Chitosan/Hydroxyapatite/Fe₃O₄ Magnetic Composite for Metal-Complex Dye AY220 Removal: Recyclable Metal-Promoted Fenton-like Degradation

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Abstract

Cross-linked Chitosan (CS) loaded with iron species has been widely used as heterogeneous Fenton catalysts for organic contaminants removal. In comparison with raw-CS based Fenton catalysts, it exhibited an improved degradation efficiency due to the stabilization of cross-linking agents. With cross-linking, however, most reactive sites of CS were occupied by cross-linking agents, making its capability decreased sharply for adsorbing the released metal ions from metal-complex dye degradation. In this work, in order to efficiently adsorb the released metal ions from metal-complex dyes and avoid a secondary pollution, a new CS-based heterogeneous Fenton catalyst (Chitosan/Hydroxyapatite/ Fe_3O_4 magnetic composite) was developed for AY220 (a model of metal-complex dyes) removal. Hydroxyapatite (HA), a well-known biocompatible material with strong ability for metal ions adsorption, was introduced to combine with CS for Fe_3O_4 loading. The total removal efficiency of AY220 by the magnetic composite can reach as high as 95.0%, and the degradation efficiency of AY220 was greatly enhanced compared with a raw-CS based catalyst and bare Fe_3O_4 . Meanwhile, the composite can efficiently adsorb Co^{2+} released from AY220 degradation, which can further promote the degradation of AY220. After five recyclable runs of the composite, the degradation efficiency of AY220 increased from 25.1% to 45.6%, demonstrating its potential usefulness in recyclable degradation of metal-complex dyes.

Keywords: Chitosan, hydroxyapatite, Fe_3O_4 , magnetic composite, metal-complex dye, Fenton reaction, dye degradation, dye removal.

1. Introduction

Metal-complex dyes as an important branch of dye industries have been widely used in wool and polyamide dyeing for their excellent color-fixing abilities, high glossiness and good acid or heat resistance properties [1]. Besides aromatic rings, they also contain toxic complex ions (such as Co^{2+} or Cr^{3+}) compared with other commercially available azo-dyes, which further increase their toxicity [2, 3], however. Accordingly, to protect the aquatic and ecological system from contamination, the efforts aimed at effectively eliminating them from the waste water before discharging into the environment are truly appealing.

The currently used methods for metal complex dyes removal mainly include adsorption, electro-coagulation and degradation [4-7]. Among them, adsorption has gained a great attention for its low cost and ease of operation. However, without proper treatment or disposal, the adsorbed organic pollutants may cause a secondary pollution. An efficient way to solve this problem is to degrade them into C and N compounds without obvious toxicity. Various degradation methods have been employed for metal-complex dyes removal from aqueous solutions, such as electrochemical treatment [4], biochemical disposal [6] and photo Fenton reaction [8]. But the characteristics of time- and energy-consuming and unrecyclable use limit their practical applications. Moreover, the released metal-complex ions during the above degradation processes may also cause a secondary pollution. Therefore, developing alternative ways of time- and energy-saving, recyclable using, and capable of

adsorbing metal ions to overcome the above drawbacks is truly imperative.

Nowadays, heterogeneous Fenton reaction (iron-based compounds as the reaction catalyst, and without external energy) as an important modification form of classical homogeneous Fenton reaction (homogeneous solution of iron ions as the reaction catalyst) has been intensively studied for their unique advantages of less ion loss, a wider pH range than those of classical Fenton reactions, and a variety of heterogeneous catalysts [9-12] have been developed. Among them, loading iron species onto solid supporters is a promising way to form heterogeneous catalysts [13-15].

Chitosan (CS), a linear natural polysaccharide obtained from full or partial deacetylation of chitin, has attracted a great interest as a solid supporter to load iron species due to its resource abundance, environmental friendliness, and excellent abilities for bonding metal ions [16-18]. However, raw CS cannot stand durative attack of $\bullet\text{OH}$ and is lack of enough mechanic strength, thus affecting its degradation efficiency [19]. Glutaraldehyde (GLA) has been then used as a cross-linking agent to stabilize CS, and thus cross-linked CS-based catalysts have been developed with improved degradation efficiency of organic contaminants [20, 21]. But these catalysts are not able to efficiently adsorb the released metal ions from dye degradation, since the amine groups (main adsorption sites for metal ions adsorption) of CS have almost been occupied by GLA or loaded iron species. Therefore, finding another material with metal ion adsorption abilities to combine with CS as the supporter is significant to make this CS-based catalyst useful for metal-complex dye degradation.

Immobilizing CS on rigid inorganic materials [22, 23] has been reported to be beneficial for its stabilizing and improving its mechanical strength and adsorption efficiency. Among various inorganic materials, hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA] has been anchored with CS to improve its stability and mechanical strength, and the as-received CS/HA composite behaved excellent in dye and metal ion removal [24, 25].

In this work, in order to efficiently adsorb the released metal ions from metal-complex dyes degradation and avoid a secondary pollution, a new CS-based heterogeneous Fenton catalyst (Chitosan/Hydroxyapatite/ Fe_3O_4 magnetic composite) was developed for AY220 (model dye of metal-complex dyes) removal. Hydroxyapatite (HA, a well-known biocompatible material with strong ability for metal ions adsorption) was introduced to combine with CS for Fe_3O_4 loading. The removal efficiency of AY220 by the magnetic composite can reach as high as 95.0%, and the degradation efficiency of AY220 was also greatly enhanced compared with raw-CS based catalyst or bare Fe_3O_4 . Meanwhile, the composite also can efficiently adsorb Co^{2+} released from AY220 degradation, which greatly promoted the degradation of AY220, demonstrating its potential usefulness in recyclable degradation of metal-complex dyes.

2. Experiment

2.1. Chemicals and materials

All reagents used in the experiment were analytical grade without further

purification. Hydrochloric acid, calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 30% (w/w) hydrogen peroxide were purchased from Kelong Chemical Industry Corporation (Chengdu, China). Chitosan, acetate, ammonium phosphatedi basic, sodium hydroxide, and ammonia solution 25-28% (w/w) were obtained from Aladdin Industrial Corporation (Shanghai, China). Iron chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was from Tianjin Damao Chemical Reagent Corporation (Tianjin, China). Acid yellow 220 (AY220) was supplied by a textile factory in Hangzhou, China. All solutions were prepared with high-purity water.

2.2. Preparation and characterization of CS/HA/Fe₃O₄

CS/HA/Fe₃O₄ composite was synthesized via co-precipitation method. Firstly, a certain amount of CS was dissolved in 2% acetic acid solution by stirring in a four-necked flask. 30 min later, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was slowly poured into the flask with continuous stirring. Before the mixed solution of FeCl_2 and FeCl_3 with the molar ratio of 1:2 was added into the flask, the pH was adjusted to 1 with hydrochloric solution ($0.1 \text{ mol} \cdot \text{L}^{-1}$) to prevent $\text{Fe}(\text{CH}_3\text{COO})_3$ and FePO_4 from precipitating. The flask was then put in a 80 °C oil bath under N₂ protection. Meanwhile, $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was dropped in simultaneously until the pH maintained above 10 with vigorous stirring for another 3 h. After cooled down to the room temperature and aged overnight with air cut off, the obtained precipitate isolated by a permanent magnet was washed repeatedly with deionized water and methanol till the pH of the filtrate close to 7. Finally, the as-received CS/HA/Fe₃O₄ composite was dried in a vacuum oven at 40 °C for 48 h. A series of CS/HA/Fe₃O₄

composites with 20%, 33.3%, 40%, 50% and 60% Fe_3O_4 contents were synthesized, and the usage of the raw materials was summarized in Table S1.

The phase structure of the CS/HA/ Fe_3O_4 composite was determined by X'Pert Pro MPD diffractometer (Philips, Netherlands). Elemental characterization on the surface of the composites was investigated by EDXS (X-Max 51-XXM0019, Oxford Instruments, UK). The dye concentration was determined by a UV-Vis spectrophotometer (UV-1750, Shimadzu, Japan). An inductively coupled plasma optical emission spectrometer (ICP-OES) (ARCOS FHS12, SPECTRO Analytical Instruments GmbH, Germany) was used for cobalt quantification. The particle size was measured by dynamic light scattering (ZEN 3090, Malvern Instrument Ltd., UK). Hysteresis loops were recorded at the room temperature with a JDAW-2000D vibrating sample magnetometer (VSM, Jilin University, China).

2.3. Adsorption experiments

2.3.1. AY220 adsorption

The adsorption studies were performed with batch equilibration method. 30 mg catalyst was added into a conical flask containing 20 mL AY220 solution (initial concentration: 500 mg L^{-1}) at 25°C and reacted with mechanical shaking. For kinetics studies, the concentration of AY220 in the supernatants after different time intervals was determined by the UV-Vis spectrophotometer at 435 nm. Adsorption isotherm experiment was carried out at dark condition. The catalyst was added into the solution of AY220 with different initial concentration ($100\text{-}1500 \text{ mg L}^{-1}$) and shaken for 12 h to ensure the adsorption equilibrium. Then the equilibrium concentration of AY220 in

the aqueous phase was measured. The AY220 adsorption removal efficiency R_a , and equilibrium adsorption capacity q_e (mg g^{-1}) were calculated as:

$$R_a = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (1)$$

$$q_e = \frac{(c_0 - c_e)V}{M_s} \quad (2)$$

where C_0 and C_e (mg L^{-1}) is the initial and equilibrium concentration of AY220 in solution, respectively, V (mL) is the volume of AY220 solution, and M_s (g) is the dosage of the catalyst.

2.3.2. Co^{2+} adsorption

Co^{2+} adsorption was also performed with batch equilibration method. 30 mg of the catalyst was added into a conical flask containing CoCl_2 solution with different initial concentrations (5, 10, 20, 30, 40, and 50 mg L^{-1}) at 25°C and reacted for 4 hours with mechanical shaking. After that, the Co^{2+} concentration in the supernatant was determined by ICP-OES as the concentration after reaction. The adsorption amount of Co^{2+} by CS/HA/ Fe_3O_4 can thus be obtained according to equation (3).

$$m_{\text{Co}} = (c_0 - c_t)V \quad (3)$$

where C_0 and C_t (mg L^{-1}) is the concentration of Co^{2+} in solution before and after reaction, respectively, V (mL) is the volume of AY220 solution, and m_{Co} (g) is the adsorption amount of Co^{2+} after reacting for 4h.

2.4. Degradation experiments

2.4.1. AY220 degradation by CS/HA/ Fe_3O_4

To examine the total removal efficiency and degradation efficiency of AY220 by

the catalyst, a certain amount of H₂O₂ (w/w: 30%) was added into 20 mL AY220 solution (initial concentration: 500 mg L⁻¹) containing 30 mg of the catalyst to react, and the supernatant and the catalyst was then collected after a given time interval by a permanent magnet, respectively. The obtained catalyst was then rinsed in 20 mL NaOH solution for 1 h (0.1 mol L⁻¹, extraction yield: 94.2%) to elute the absorbed AY220. Meanwhile, the AY220 concentration in the supernatant (denoted as C_t) and that absorbed by the catalyst (denoted as C_{at}) after reacting for a given time were all determined with the UV-Vis spectrophotometer. Based on the above process, the total removal efficiency and degradation efficiency of AY220 by the catalyst can thus be calculated as:

$$R = \frac{(c_0 - c_t)}{c_0} \times 100\% \quad (4)$$

$$R_d = \frac{c_0 - (c_t + c_{at})}{c_0} \times 100\% \quad (5)$$

where R and R_d is the total removal efficiency and degradation efficiency of AY220 by the catalyst, respectively. C₀ is the initial concentration of AY220, C_t and C_{at} is the AY220 concentration in the supernatant and absorbed by the catalyst after a given time interval, respectively.

2.4.2. AY220 degradation by recyclable used CS/HA/Fe₃O₄

After the catalyst was used for AY220 removal for the first time, it was then eluted and washed with NaOH solution and deionized water successively till the pH close to 7 for its recyclable use. The experimental details, as well as the calculation of the total removal efficiency and degradation efficiency are all the same as presented in

2.4.1.

2.4.3. AY220 degradation by CS/HA/Fe₃O₄ with adsorbed Co²⁺ on its surface and equivalent Co²⁺ in solution

The catalyst with adsorbed Co²⁺ on its surface (obtained from 2.3.2) was used for AY220 removal after washed by deionized water. For comparison, the catalyst without adsorbed Co²⁺ was then added to AY220 solution containing equal amount of Co²⁺ as that of being adsorbed (the adsorbed amount of Co²⁺ calculated from equation 3) to remove AY220. Both the experimental details were the same as 2.4.1, and the AY220 degradation efficiency was also calculated according to Equation (5).

3. Results and discussion

3.1.Characterization of the catalyst

Fig.1 gives the XRD patterns of CS, HA, Fe₃O₄ and CS/HA/Fe₃O₄ composite. A broad peak assigned to chitosan around 20° (Fig.1b) almost disappeared in the XRD pattern of CS/HA/Fe₃O₄ (Fig.1a), indicating that the intramolecular hydrogen bonds of CS between -NH₂ and -OH groups were broken or destroyed by the inorganic phases of HA and Fe₃O₄[26]. The addition of HA and Fe₃O₄ affected the crystallinity of CS and made its XRD peak become extremely weak as shown in Fig.1a. All the characteristic peaks of HA (denoted as "1" in Fig.1c) and Fe₃O₄ (denoted as "2" in Fig.1d) can be seen in the composite material, and were all broadened in the composite (Fig.1a), further confirming the strong interaction between inorganic phases and CS of the composite [27].

Fig.1. X-ray diffraction patterns of CS/HA/Fe₃O₄(a), CS(b), HA(c),and Fe₃O₄ (d) and main peaks of HA (denoted as 1), and Fe₃O₄ (denoted as 2).

The magnetic hysteresis loops of Fe₃O₄ and CS/HA/Fe₃O₄ composite measured at the room temperature are shown in Fig. 2. The saturation magnetization (M_s) is found to be 60.05, 14.82 emu g⁻¹ for Fe₃O₄ and CS/HA/Fe₃O₄ composite, respectively. Although the saturation magnetization value of the CS/HA/Fe₃O₄ composite is lower than that of Fe₃O₄, it could also be rapidly separated from its water dispersion by an external magnet in several seconds, as displayed in the upper inset of Fig. 2. The reason of the decreased saturation magnetization value for the CS/HA/Fe₃O₄ composite can be ascribed to the presence of non-magnetic chitosan and hydroxyapatite. The above results indicated that CS/HA/Fe₃O₄ composite exhibited enough magnetic response to meet the need of magnetic separation.

Fig.2. Magnetic hysteresis loops of Fe_3O_4 and CS/HA/ Fe_3O_4 (insets: magnetic separation of CS/HA/ Fe_3O_4 from the aqueous suspensions).

3.2. Optimization of the related parameters

3.2.1. Effect of CS to HA weight ratio

Since the role of HA in the composite was to stabilize CS and provide adsorption sites for adsorbing Co^{2+} released from AY220 degradation, the CS to HA weight ratio was thus firstly optimized according to the adsorption results shown in Fig.3. From Fig.3, it can be seen that the maximum adsorption for AY220 was obtained with 50% CS, and this may be resulted from the increasingly homogeneous encapsulation of the HA particles into the CS [28]. Therefore, the CS to HA weight ratio in the tri-phase composite was then set as 1:1 during the following experiments.

Fig.3. Effect of CS weight content in CS/HA composites on AY220 removal. Initial AY220 concentration: 500 mg L⁻¹; adsorbent dosage: 30 mg/20 mL; and treatment time: 120 min.

3.2.2 Effect of Fe₃O₄ weight content and H₂O₂ concentration

Fig.4. Effect of Fe₃O₄ weight content and H₂O₂ concentration on AY220 removal. Initial AY220 concentration: 500 mg L⁻¹; adsorbent dosage: 30 mg/20 mL; and treatment time: 120 min.

As Fe₃O₄ is the loaded iron species on the CS/HA supporter to initiate H₂O₂ generating hydroxyl radicals (main oxidation species for degradation of AY220), the

effects of its weight content and the H_2O_2 concentration on AY220 removal should be examined. As shown in Fig.4, it was clear that the AY220 removal efficiency increased with the H_2O_2 concentration for all CS/HA/ Fe_3O_4 composites with different Fe_3O_4 contents, and this was possibly caused by the increased hydroxyl radicals from increased H_2O_2 [29, 30]. Specifically, for CS/HA/ Fe_3O_4 composite with 40% Fe_3O_4 weight ratio, the dye removal efficiency increased sharply with the H_2O_2 concentration and became higher than that of all other composites with different Fe_3O_4 contents at $0.05 \text{ mol L}^{-1}\text{H}_2\text{O}_2$. After that, the AY220 removal efficiency continued to increase and reached a stage at 0.25 mol L^{-1} of H_2O_2 . Herein, the Fe_3O_4 content and the H_2O_2 concentration was set at 40% and 0.25 mol L^{-1} , respectively.

3.2.3. Effect of pH and catalyst dosage

The effect of the sample pH on the dye removal was determined from pH 3 to pH 11 and the results were presented in Fig.5a. Although the dye removal efficiency decreased sharply from 80% to 20% when the pH increased from 9 to 11, it almost retained over 80% in the pH range of 3-9. Compared with the classical homogenous Fenton catalyst (optimal pH value for reaction is about 3), using CS/HA as the supporter to load Fe_3O_4 as a heterogeneous Fenton catalyst indeed extended the pH range for dye removal. According to the Haber-Weiss circle, the increasing of hydroxide ions caused by the increasing of pH would slow down the Fenton-like reaction and produced less $\text{OH}^\bullet$, making the dye degradation decreased and thus the removal efficiency [20, 31]. Since the real sample pH was about 5 during the wool dyeing process when AY220 was used, pH 5 was thus convenient for practical use.

Fig.5. Effect of sample pH (a) and catalyst dosage (b) on AY220 removal by CS/HA/Fe₃O₄. Initial AY220 concentration: 500 mg L⁻¹; adsorbent dosage: 30 mg/20 mL; and treatment time: 120 min.

The influence of CS/HA/Fe₃O₄ dosage on the dyes removal was also investigated. As shown in Fig.5b, the removal efficiency of AY220 increased from less than 65% to over 95% with the catalyst dosage increasing from 10 mg/20 mL to 40 mg/20 mL. This was due to the increasing amount of active sites for both the formation of •OH and the adsorption of the dye [11]. The maximum removal efficiency was obtained when the dosage was 30 mg/20 mL, which then was used in this work.

3.3. Adsorption performance

Because CS/HA can simultaneously provide adsorption sites for both AY220 dyes and H₂O₂, the H₂O₂ decomposition can thus be initiated to produce hydroxyl radicals

for attacking the adsorbed dye, which then promotes the degradation of AY220. Therefore, the adsorption performance of the CS/HA/Fe₃O₄ should be investigated for the reason that both adsorption and catalysis coexist during the process of heterogeneous Fenton-like reaction.

3.3.1. Adsorption kinetics

Fig.6 shows the adsorption kinetics for AY220. It was obvious that the dye was rapidly adsorbed during the first 40 min and almost reached equilibrium in 160 min. No significant changes were observed after 200 min. The time dependence for the adsorption of AY220 by CS/HA/Fe₃O₄ composite can be well described by a pseudo-second-order model (the coefficient R^2 is found to be 0.9989), which suggested that chemisorption could be the rate controlling step [32]:

$$\frac{t}{q_e} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e and q_t is the adsorption capacity (mg g⁻¹) at equilibrium and at time t (min), respectively. K (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order adsorption. The linear plot of t/q versus t is shown in the inset of Fig.6.

Fig.6. Adsorption kinetics for AY220 on CS/HA/Fe₃O₄ and the fitted curve (inset in Fig.5).

Initial AY220 concentration: 500 mg L⁻¹; adsorbent dosage: 30 mg/20 mL; and pH value: 5.

3.3.2. Adsorption isotherm

AY220 aqueous solutions with different initial concentrations from 100-1500 mg L⁻¹ were used for the adsorption experiments. Fig.7 shows the isothermal adsorption of AY220 dye on CS/HA/Fe₃O₄ composite. For better understanding the adsorption patterns, Langmuir, Freundlich and Temkin equations were employed to simulate the adsorption isotherms. The Langmuir isotherm was expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}c_e}$$

where C_e is the equilibrium concentration of the AY220 solution (mg L⁻¹), q_{max} (mg g⁻¹) and b (L mg⁻¹) is the theoretical maximum adsorption capacity and Langmuir equilibrium constants, respectively.

The Freundlich isotherm was expressed as:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e$$

where k_F and n are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption. The degree of nonlinearity between k_F and $(1/n)$ can be determined from the linear plot of $\ln q_e$ versus C_e .

The Temkin isotherm was presented as:

$$q_e = B \ln k_T + B \ln c_e$$

Where B and K_T are Temkin adsorption isotherm constants, and their values can be obtained through plotting $\ln C_e$ versus q_e .

The values of $q_{\max}$, b , k_F , $1/n$, B , K_T and the correlation coefficients for the above isotherms are given in Table 2.

Table 2 Langmuir, Freundlich and Temkin parameters of removal of AY220 by CS/HA/Fe₃O₄

Langmuir model			Freundlich model			Temkin model		
$q_{\max}$	b	R^2	K_F	$1/n$	R^2	B	K_T	R^2
271.0	10.51	0.9621	79.28	0.217	0.9704	43.58	1.956	0.9967

Within the investigated concentration range, Temkin model was best fitted to the removal behaviour of AY220 by CS/HA/Fe₃O₄ (Temkin fitted curve was shown in the inset of Fig.7) based on the value of R^2 , which indicated that AY220 was adsorbed on the uneven surface of CS/HA/Fe₃O₄ composite with a monolayer adsorption pattern [33].

Fig.7. Adsorption isotherm for AY220 by CS/HA/Fe₃O₄, and Temkin fitted curve of the composite (inset in Fig.6). Adsorbent dosage: 30 mg/20 mL and pH value: 5

3.4. Catalytic activity

3.4.1. Enhanced degradation efficiency by CS/HA/Fe₃O₄

Fig.8 gives the catalytic degradation efficiencies of AY220 by CS/HA/Fe₃O₄ and Fe₃O₄. In comparison with bare Fe₃O₄, CS/HA/Fe₃O₄ exhibited an enhanced degradation efficiency of AY220. In fact, the enhanced degradation efficiency of Fe₃O₄ after being loaded on the supporter was also reported by Hu et al. [11] using nano-Fe₃O₄/MWCNTs to degrade 17-methyltestosterone in aqueous solution. The enhanced degradation efficiency of CS/HA/Fe₃O₄ may relate to the increased active sites provided by a good dispersion of Fe₃O₄ on the CS/HA supporter rather than an aggregation of bare Fe₃O₄ in aqueous solution [34] (aggregation of bare Fe₃O₄ made its hydrodynamic radius bigger than that of CS/HA/Fe₃O₄, as shown in Fig.S1). On the other hand, Co²⁺ ions released during the AY220 degradation process also possibly cause the increased degradation efficiency of AY220 owing to the initiation of H₂O₂ by the absorbed Co²⁺, thus promoting the generation of hydroxyl radicals. Moreover, the degradation efficiency of AY220 by CS/HA/Fe₃O₄ was also much higher than that of the raw-CS based catalyst (CS/Fe₃O₄ composite) (Fig.S2), and this further confirmed the combination of HA with CS indeed improved the stability of CS.

Fig.8. Enhanced degradation of AY220 by CS/HA/Fe₃O₄ compared with Fe₃O₄. Initial AY220 concentration: 500 mg L⁻¹; catalysts dosage: 30 mg/20 mL of CS/HA/Fe₃O₄ and 12 mg/20 mL of Fe₃O₄; pH value: 5; and H₂O₂ concentration: 0.25 mol L⁻¹.

3.4.2 Enhanced degradation efficiency by recyclable-used CS/HA/Fe₃O₄

Variation of the degradation efficiency of AY220 by the catalyst with the increasing recyclable time of the catalyst was shown in Fig.9. As it can be seen from Fig.9, with the recyclable time increasing from Cycle 1 to Cycle 5, the degradation efficiency of AY220 enhanced significantly from 25.1% to 45.6%, which is possibly due to the accumulation of absorbed Co²⁺ ions on the catalyst surface after several recycles [10] and the synergistic effect of the adsorbed Co²⁺ and the loaded Fe₃O₄ [12].

Fig.9. Variation of degradation efficiency of AY220 with the increasing recyclable time of the catalyst.

The change of the total Co²⁺ concentration (including chelated or free Co²⁺) in the supernatant after being treated by CS/HA/Fe₃O₄ in absence or presence of H₂O₂ was given in Fig.10. It was observed that the total Co²⁺ concentration all decreased

with the treatment time, which indicated that AY220 can be removed efficiently by the composite no matter whether H_2O_2 is present or not. However, in the presence of H_2O_2 , the total Co^{2+} concentration began to decrease sharply after treatment for 30 min, and decreased much lower than that without H_2O_2 after 2 h, which implied the Co^{2+} released during the Fenton-like degradation may be absorbed by $\text{CS}/\text{HA}/\text{Fe}_3\text{O}_4$. Moreover, the surface Co/S ratio of $\text{CS}/\text{HA}/\text{Fe}_3\text{O}_4$ in the presence of H_2O_2 increased from 0 to 0.71 (higher than 0.5 of AY220, determined by EDS) after dye treatment further confirmed the adsorption of Co^{2+} by the catalyst. Meanwhile, the surface Ca/P ratio of $\text{CS}/\text{HA}/\text{Fe}_3\text{O}_4$ decreased from 1.63 to 1.24 after treatment implied the adsorption mainly attribute to ion exchange between Ca^{2+} in HA and Co^{2+} in the supernatant. The possible absorption process was illustrated in Fig.11.

Fig.10. The total Co^{2+} concentration changing in the supernatant after treatment by $\text{CS}/\text{HA}/\text{Fe}_3\text{O}_4$ in absence and in presence of H_2O_2

Fig.11. Scheme of the adsorption of free Co^{2+} released from AY220 degradation by CS/HA/Fe₃O₄ in the presence of H₂O₂

Furthermore, the effect of the adsorption amount for Co^{2+} in CoCl₂ solutions by the catalyst on its degradation efficiency of AY220 was also evaluated (the adsorption amount for Co^{2+} and the degradation efficiency of AY220 by the catalyst after adsorbed Co^{2+} in CoCl₂ solutions with different initial concentrations was shown in Fig.S3), and the result was shown in Fig.12. With increasing of the adsorption amount for Co^{2+} from 77.4 to 189 μg , the degradation efficiency of AY220 by the catalyst increased greatly and reached 51%, and this indicated that the accumulation of free Co^{2+} on the catalyst surface after recyclable use was indeed directly correlated with its improved dyes degradation efficiency.

Fig.12. The effect of the adsorption amount for Co²⁺ by the catalyst on its degradation efficiency.

Finally, the degradation efficiency of AY220 by the CS/HA/Fe₃O₄ with Co²⁺ adsorbed on its surface and equivalent Co²⁺ in solution was compared. The results was given in Fig.13. The CS/HA/Fe₃O₄ with Co²⁺ showed a much higher degradation efficiency for AY220 than that without Co²⁺, which suggested that a synergistic effect between adsorbed Co²⁺ and loaded Fe₃O₄ could exist during the dye degradation. When no Co²⁺ was adsorbed on the catalyst, the H₂O₂ initiation mainly involved in the following two independent processes (eq 7 and eq 8):

However, for the catalyst with Co^{2+} adsorbed, the hydroxyl radical generation progress is different. The adsorbed Co^{2+} ($\text{Co}^{2+}_{\text{sur}}$) firstly initiate H_2O_2 to generate hydroxyl radicals and Co^{3+} (eq 9), then Fe^{2+} loaded on the catalyst was oxidized by Co^{3+} (eq 10) due to the higher redox potential of $\text{Co}^{3+}/\text{Co}^{2+}$ (1.842 V) than that of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.770 V), promoting the $\bullet\text{OH}$ generation through initiation of H_2O_2 by Co^{2+} . Meanwhile, Fe^{2+} and Fe^{3+} also react with H_2O_2 as eqs 11-13 and further accelerate the generation of $\bullet\text{OH}$. Therefore, the above reaction all contribute to the much higher AY220 degradation efficiency than using the catalyst without Co^{2+} adsorbed, and the recyclable metal-promoted Fenton-like degradation procedure was illustrated in Fig.14.

Fig.13. Degradation efficiency of AY220 by CS/HA/Fe₃O₄ with Co²⁺ adsorbed on its surface and in the solution under different Co²⁺ treatment concentration.

Fig.14. Schematic diagram of recyclable metal-promoted Fenton-like degradation procedure.

3.5. The total removal efficiency of AY220 by recyclable-used CS/HA/Fe₃O₄

As mentioned above that both adsorption and catalysis coexist during the process of heterogeneous Fenton-like reaction, the total removal efficiency except degradation efficiency of AY220 by recyclable-used CS/HA/Fe₃O₄ was also examined, and the result was given in Fig.15. It was clearly shown that the total removal efficiency of AY220 decreased from 95.0% to 80.5% after 5 runs, which indicated the adsorption

efficiency decreased during the recyclable process. The possible reason may be ascribed to the destroyed organic phase, generated pore, and the saturated adsorption sites caused by the Fenton oxidation process [35]. However, the removal efficiency of AY220 by CS/HA/Fe₃O₄ still retained above 80% after 5 runs, and this implied its good recyclability for practical application.

Fig.15. Total removal efficiency of AY220 by recyclable-used CS/HA/Fe₃O₄.

4. Conclusion

In this work, HA instead of a cross-linking agent was introduced to combine with CS to form a dual-phase composite (CS/HA) as a supporter for Fe₃O₄ loading, and a new CS-based heterogeneous Fenton catalyst (CS/HA/Fe₃O₄ magnetic composite) was thus developed for AY220 degradation/removal. The total removal efficiency of AY220 by the CS/HA/Fe₃O₄ magnetic composite can reach as high as 95.0%. Meanwhile, it degraded AY220 without external energy and with a greatly enhanced degradation efficiency compared with the raw-CS based catalyst and bare Fe₃O₄. Moreover, it can efficiently adsorb Co²⁺ released from AY220 degradation, and with

the increasing of Co^{2+} adsorbed on its surface after 5-time recyclable runs, its degradation efficiency of AY220 increased from 25.1% to 45.6%, and this showed its recyclable metal-promoted degradation enhancement and a great potential in removal of metal complex dyes.

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