Synthesis, characterization and photocatalytic activity of Co(III) 5,10,15,20-tetrakis(carboxyphenyl)porphyrin-supported chitosan

Hossein Ghafuri, Rahmatollah Rahimi, Ziba Felfelian, Mahboubeh Rabbani

Department of Chemistry, Iran University of Science and Technology, Narmak, Tehran 16846-*13114, Iran*

Absteract:

In this work, Co(III) 5,10,15,20-tetrakis(carboxyphenyl)porphyrin was synthesized and immobilized on chitosan. The synthesized composite was characterized by FT-IR and UV-Vis and DRS spectrometers. It is expect that porphyrin act as visible light antenna and to modify the photoresponse properties of chitosan particles. Adsorption and photodegradation of methylene blue (MB) over TCPP- chitosan were systematically investigated.

Keywords: Porphyrin, Metaloporphyrin, Methylene blue, Photodegradation.

1. Introduction:

Porphyrin, a square planar aromatic macrocycle consisting of four pyrroles and four methine carbons, is the most significant pigment to be found in nature. Owing to numerous advantageous properties such as structural active, attractive absorption and emission properties, Immobilization of metalloporphyrins onto various supports, which can be inorganic, organic or hybrid materials, not only facilitates catalyst recovery and reuse but also improve catalytic activity and selectivity because of the influence of the microenvironment of the support [1-4]. In recent years, many studies have focused on exploring the relationship between the structure of porphyrin and the corresponding catalytic efficiency [5,6]. In particular, the effect of the support's microenvironment on the catalytic properties of metalloporphyrins has been investigated.

Synthetic colors are used in various industries such as the manufacture of cosmetics, leather, food, leather, plastic, paper and textile industries. Synthetic wastewater containing dyes ecological and public health threat. Methylene blue is a chemical dye that used widely in chemical industry, because of its aromatic, often toxic, carcinogenic, mutagenic and resistant to degradation is a biological. Adsorption process for the removal of dyes from wastewater is one of the effective methods.

In this paper, Co(III) 5,10,15,20-tetrakis(carboxyphenyl)porphyrin was immobilized on chitosan to modify the photoresponse properties of chitosan particles. Adsorption and photodegradation of methylene blue (MB) over TCPP- chitosan were systematically investigated.

2. Experimental method

2.1. Materials

All of the Chemicals used in this work were analytical grade reagents and used without further purification and purchased from Merck company. Deionized water was used to prepare all solutions.

2.2. Synthesis of CoTCPP

TCPP was prepared according to a procedure similar to that previously described in reference [7]. $CoCl_2 \cdot 6H_2O$ (0.0958 g, 6 mmol), and TCPP (0.0905 g, 1 mmol) were dissolved in DMSO, followed by refluxing for 24 hours. After the solution was cooled to room temperature, HCl (1 M) was added to the solution to cause deposition of the crude product as a purple solid, which was collected by filtration, washed with distilled water, so precipitation was obtained, redissolved in NaOH (0.1 M) followed by addition of HCl (1 M), which caused deposition of the product as a purple solid. This was collected by filtration and dried in vacuo [8].

2.3. Synthesis of CoTCPP immobilized on chitosan

A mixture of diluted acetic acid (5 ml) and chitosan (0.1 g) in a three-neck flask with an electro-magnetic stirrer was stirred at room temperature for 15 min. Then 10 ml of distilled water were added to form the colloidal solution. Then 1% NaOH solution was slowly added until the colloidal solution became neutral. Moreover, 0.050 g of tetrakis(4-carboxyphenyl)porphyrin was dissolved in benzene (60 ml) and slowly added into the reaction system. After stirring for 2 h, the reaction was stopped, and the reaction solution was filtered and washed with distilled water [9].

2.4. Characterization of CoTCPP and CoTCPP-Chitosan

The samples were characterized by FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer.

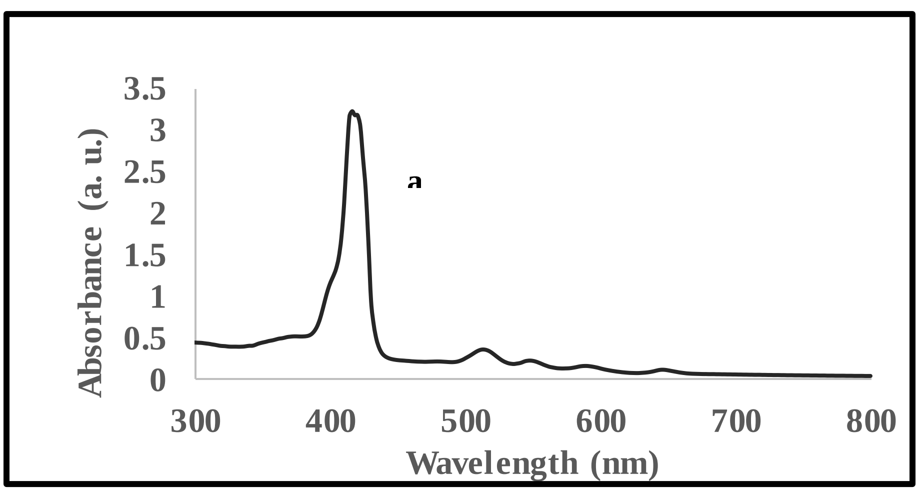
2.5. Photodegradion of MB by CoTCPP and CoTCPP- Chitosan

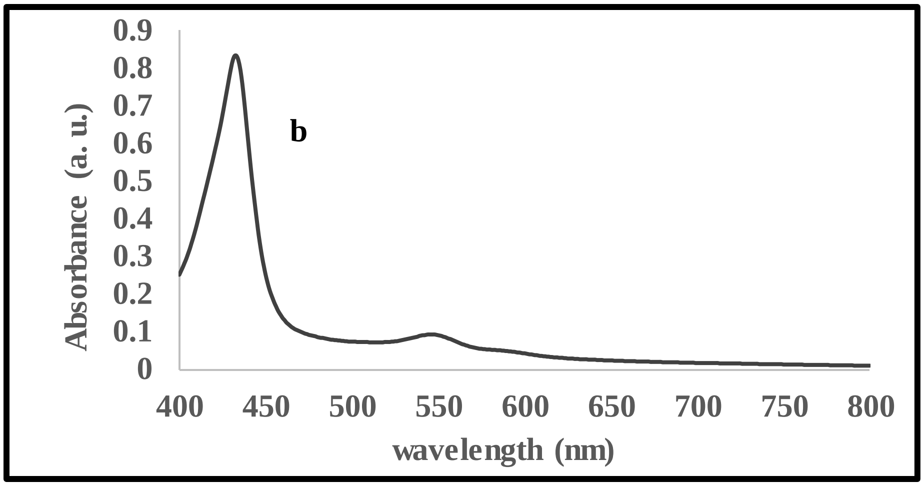
The photocatalytic activities of CoTCPP and the supported catalysts were measured by the degradation of methylene blue (MB) aqueous solution under visible light irradiation, respectively. The experimental set up placed in a black box consisted of a 200 ml beaker irradiated by a 5 W, LED lamp; methylene blue aqueous solution was mixed with photocatalyst powder (10 gl^{-1}) in the above 200 ml beaker. The photoreactivity runs lasted 240 min; the quantitative determination of methylene blue was performed by measuring its absorption at with UV spectrophotometer.

3. Results and discussion

3.1. UV-vis spectra of TCPP, CoTCPP and CoTCPP- Chitosan

As Fig 1 shows the UV-Vis spectra of the TCPP, CoTCPP and CoTCPP-Chitosan measured in the range of 400-800 nm, respectively. The UV–visible spectrum of TCPP is containing a Soret peak in 422 nm and four Q peaks in 504, 556, 604 and 652 nm. However, UV–visible spectrum of CoTCPP, the Soret bond of the porphyrin are red-shifted and Q bands are reduced, Soret band appearance at 434 nm and Q band in 548 and 578 nm.





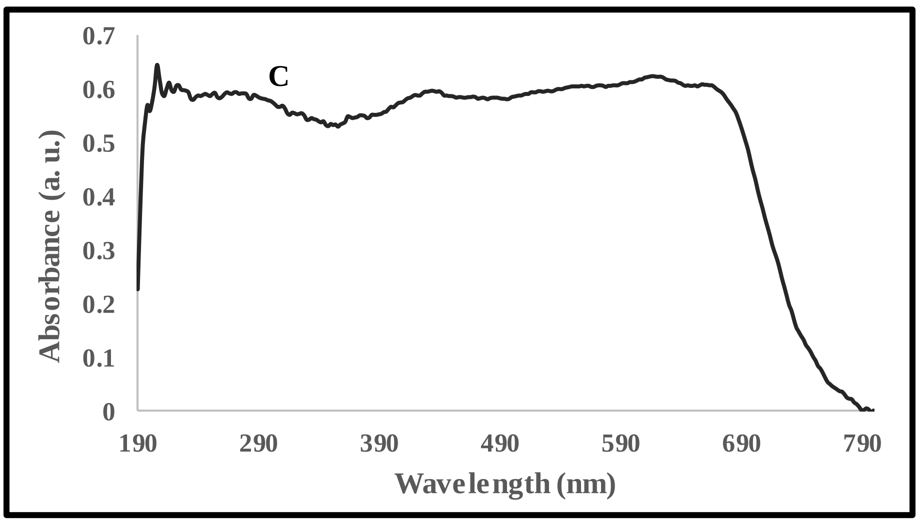


Fig. 1. UV-Vis spectra a) TCPP, b) CoTCPP, c) CoTCPP-chitosan

3.2. FT-IR spectra of CoTCPP and CoTCPP-Chitosan

Fig.2 shows the FT-IR spectra of the CoTCPP and CoTCPP-Chitosan measured in the range of 400–4000 cm^{-1}. The appearance of a sharp band at 1700 cm^{-1} in the FT-IR spectra confirms the synthesis of CoTCPP it is the characteristic absorption band for the C=O stretching vibration, Additionally broad absorption peaks centered at around 3100 cm^{-1} is caused by the O–H stretching vibration, The appearance of strong pick at 1650 cm^{-1} shows stretch vibration of C=O.

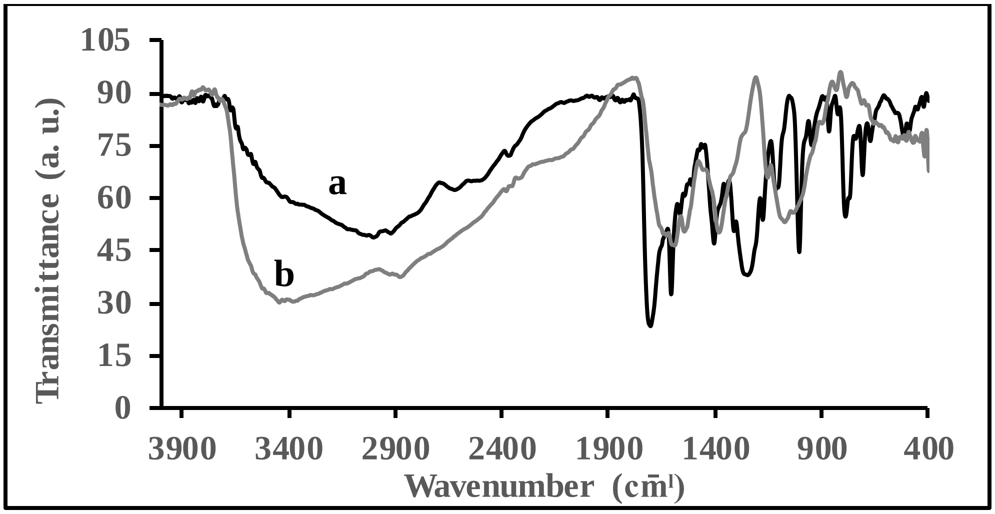
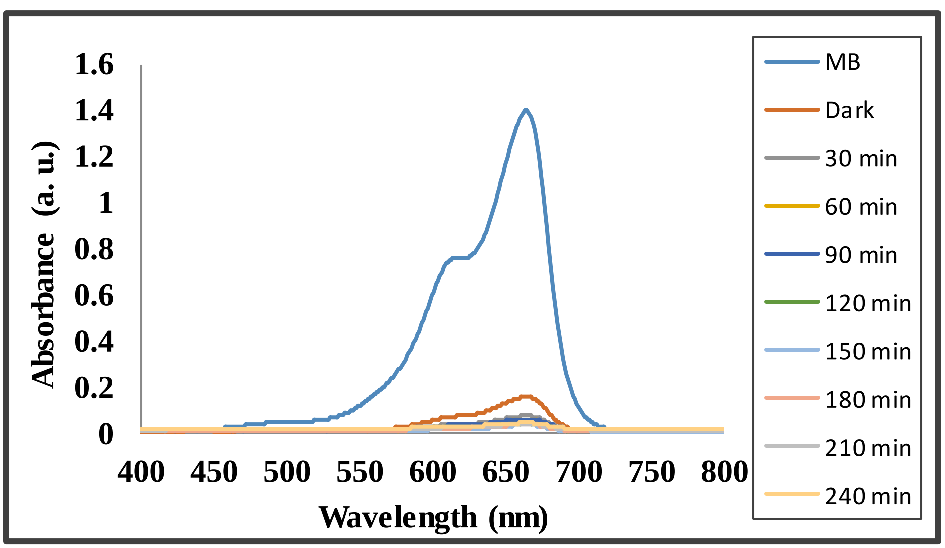


Fig. 2. FT-IR spectra, a) CoTCPP, b) CoTCPP-Chitosan

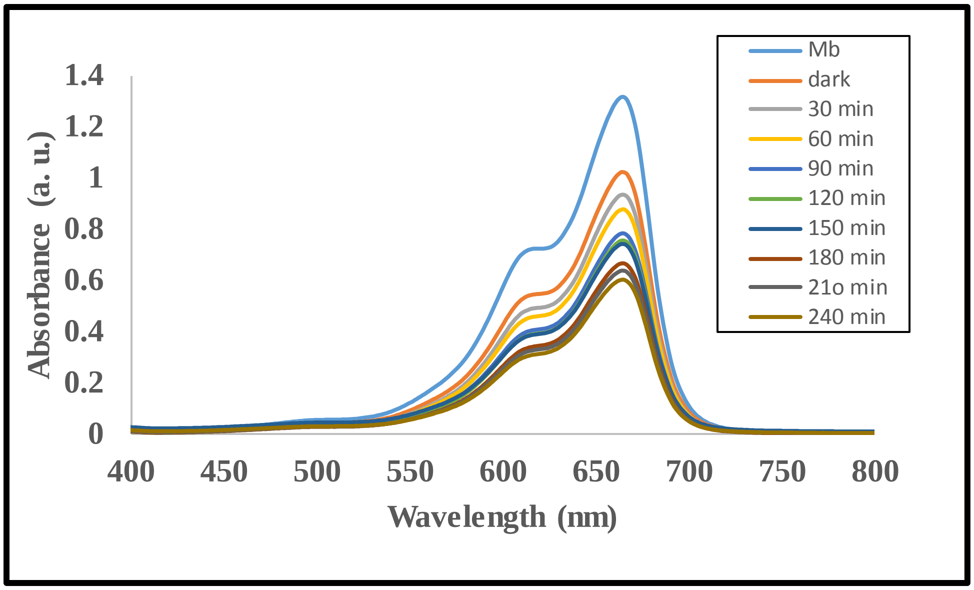
3.3. Deagradation of MB by CoTCPP and CoTCPP-Chitosan

The UV-Vis spectra of methylene blue during degradation by CoTCPP and CoTCPP supported on chitosan were shown in Fig. 3a and Fig. 3b, respectively.

As been shown in this figure, degradation activity of pure porphyrin is higher than porphyrin supported on surface chitosan, because in this study for ever photoreaction the same amount of photocatalyst was used and on other hands, the amount of porphyrin content on chitosan is very low. Therefore, it can be found that porphyrin/chitosan is a good photocatlyst for degradation of MB. Also, this catalyst can be separated easily rather than pure porphyrin.



(a)



(b)

Fig. 3. The absorption spectra of the MB solution, (a) CoTCPP, (b) CoTCPP-chitosan

The absorption spectra of the MB solution after 4 h degradation in different conditions were shown in Fig. 4. The removal efficiency of photocatalysts was demonstrated in Fig. 5.

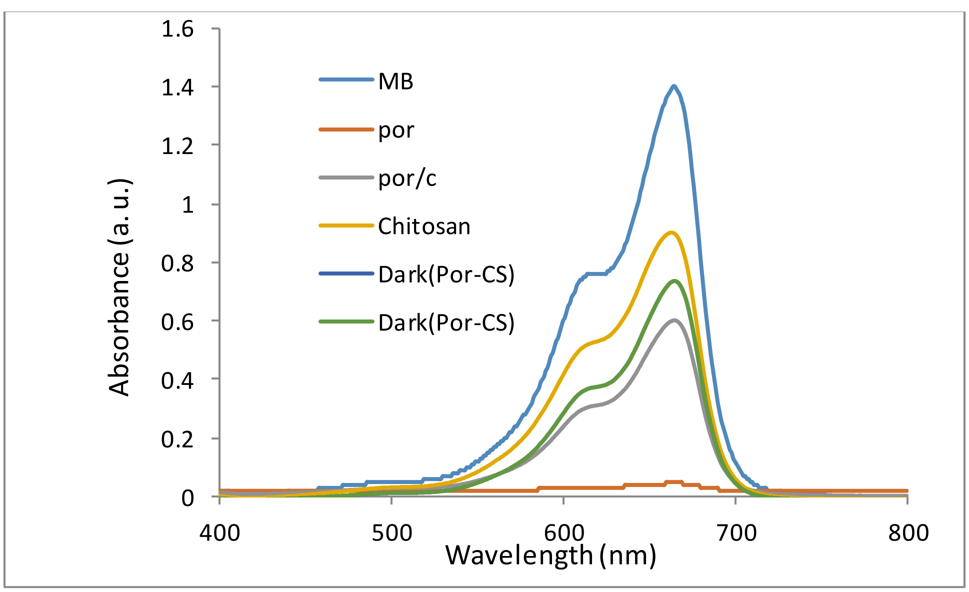


Fig. 4. The absorption spectra of the MB solution after 4 h degradation in different conditions.

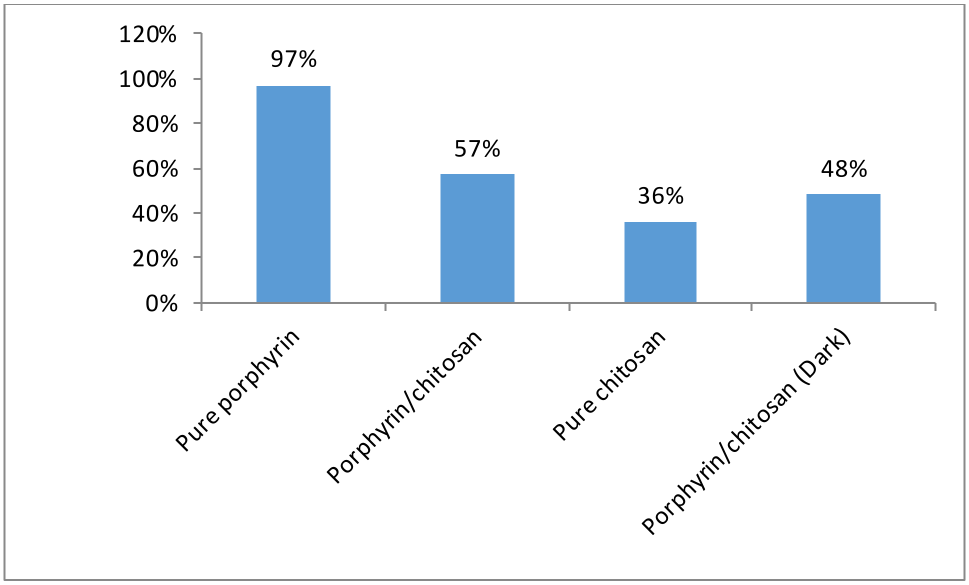


Fig. 5. The removal efficiency of photocatalysts

4. Conclusions

Co(III) 5,10,15,20-tetrakis(carboxyphenyl)porphyrin supported on chitosan prepared easily. Chitosan is a cheap and plentiful, and possesses particular microstructure with excellent function. Stabilization porphyrin on surface of chitosan with strong aromaticity and rich metal coordination chemistry can make a strong catalysis for Degradation of organic pollutants.

References:

[1] E.M. Serwicka, J. Poltowicz, K. Bahranowski, Z. Olejniczak, W. Jones, *Appl. Catal. A*: Gen. 275 **(2004)** 9.

[2] J. Haber, J. Poltowicz, J. Mol. *Catal. A: Chem*. 220 **(2004)** 43.

[3] J. Haber, L. Matachowski, K. Pamin, J. Poltowicz, *Catal. Tad*. 91 **(2004)** 195.

[4] T.M. Nenoff, M.C. Showalter, K.A. Salaz, *J. Mol. Catal. A: Chem*. 121 **(1997)** 123.

[5] R.R.L. Martins, M.G.P.M.S. Neves, A.J.D. Silvestre, M.M.Q. Simoes, *J. Mol. Catal. A: Chem*. 172 **(2001)** 33.

[6] R.R.L. Martins, M.G.P.M.S. Neves, A.J.D. Silvestre, M.M.Q. Simoes, *J. Mol. Catal. A: Chem*. 137 **(1999)** 41.

[7] R. Rahimi, M. Mahjoub-Moghaddas, S. Zargari, *Journal of Sol-Gel Science and Technology*, 65 **(2013**) 420.

[8] Takashi Nakazono,a Alexander Rene Parentab and Ken Sakai, *Chem. Commun*, 49 **(2013)** 6325

[9] C. C. Guo, G. Huang, X. B. Zhang, D. C. Guo, *Applied Catalysis A: General* 247 **(2003)** 261–267