



Efficient removal of dyes in water using chitosan microsphere supported cobalt (II) tetrasulphthalocyanine with H₂O₂

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ABSTRACT

A new efficient catalyst, CoTSPc@chitosan, was developed by immobilizing water soluble cobalt (II) tetrasulphthalocyanine onto adsorbent chitosan microspheres covalently for the heterogeneous catalytic oxidation of C. I. Acid Red 73 with H₂O₂. The result indicated that the COD removal and discoloration of C. I. Acid Red 73 made 55 and 95% respectively in the presence of CoTSPc@chitosan with H₂O₂ in 4 h. In addition, CoTSPc@chitosan–H₂O₂ system could proceed efficiently in a relatively wide pH range and remain high catalytic activity after 6 reuse cycles. Furthermore, the adsorption study of CoTSPc@chitosan confirmed that chitosan was an outstanding support which contributed a lot to the removal reaction. In conclusion, the combination of adsorption process and catalytic oxidation made the CoTSPc@chitosan–H₂O₂ system achieve a simple, efficiently and environmentally friendly water treatment.

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1. Introduction

Wastewater discharged from dyeing processes can be one of the biggest contributors to textile effluents, comprising mainly residual dyes and auxiliary chemicals. Thus, wastewater from dyeing industries creates a great problem of pollution [1]. It is known that wastewaters containing dyes are very difficult to treat, since the dyes are recalcitrant molecules, resistant to aerobic digestion, and stable to oxidizing agents. In recent years, catalytic oxidation has been recognized as an effective method of removal of dyes in water [2,3]. Especially, the interest in catalytic oxidation based on the Fenton-like reaction is continuously growing because of the possibility of utilization of an environmentally friendly oxidant like hydrogen peroxide and readily available complexes as catalysts [4,5].

Metal complexes of phthalocyanines with facile preparation methods characterized by large scale, high thermal stability, effective catalytic degradation of organic pollutants have attracted great interest for environment applications [6]. Nevertheless these homogeneous metallophthalocyanine-based catalysts are hardly recovered at the end of reaction for reuse [7,8] and suffer from limited lifetime activity due to the formation in solution of inactive

aggregates and bridged μ -oxo dimers, which significantly affects their catalytic properties [9,10]. Therefore, anchoring of metallophthalocyanines in solid supports provides a promising approach to overcome such drawbacks, where the macrocycle can be isolated and its catalytic site can be protected. Accordingly, the methods about anchoring of phthalocyanine onto various supports like carbon fibers [11], silica [12], clays [13], resins [14] and zeolites [15] via covalent bond or axial ligation of the metal center were investigated. However, there is still a need to develop new efficient heterogeneous catalysts in more simple and efficient way.

Chitosan, the partial deacetylation product of chitin, is a polysaccharide composed by polymers of glucosamine and N-acetyl glucosamine. The functional amino group at the C-2 provides chitosan an outstanding capacity and high rate of adsorption [16]. Meanwhile, chitosan is a kind of low-cost and even cost-effective material which could be obtained from the wastes of the seafood processing industry, mainly shells of crabs, shrimp, prawns, and krill [17]. Accordingly, chitosan has received increasing interests and deserved particular attention to remove dyes in waste water. Furthermore, compared with other low-cost adsorbents with high adsorption capacity like non-conventional activated carbons from solid wastes, industrial by-products, agricultural solid waste, clays and zeolites reported in reviews [18,19], the potential as development of new complexing materials makes a distinguishing feature of chitosan. As the review summarized [20], versatile chitosan could be manufactured into films, membranes, fibers, gels, nanoparti-

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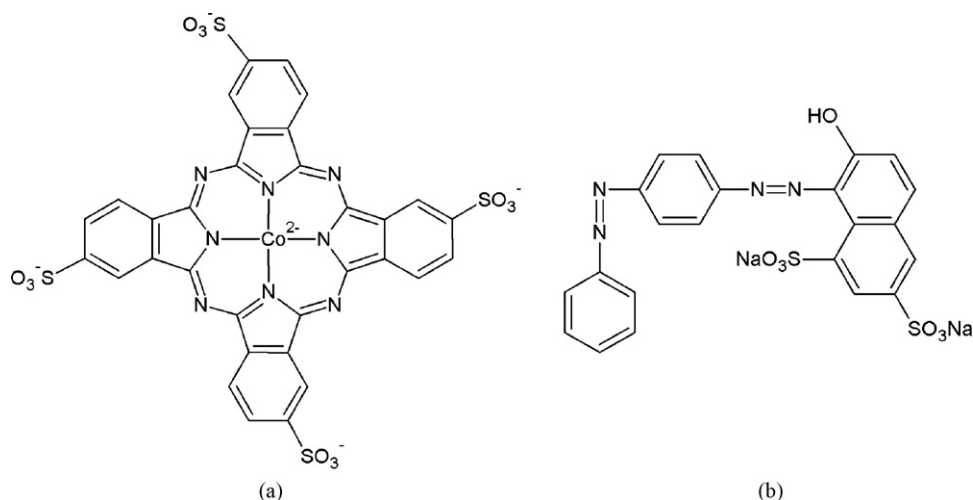


Fig. 1. The chemical structures of cobalt (II) tetrasulfophthalocyanine (a) and C. I. Acid Red 73 (b).

cles, or especially the presence of amino groups coupled with the hydrophilic nature of chitosan was used to prepare supported aqueous phase catalysts and other bifunctional materials [13]. Chitosan-phthalocyanine complex were applied to the preparation of organic matter as reported [22], but no study about chitosan supported metallophthalocyanine for degradation of organic pollutants has been proposed.

Due to the cobalt phthalocyanine derivatives are more affordable, simpler to prepare in large scale, and more chemically stable as reported [11,40,42]. Herein we report the efficient removal of dye C. I. Acid Red 73 in water using chitosan microsphere supported cobalt (II) tetrasulfophthalocyanine with H₂O₂. In this work, a combination of adsorption and catalytic oxidation process was investigated to provide a simple, effective, and economic method for water decontamination. The effect of pH, adsorption isotherms, and recycling use of chitosan supported catalysts were discussed in order to understand the removal mechanism of C. I. Acid Red 73 and optimize the catalytic degradation system.

2. Experimental

2.1. Materials and reagents

Cobalt tetrasulfophthalocyanine (CoTSPc, Fig. 1) was prepared by template synthesis starting from CoCl₂·6H₂O, 4-sulfophthalic acid and urea according to the procedures for the synthesis of metallophthalocyanine [21]. 4-Sulfophthalic acid was purchased from Tokyo Chemical Industry Co., Ltd. Chitosans were obtained from Zhejiang Golden-shell Biochemical Co., Ltd. (Zhejiang, China). Doubly distilled water was used throughout this study. Other chemicals were of laboratory reagent grade and used without further purification.

2.2. Preparation of chitosan microsphere

Chitosan was characterized by its deacetylation degree (DD) which amounts to 91.02%. The chitosan microspheres were formed from an aqueous solution of chitosan by dissolving 2 g of chitosan in 100 mL of a 0.05 M acetic acid solution. Total dissolution was obtained by stirring overnight at room temperature. Gelation of the millimetric microspheres was obtained by dropping the chitosan solution into a 2 M NaOH solution through a 0.7 mm gauge syringe needle. The chitosan microspheres were left in the alkaline solution for 2 h, filtered and washed with redistilled water. Then the microspheres were dehydrated by immersion in a series of succes-

sive ethanol–water baths of increasing alcohol concentration (10, 50, and 100%) for 15 min each. At last, the chitosan microspheres were dried under vacuum conditions at room temperature [22].

2.3. Immobilization of CoTSPc onto chitosan microspheres

The chitosan based CoTSPc oxidation catalysts (CoTSPc@chitosan) were prepared as following procedures by covalent bond. First, 10 mM CoTSPc solution was prepared by dissolving 0.104 g of CoTSPc in 10 mL redistilled water under stirring. Then 0.5 g of chitosan microspheres was added into 10 mL of CoTSPc solution under stirring at 25 °C for 24 h. The CoTSPc@chitosan solids were collected by filtration and dried in 80 °C. CoTSPc loading (10.6 μmol/g) was determined by monitoring the change in the strong absorption band at 667 nm.

2.4. Catalytic oxidation degradation procedures of C. I. Acid Red 73

The catalytic oxidation of the C. I. Acid Red 73 (Fig. 1) was carried out in a 50 mL flask which was sealed and agitated at 100 rpm in the thermostatic shaker maintaining the $T = 25$ °C. The typical reaction mixture contained the following initial concentrations or amount: C. I. Acid Red 73 (50 mg/L, 10 mL); CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc); and hydrogen peroxide (100 mM). For the runs of cyclic reaction, the 0.1 g of catalysts was added and was collected by filtration and dried in 80 °C. The buffer solution of pH = 4, pH = 6, pH = 7 and pH = 8 were prepared by 0.01 M C₄H₂O₇–0.02 M Na₂HPO₄ in different proportions referring to the literature [35], and this series of buffer was applied in the experiments which focused on the effect of pH (Section 3.3). The concentration of C. I. Acid Red 73 of different samples was analyzed on UV–vis spectrophotometer (Shimadzu, UVPC2010, Japan) at the wavelength of maximum absorbance (λ_{\max}) 506 nm. The COD residue was analyzed by COD detector (Lovibond, ET99718 COD, Germany). The cobalt content (including free cobalt ions and cobalt in compound) in the aqueous phase was detected by Inductively Coupled Plasma Mass Spectrometry (Agilent, 7500a, American).

2.5. Sorption isotherms

The sorption isotherms of C. I. Acid Red 73 on CoTSPc@chitosan or chitosan in water were carried out using the batch slurry method [23]. The slurry containing 0.05 g of catalyst and 10 mL of dye solution at various concentrations was agitated at 100 rpm in the

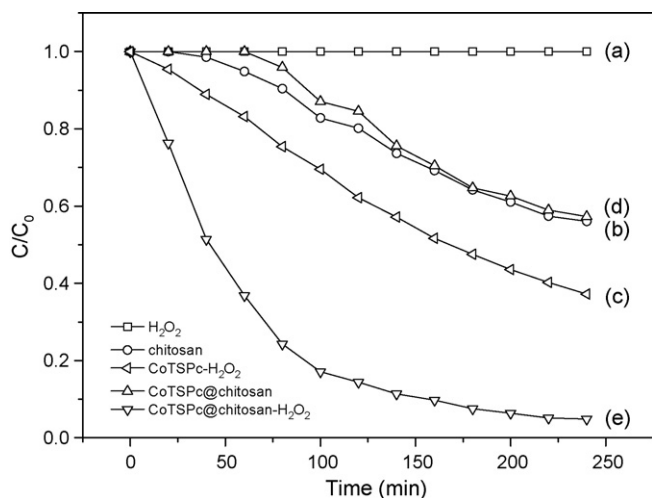


Fig. 2. The concentration changes of C. I. Acid Red 73 (initial concentration 50 mg/L, 10 mL, pH = 7, $T = 25^\circ\text{C}$) under different systems: (a) H_2O_2 (100 mM); (b) chitosan (0.1 g); (c) CoTSPc (106 μM) and H_2O_2 (100 mM); (d) CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc); (e) CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc) and H_2O_2 (100 mM).

thermostatic shaker and maintained at temperature 25°C until equilibrium was reached. The adsorption amount of C. I. Acid Red 73, Q_e , was calculated by the equation:

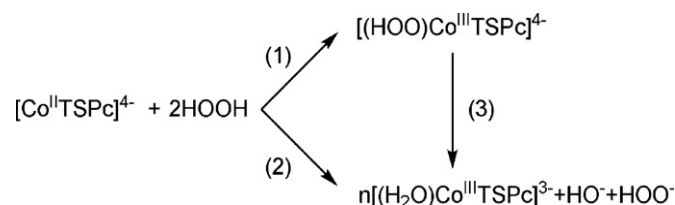
$$Q_e = \frac{(C_0 - C_e)V}{m}$$

where Q_e is the dye concentration in the sorbent at equilibrium (mg/g), C_0 is the initial dye concentration in the liquid phase (mg/L), C_e is the liquid-phase dye concentration at equilibrium (mg/L), and m is the mass of sorbent used (g).

3. Results and discussion

3.1. Catalytic oxidation degradation of C. I. Acid Red 73

As shown in Fig. 2, C. I. Acid Red 73 was persistent and stable in the presence of H_2O_2 without any catalyst. And the concentration of C. I. Acid Red 73 was decreased by about 56% when the supported catalyst CoTSPc@chitosan was present according to its high adsorption ability, showing the similar removal performance as chitosan was present alone. The influences on chitosan microspheres surface by alkaline solution in the process of preparation possibly slowed down the protonation of amine groups in chitosan, resulting in the low adsorption rate in the beginning. The homogeneous catalysis of CoTSPc in the presence of H_2O_2 was also carried out, while the concentration of CoTSPc was the same as that in the chitosan supported. It can be seen that ca. 60% of C. I. Acid Red 73 was removed in the reaction, and the speculative mechanism of catalysis was shown in Scheme 1 [24,40,41]. The main step of the mechanism was the oxidation of CoTSPc by hydrogen peroxide to form $[(\text{HOO})\text{Co}^{\text{III}}\text{TSPc}]^{4-}$ and $[(\text{H}_2\text{O})\text{Co}^{\text{III}}\text{TSPc}]^{3-}$ (as proved by UV-vis spectroscopy) associated with the generation of HO^\bullet and



Scheme 1. The possible mode of activation of CoTSPc by H_2O_2 .

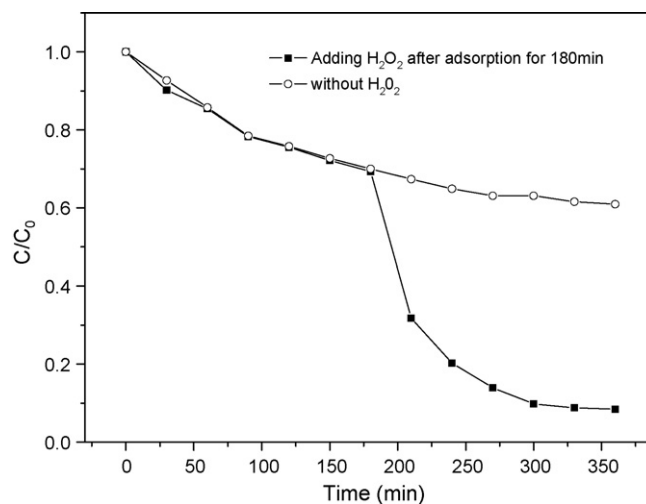


Fig. 3. Effect of adding H_2O_2 on concentration changes of C. I. Acid Red 73 (initial concentration 50 mg/L, 10 mL, pH = 7, $T = 25^\circ\text{C}$) in the presence of CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc).

HOO^\bullet radicals. Both the $[(\text{HOO})\text{Co}^{\text{III}}\text{TSPc}]^{4-}$ intermediate and radicals then reacted with the dyes. Relatively, when C. I. Acid Red 73 was exposed to catalyst CoTSPc@chitosan and oxidant H_2O_2 together, the concentration declined sharply and ca. 95% of target was removed. The results presented here demonstrated the immobilization of CoTSPc could obviously accelerate the oxidation of C. I. Acid Red 73 in the presence of H_2O_2 .

Meanwhile, Fig. 3 shows that the process of adsorption nearly reached the dynamic equilibrium and about 25% of C. I. Acid Red 73 was adsorbed from aqueous to catalyst support after adsorption for 180 min with CoTSPc@chitosan alone. After adding H_2O_2 to the adsorption equilibrium system, the removal of C. I. Acid Red 73 increased rapidly to 90%. Above experiment (Fig. 2) indicated that the H_2O_2 alone could not oxidize the dyes, while the homogeneous catalysis of CoTSPc in the presence of H_2O_2 removed ca. 60% of C. I. Acid Red 73. Therefore, the result suggested that the catalytic oxidation brought by CoTSPc supported on chitosan with H_2O_2 could take place effectively after the adsorption of C. I. Acid Red 73 to CoTSPc@chitosan reached equilibrium.

The COD removal of C. I. Acid Red 73 in chitosan and CoTSPc@chitosan systems were around 30 and 55%, respectively, as shown in Fig. 4. This fact indicates that at the concentrations of

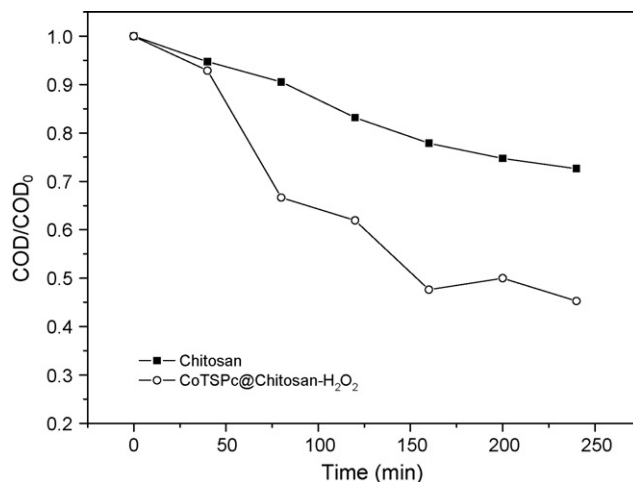


Fig. 4. COD residue of C. I. Acid Red 73 in the presence of CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc) with H_2O_2 (100 mM).

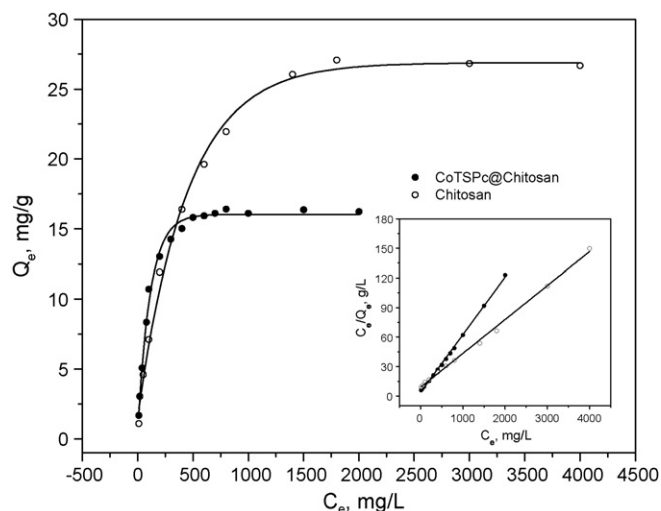


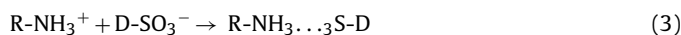
Fig. 5. Sorption of C. I. Acid Red 73 onto chitosan and CoTSPc@chitosan at $T = 25^\circ\text{C}$, $\text{pH} = 7$. Inset shows the Langmuir isotherm linear plots.

CoTSPc@chitosan used, the catalyst system not only degraded the azo linkage ($-\text{N}=\text{N}-$) but also could decompose the reaction products completely for the greater part. It has been reported that introduction of sulfo group at the periphery of the mole makes the metallophthalocyanine soluble and realizes the oxidation of organic substrates in the presence of H_2O_2 under aqueous media, an obvious green alternative to organic solvents [25]. Our results here have investigated that the immobilizing of CoTSPc on chitosan could realize the reclamation of soluble phthalocyanine from the aqueous solution on the basis of maintaining high reactivity of catalysts.

3.2. Adsorption process of C. I. Acid Red 73

The high efficiency of chitosan for its ability to interact with dyes has been studied by numerous scientists [26–28]. In particular, its outstanding removal capacity for anionic dyes such as acid, reactive and direct dyes has been demonstrated. Thus it is necessary to investigate the great contribution of chitosan in the removal of C. I. Acid Red 73.

The possible mechanisms of the adsorption process of chitosan and C. I. Acid Red 73 in aqueous solution are likely to be ionic interactions of the dye ions with the amino groups on the chitosan as the following proceeds [28]



First, the sulfonate groups of C. I. Acid Red 73 dissociate and are converted to anionic ions (1). In the presence of H^+ , the amino groups of chitosan became protonated (2). Then the adsorption proceeds due to the electrostatic attraction between these two counterions (3).

The equilibrium saturation capacities of C. I. Acid Red 73 in each of the systems are demonstrated in Fig. 5, showing the monolayer saturation or maximum adsorption is reached in CoTSPc@chitosan and chitosan systems. In this case, a higher adsorption capacity is observed for chitosan than that of CoTSPc@chitosan and the difference in the degree of adsorption between them may mainly be attributed to the quantity of unoccupied amino groups on chitosan. As shown in the inset of Fig. 5, the linear plots of specific sorption C_e/Q_e against the equilibrium concentration C_e for C. I. Acid Red 73

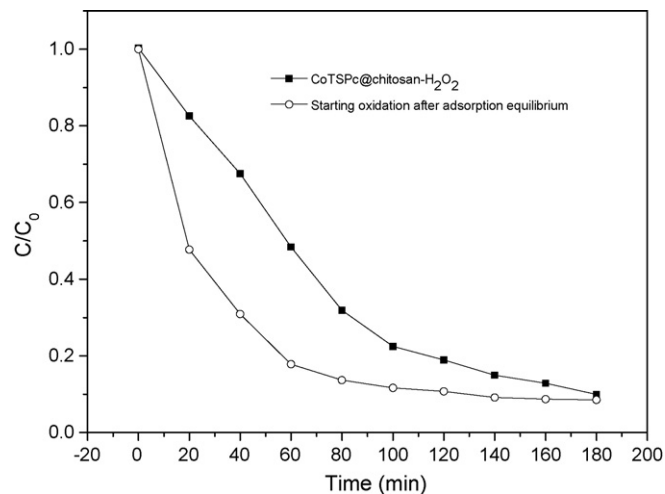


Fig. 6. Effect of achieving adsorption equilibrium previously on C. I. Acid Red 73 (initial concentration 50 mg/L, 10 mL, $\text{pH} = 7$, $T = 25^\circ\text{C}$) removal in the presence of CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc) with H_2O_2 (100 mM).

are shown. The values of the correlation coefficients strongly support the fact that the two sorption systems above closely follow the Langmuir model.

Although the loading of CoTSPc certainly decreased the saturation adsorption capacities of chitosan, there is no marked difference in the adsorption process of C. I. Acid Red 73 between CoTSPc@chitosan and chitosan systems by comparing with the results presented in Fig. 2. Meanwhile, an experiment about the effect of adsorption on C. I. Acid Red 73 removal in CoTSPc@chitosan system was investigated and the results were shown in Fig. 6. When the oxidation process was initiated after the adsorption of dye achieving equilibrium, it could be seen that the reaction speed of C. I. Acid Red 73 removal increased a lot at the beginning of reaction. The certainly increase could be mainly attributed to the enrichment of dye onto the catalysts which would accelerate its oxidation by the oxidizer generated nearby in situ. In this regard, the results confirmed that chitosan is an outstanding support for CoTSPc loading and contributed a lot to the removal of C. I. Acid Red 73 in water.

3.3. Effect of pH on C. I. Acid Red removal

pH is one of the important parameters controlling the adsorption process of chitosan and influencing the catalytic properties of CoTSPc. As shown in Fig. 7, the concentration of C. I. Acid Red 73 respectively decreased about 50–95% at the pH range from 4 to 8 and the reaction under $\text{pH} = 7$ achieved the best. Compared with the CoTSPc@chitosan system under $\text{pH} = 8$, the reaction in the condition of $\text{pH} = 4$ resulted in a worse state although it processed better in the beginning.

Two important factors are likely responsible for the observed phenomenon above. Firstly, hydrogen atoms (H^+) in the solution could protonate the amine groups ($-\text{NH}_2$) under acidic conditions inducing the improvement of adsorption efficiency. Relatively, the adsorption ability would be limited to a certain extent in alkaline solution according to the published study [29,30]. Secondly, CoTSPc are in known to exist as dimers in equilibrium with monomers in aqueous solutions [31]. And the monomers would transform to be superior when the solutions became alkaline, enhancing the catalytic activity and stability of CoTSPc [32].

Thus, the adsorption process may play a primary role in the reaction of color removal under acidic condition while the catalytic oxidation would turn into main dominant factor in alkaline

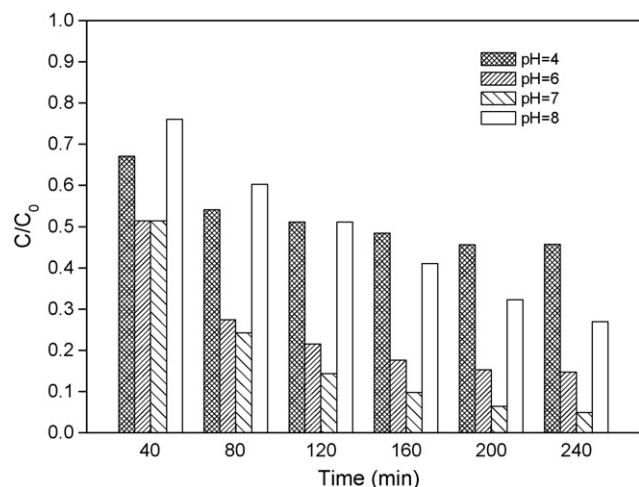


Fig. 7. Effect of pH on C. I. Acid Red 73 (initial concentration 50 mg/L, 10 mL, pH = 7, $T = 25^\circ\text{C}$) removal in the presence of CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc) with H_2O_2 (100 mM).

solution. The combination of adsorption process and catalytic oxidation would advantage the CoTSPc@chitosan system proceed at a relatively wide pH range and achieve best effect under nearly neutral condition. Comparing with other systems [11,33,34] like Fenton systems which should take place in acid solutions or the homogeneous phthalocyanine systems which mostly keep active in alkaline conditions, the CoTSPc@chitosan system take the advantage of excellent performance in neutral conditions.

3.4. Effect of H_2O_2

Meanwhile, the effect of H_2O_2 concentration on catalytic oxidation has been studied and discussed as presented in Fig. 8. As expected, the C. I. Acid Red 73 removal could be accelerated by the increase of H_2O_2 till the growing tendency slowed down when H_2O_2 concentration was of 100 mM. On the contrary, the removal efficiency began to decline when the H_2O_2 concentration amount to 200 mM. It is because that the metallophthalocyanine could not possess an intrinsic chemical stability and even cause deactivation

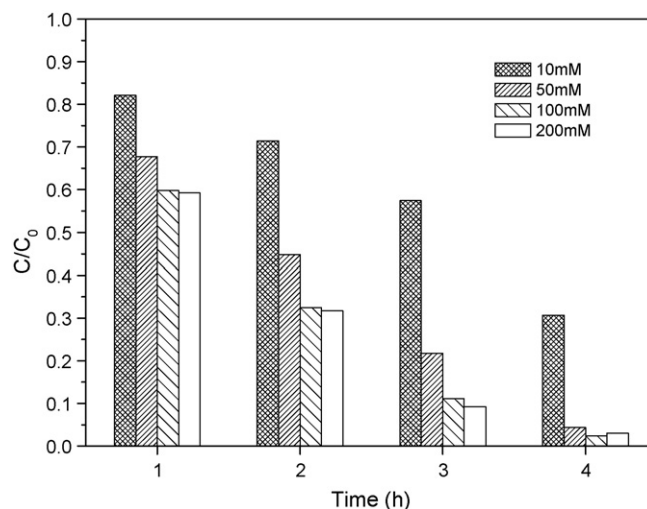


Fig. 8. Effect of H_2O_2 concentration on C. I. Acid Red 73 (initial concentration 50 mg/L, 10 mL, pH = 7, $T = 25^\circ\text{C}$) removal in the presence of CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc).

in high concentration of oxidants as reported by similar literatures [25]. Therefore, the concentration of H_2O_2 should be controlled exactly in order to achieve high removal efficiency.

3.5. Effect of visible light

Metallophthalocyanines were proved to be highly promising in photocatalytic activity due to their intense absorption in the red region of visible light [14,36,37]. And dyes removal process was exposed to indoor natural light in our experiments, so we carried out the control experiments in the dark. The result (Fig. 8) showed that the concentration of dyes declined quickly in dark as well as in natural light, indicating that CoTSPc@chitosan- H_2O_2 system could also maintain high removal efficiency in dark.

By referring to the photooxidation research using metallophthalocyanines as photocatalyst, the oxidation efficiency was found to depend on the light intensity [38]. Additionally, almost all the researches focusing on the photocatalytic activity used intense light source just like high power halogen lamp [36–39]. Then we

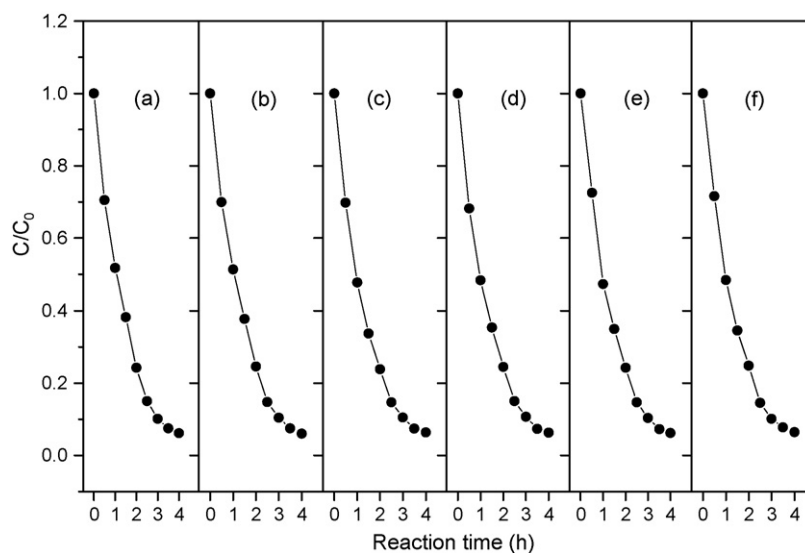


Fig. 9. Recycling experiment for C. I. Acid Red 73 removal (initial concentration 50 mg/L, 10 mL, pH = 7, $T = 25^\circ\text{C}$) in the presence of CoTSPc@chitosan (0.1 g, containing 106 μM CoTSPc) with H_2O_2 (100 mM).

regarded that the metallophthalocyanines could not get excited by indoor natural light to interact with ground state oxygen which would generate the singlet oxygen. And it also revealed that the CoTSPc@chitosan–H₂O₂ system without the photocatalytic process would overcome the drawbacks found in light sensitive system.

3.6. Recycling experiment

The reuse and stability of the catalyst are one of the important factors to be considered for practical use in water purification. The results shown in Fig. 9 indicate that the supported catalyst CoTSPc@chitosan was recyclable for consecutive sorption and catalytic oxidation of C. I. Acid Red 73, the catalyst activity was still excellent after 6 runs.

The data on the complex leaching is another essential point to evaluate the catalytic performance. First, no CoTSPc absorbance peak in the range from 600 to 800 nm was observed by UV–vis spectrometer in the reaction solution. Additionally, the cobalt content (including free cobalt ions and cobalt in compound) in the aqueous phase was detected by Inductively Coupled Plasma Mass Spectrometry (ICP–MS). The result was that the solution after catalytic reaction contained 0.04 ppm cobalt, equaling to only 1/150 of the cobalt in CoTSPc which was supported on chitosan proportionally. Thus, the outstanding adsorption ability of chitosan and the high catalytic capability of CoTSPc made the CoTSPc@chitosan a novel, simple, efficiently and practical catalyst.

4. Conclusion

CoTSPc@chitosan–H₂O₂ system, developed by immobilizing of cobalt (II) tetrasulfophthalocyanine onto chitosan microspheres covalently, corresponds to the criteria of green chemistry and sustainable development. It offers the capabilities and advantages of: (1) using of hydrogen peroxide as an environmentally friendly oxidant and chitosan as an cost-effective support; (2) efficient removal of the C. I. Acid Red 73 in aqueous solution; (3) being active in a wide pH range and of outstanding performance in neutral conditions; (4) being efficient without light source; (5) easy separation of catalyst from reaction mixture and possibility of recycling. Therefore, this study provides a simple, efficient and environmentally friendly treatment for waste water containing dyes.

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