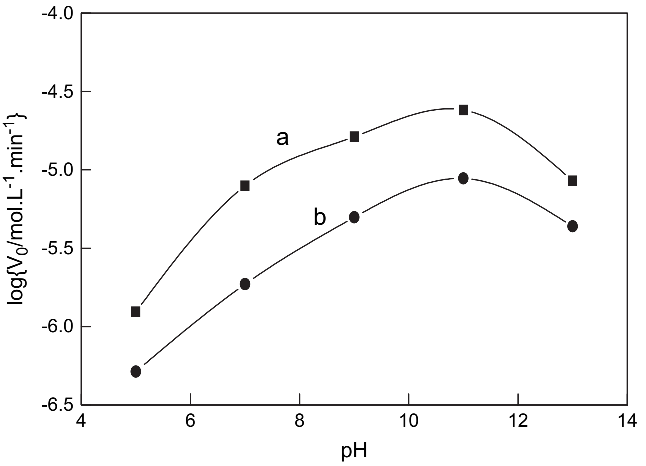


Fig. 2. Effect of pH on the catalytic activity of Co_2Pc_2 and Fe_2Pc_2 to oxidize MEA ($T = 25$ °C, $[O_2]_0 = 8.59 \times 10^{-3}$ mol L^{-1}, a: Co_2Pc_2 and b: Fe_2Pc_2).

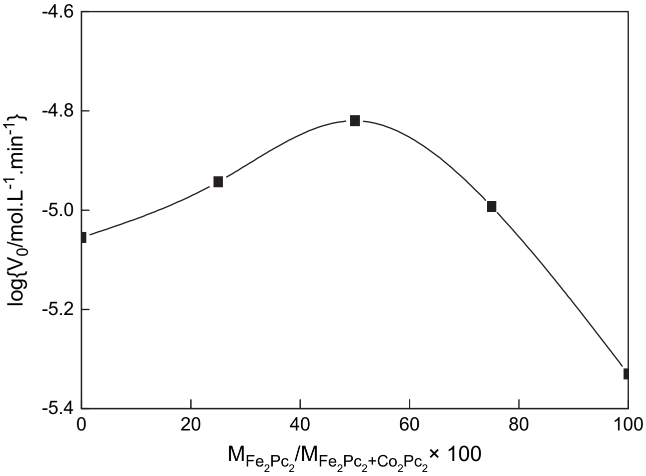


Fig. 4. Dependence of the Co_2Pc_2 and Fe_2Pc_2 ratio on the catalytic activity to oxidize MEA ($T = 25$ °C, pH = 11, $[O_2]_0 = 8.59 \times 10^{-3}$ mol L^{-1}).

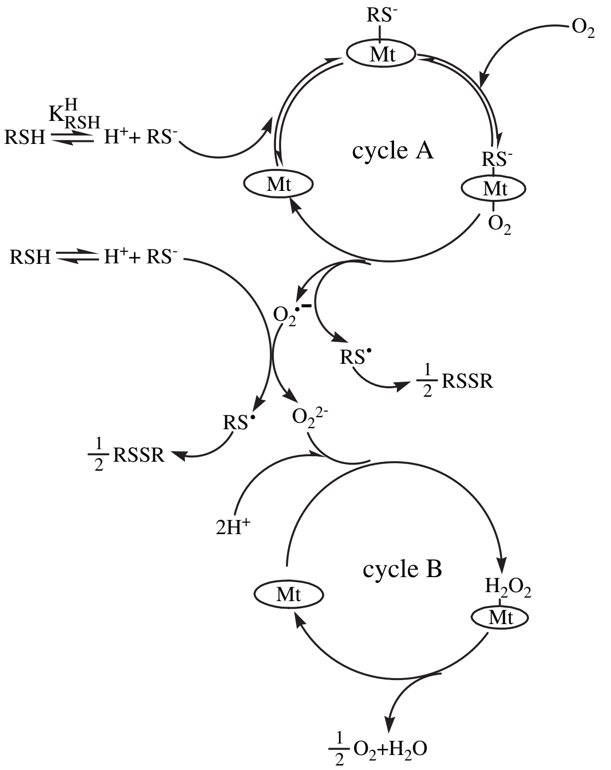


Fig. 5. Mechanism of catalytic oxidation of mercaptan (RSH) by metallophthalocyanine.

the rate-determining step, the succeeding steps are rapid: $O_2^{\bullet -}$ reacts with the other RS^-, forming RSSR and O_2^{2-}. O_2^{2-} reacts with H^+, giving H_2O_2. Finally, H_2O_2 is decomposed by the catalysis-like reaction to O_2 and H_2O. Fig. 5 demonstrated that the whole catalytic reaction was composed of cycles A and B. The higher catalytic ability of $FeCoPc_2$ probably owned to synergistic effect in both cycles A and B. In order to further confirm our presumption, the catalytic ability of Co_2Pc_2 and Fe_2Pc_2 on H_2O_2 was investigated at pH 11 and 25 °C. In the same airtight system, 150 mL Co_2Pc_2 or Fe_2Pc_2 (1.0×10^{-5} mol L^{-1}) aqueous solution was added, and 10 mL H_2O_2 (20%, w/w) was put into the same reactor. The catalytic ability of Mt_2Pc_2 was evaluated by oxygen evolved (Fig. 6). The oxygen evolved of Fe_2Pc_2 was obviously higher than that of Co_2Pc_2. Especially at the beginning of the reaction, the oxygen evolved from Fe_2Pc_2 was approximately three times as much as that of Co_2Pc_2. However, oxygen evolved got stable gradually with the reaction going on, which attributed to the remarkable decrease of H_2O_2. Obviously, Fe_2Pc_2 on H_2O_2 had much higher catalytic ability than Co_2Pc_2 in cycle B, but Fig. 3 revealed that the catalytic ability of Co_2Pc_2 on MEA was much better than that of Fe_2Pc_2 in the whole reaction, so it was evident that the catalytic ability of Co_2Pc_2 on MEA was greater than that of Fe_2Pc_2 in cycle A. It was easy to explain why the mixture had much higher catalytic ability than individual Co_2Pc_2 and Fe_2Pc_2. In the process of the whole reaction, Co_2Pc_2 was adept in cycle A, but Fe_2Pc_2 specialized in cycle B. The synergistic effect between Co_2Pc_2 and Fe_2Pc_2 resulted in higher catalytic oxidation ability of $CoFePc_2$ on MEA.

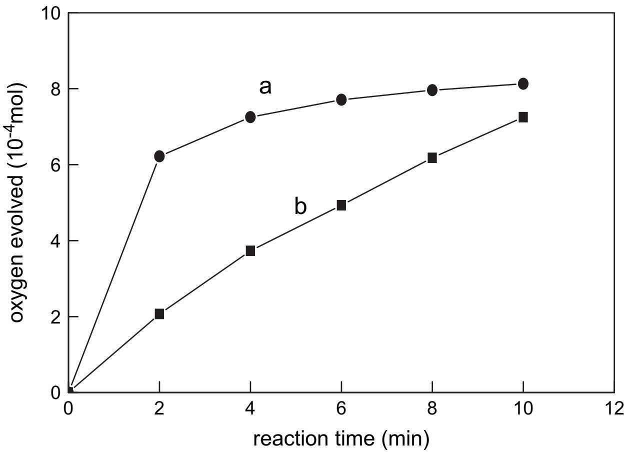


Fig. 6. Rate of decomposing H_2O_2 by binuclear metallophthalocyanines (pH = 11, T = 25 °C, $[H_2O_2]_0$ = 1.84 mol L^{-1}, a: Fe_2Pc_2 and b: Co_2Pc_2).

3.3. Deodorant performance of Mt_2Pc_2F

In aqueous solution, Mt_2Pc_2 had excellent catalytic oxidation ability on MEA. However, Mt_2Pc_2 as an artificial enzyme is a small molecule and is generally available only as powder or in solution, so it is inconvenient to directly eliminate the most common malodors of CH_3SH and H_2S. A better strategy is needed to fix them onto support that can be used repeatedly. SF is natural macromolecules, and it probably offers ideal frames for construction of versatile and robust catalytic sites. SF is selected as the support to prepare Mt_2Pc_2F. Mt_2Pc_2F is expected to efficiently remove CH_3SH and H_2S at room temperature. Co_2Pc_2 was supported on SF and CSF, respectively, obtained Co_2Pc_2SF and Co_2Pc_2CSF, and their deodorant performances on CH_3SH were tested, as shown in Fig. 7. It illustrated that SF without supporting Co_2Pc_2 only eliminated a little CH_3SH, and both Co_2Pc_2SF and Co_2Pc_2CSF had better catalytic ability on CH_3SH. In addition, it also indicated that the catalytic ability of Co_2Pc_2CSF on CH_3SH was much better than that of Co_2Pc_2SF, which may be attributable to different

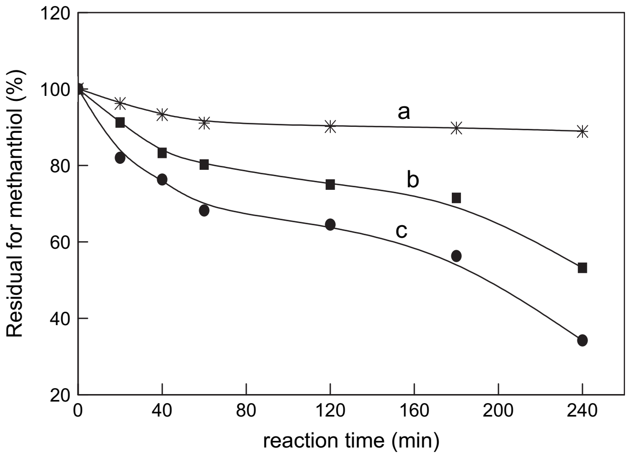


Fig. 7. Speed of oxidizing CH_3SH by SF loaded Co_2Pc_2 ($[CH_3SH]_o$ = 100 ppm, T = 25 °C, a: SF, b: Co_2Pc_2SF, and c: Co_2Pc_2CSF).

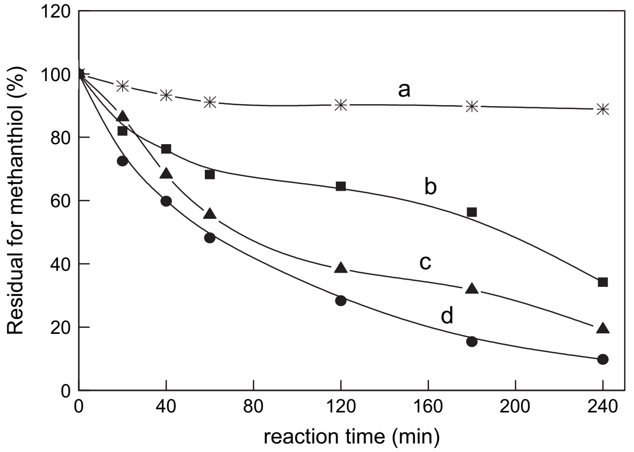


Fig. 8. Rate of oxidizing CH_3SH by Mt_2Pc_2CSF ($[CH_3SH]_o = 100$ ppm, $T = 25$ °C, a: SF, b: Co_2Pc_2CSF, c: Fe_2Pc_2CSF, and d: $CoFePc_2CSF$).

microenvironments. Some groups in SF such as amino coordinated easily with the central metal ion in metallophthalocyanine, so the rival effect, amino scrambled for the central metal ion with CH_3SH, occurred, leading to the decrease of the catalytic ability for metallophthalocyanine. After SF were treated by MA, most of coordination groups such as amino were shielded, and the catalytic ability of metallophthalocyanine was improved, so the deodorant performance of Co_2Pc_2CSF on CH_3SH was better than that of Co_2Pc_2SF.

Co_2Pc_2 and Fe_2Pc_2, respectively, were loaded on 2 g CSF to obtain Co_2Pc_2CSF and Fe_2Pc_2CSF, and their deodorant performances on CH_3SH and H_2S were tested at room temperature, as shown in Figs. 8 and 9. In comparison with SF, both Fe_2Pc_2CSF and Co_2Pc_2CSF had excellent deodorant ability on CH_3SH and H_2S. Figs. 8 and 9 indicated that the deodorant performances of Fe_2Pc_2CSF on CH_3SH and H_2S were better than that of Co_2Pc_2CSF. Furthermore, when equally molar Fe_2Pc_2 and Co_2Pc_2 were mixed and supported on CSF, cationic silk fibres supported mixed binuclear metallophthalocyanine ($CoFePc_2CSF$) was obtained, and the best deodorant activity can be obtained, as shown in Figs. 8 and 9. It could be explained that synergistic effect existed, analogous to $CoFePc_2$ in aqueous solution. At room temperature, Mt_2Pc_2CSF can be used repeatedly. In order to further investigate the repeated use, $CoFePc_2CSF$ was selected to test the catalytic ability on CH_3SH. $CoFePc_2CSF$ (2 g) was suspended in a 5 L flask, and quantitative methanthiol was injected into the flask. Most of CH_3SH was removed after about 240 min, so the supplement of methanthiol was added to keep the initial concentration of 100 ppm. The initial and subsequent concentrations of CH_3SH were measured using a gas detector tube. The same procedure was repeated five times, and their results were shown in Fig. 10. It proved that there was no remarkable decrease for catalytic activity of Mt_2Pc_2. Therefore, Mt_2Pc_2CSF had great deodorant ability on CH_3SH, and Mt_2Pc_2 acted as a catalyst in the oxidation for malodors.

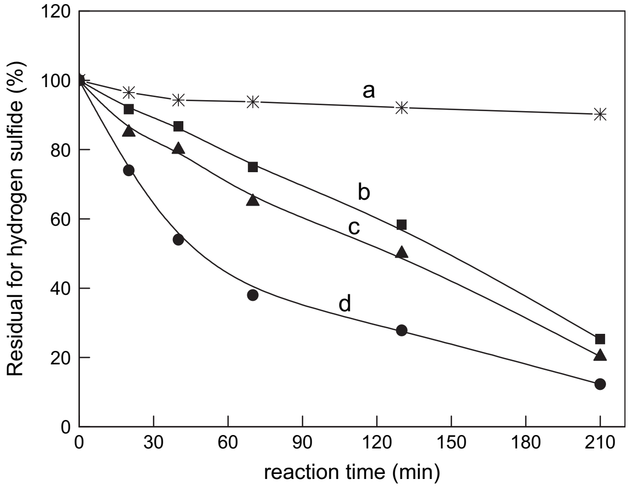


Fig. 9. Rate of oxidizing H_2S by Mt_2Pc_2CSF ($[H_2S]_o = 100$ ppm, $T = 25$ °C, a: SF, b: Co_2Pc_2CSF, c: Fe_2Pc_2CSF, and d: $CoFePc_2CSF$).

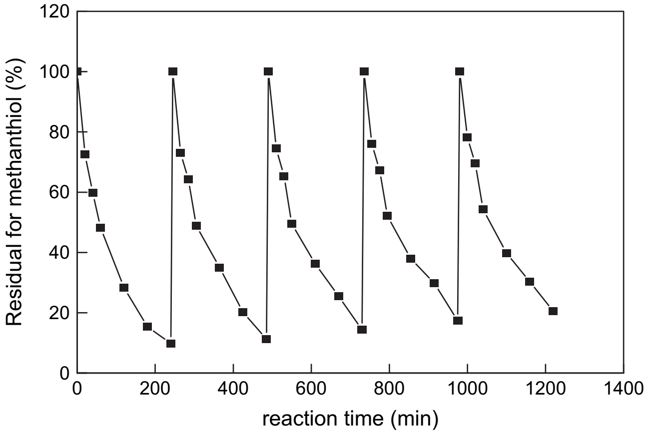


Fig. 10. Deodoring speed for CH_3SH in five runs by $CoFePc_2CSF$ ($T = 25$ °C).

4. Conclusions

Two kinds of binuclear metallophthalocyanines, Fe_2Pc_2 and Co_2Pc_2, showed high catalytic oxidation ability on MEA in aqueous solution. It was significantly found that the catalytic oxidation ability of Co_2Pc_2 and Fe_2Pc_2 mixture was the greatest at the molar ratio 1:1, which attributed to synergistic effect between Fe_2Pc_2 and Co_2Pc_2. At room temperature, the deodorant performance of Co_2Pc_2CSF was better than that of Co_2Pc_2SF. Mt_2Pc_2CSF had perfect deodorant performances on CH_3SH and H_2S, and even the deodorant performance of $CoFePc_2CSF$ was the best.

Acknowledgments

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