

Preparation of EDTA modified cotton fiber iron complex and catalytic properties for aqueous Cr(VI) reduction and dye degradation

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ABSTRACT

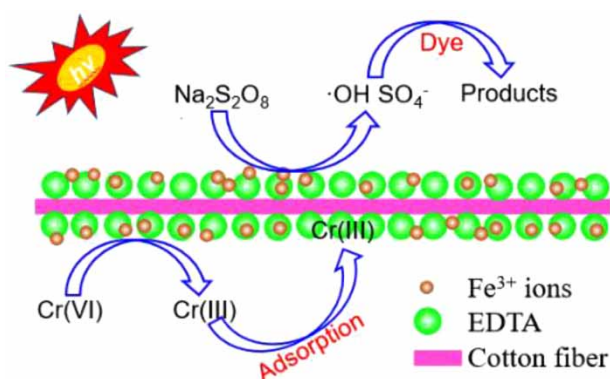
Cotton fabric was modified with Na₂EDTA using a hydrothermal method to introduce surface hydroxyl groups, and subsequent coordination of Fe(III) ions to produce an Na₂EDTA modified cotton-fiber-Fe complex (Fe-EDTA-Cotton). After characterization by SEM and FTIR, Fe-EDTA-Cotton was used as a heterogeneous photocatalyst to reduce Cr(VI) and degrade Reactive Red 195 oxidatively, to evaluate its catalytic activity. The results indicated that high Na₂EDTA and/or NaH₂PO₄ concentrations, and/or high hydrothermal temperature increased the carboxyl group content (Q_{COOH}) of the cotton fiber; high Fe content and elevated temperature could enhance coordination. Fe-EDTA-Cotton had a significant photocatalytic function in reducing Cr(VI). Increasing the Q_{Fe} value of the complex or stronger irradiation favored photocatalytic reduction of Cr(VI) species. Increasing the system's pH did not help the reduction reaction. Fe-EDTA-Cotton could also remove Cr(VI) and Reactive Red 195 simultaneously from aqueous solution, and showed strong photocatalytic capacity. The reduction or oxidation reaction could be regulated by changing Na₂S₂O₈ concentration in the reaction system, which might provide a new way to treat wastewater containing organic pigments and Cr(VI) species.

Key words: Cr(VI) removal, EDTA modified cotton, Fe complex, oxidative degradation of dye, photocatalytic reduction

HIGHLIGHT

- Hydrothermal process enhanced EDTA modification of cotton fabric.
- EDTA-modified cotton fiber Fe complex was prepared.
- Cr(VI) removal was improved by its synergistic effect.
- Fe complexes can remove Cr(VI) and organic dyes from aqueous solution in one bath.
- The work might provide a new way to purify the wastewater containing organic pigments and Cr(VI) species.

GRAPHICAL ABSTRACT



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INTRODUCTION

With the development of industry, heavy metal ions in water have caused serious environmental pollution, and pose a significant threat to human and aquatic life and health. Hexavalent chromium (Cr(VI)) is a highly toxic heavy metal ion, which can cause DNA damage through food chain enrichment in humans as it is non-biodegradable. It can lead to mutagenesis and carcinogenesis in humans (Jing *et al.* 2017). Moreover, a maximum acceptable level for total Cr species in wastewaters has been mandated at 0.1 to 0.2 mg L⁻¹ in many countries to minimize their harm to both humans and the natural environment (Jing *et al.* 2017; Wang *et al.* 2017). Cr(VI) and trivalent chromium (Cr(III)) are the most stable forms in the aquatic environment, and Cr(VI) is about 1,000 times more poisonous than Cr(III). Since about 2000, many techniques such as adsorption (Mao *et al.* 2012), ion-exchange (Petruzzelli *et al.* 1995), chemical reduction (Lakshminathiraj *et al.* 2008; Kim *et al.* 2019) and precipitation (Palmer & Wittbrodt 1991) have been employed for Cr species removal from aqueous media. Reduction of Cr(VI) with nano-TiO₂ or Fe ions and their complexes as photocatalysts has been a major focus of investigation, due to their excellent chemical and optical properties, and low cost (Marinho *et al.* 2016, 2017; Ye *et al.* 2017). Although they show strong Cr(VI) reduction ability, it is difficult to separate and recycle nano-TiO₂ particles or Fe ions from solution when the reaction is complete, which limits their application in actual wastewater treatment. Thus, there is real practical significance in searching for novel, bifunctional, heterogeneous photocatalysts with strong reduction and adsorption capacity, to improve chromium ion removal rates and reduce secondary environmental pollution.

The molecular structure of ethylenediaminetetraacetic acid (EDTA) contains four carboxyl and two amino groups, as coordination functional groups, has high affinity for many divalent or trivalent metal ions, and can form highly stable complexes (Yang *et al.* 2014). EDTA has, therefore, been used widely as a chelating agent for heavy metal ion removal from water. EDTA complexes are photoactive to UV and visible light, and Fe(III)-EDTA complexes are converted to Fe(II) after exposure to light and can be used as an efficient photocatalyst for Cr(VI) (Beiyuan *et al.* 2018). Studies have also shown that EDTA has poor biodegradability as a synthetic chelating agent, and the metal-EDTA complexes formed in wastewater treatment are difficult to remove by traditional biological or chemical processes, thus causing serious pollution problems (Klüner *et al.* 1998; Beiyuan *et al.* 2018). EDTA immobilization on fiber carrier surfaces not only yields good metal-ion adsorption performance but can also improve solid-liquid separation after reaction, avoiding secondary environmental pollution. Moreover, EDTA molecules not coordinated with Fe(III) on the fiber surface can effectively capture Cr(III) in aqueous solution, thereby removing Cr(III) from solution.

Fe(III)-EDTA can also be used as a heterogeneous reaction catalyst in the oxidative degradation of organic pollutants such as dyes. It is worth noting that cotton is a natural fiber offering the benefits of easy degradability, low cost, large specific surface and high porosity, which is advantageous for contact between pollutants and the fiber surface's active sites in the reaction process (Dong *et al.* 2020). On that basis, cotton fabric was modified with Na₂EDTA using a hydrothermal method to introduce surface hydroxyl groups, and subsequent coordination of Fe(III) ions to produce an Na₂EDTA-modified cotton-fiber-Fe complex for this study. This was used as a heterogeneous photocatalyst in Cr(VI) reduction and the oxidative degradation of Reactive Red 195 to investigate its catalytic reduction and oxidation performance.

METHODS

Reagents and materials

Commercially scoured, boiled and mercerized, 100% cotton plain fabric (156.8 g m⁻²) was employed. Na₂EDTA, NaH₂PO₄ (SHP), FeCl₃·6H₂O, Na₂S₂O₈ (SPS), K₂Cr₂O₇, diphenylcarbazide and NaOH were all analytical grade reagents, used as received without further purification. A commercially available azo dye, Reactive Red 195 (RR195), was used after purification by re-precipitation.

Preparation of Fe complex on modified cotton fiber

The EDTA modified cotton-fiber-Fe complex was prepared according to previous research (Dong *et al.* 2019). Typically, 1.0 g of cotton fiber was immersed for 20 minutes in a mixed solution containing specified concentrations of Na₂EDTA and SHP, then transferred to a 100 mL, Teflon-lined, stainless-steel autoclave and heated at 200 °C (except for special instructions) for 1 hour, before cooling to room temperature. The modified cotton fiber (EDTA-Cotton) obtained was then placed in 50 mL of an aqueous solution containing 0.10 mol L⁻¹

Fe(III) ion, held at 55 °C and stirred continuously for 3 hours, to prepare the EDTA-Cotton Fe complex (Fe-EDTA-Cotton). Finally, the carboxylic acid content (Q_{COOH} , mmol g^{-1}) on the EDTA-Cotton surface and the Fe content (Q_{Fe} , mmol g^{-1}) of the resulting Fe-EDTA-Cotton were calculated using the method described by Dong *et al.* (2019).

Characterization

The cotton fabric was analyzed by SEM, FTIR and DRS, before and after modification and coordination. For SEM observation, a Zeiss Gemini 500 scanning electron microscope operating at 15 kV was used to investigate the sample surface structure. For FTIR analysis, a Nicolet iS50 FT-IR spectrometer was used to determine surface chemical constituents. A Hitachi UH4150 UV-vis-NIR spectrometer was used to assess the light adsorption ability of fibrous samples by measuring their diffuse reflectance UV-Vis spectra (DRS), with barium sulfate as the reference.

Photocatalytic experiments

The photocatalytic measurements were carried out using Cr(VI) and RR195 as target pollutants under visible light irradiation from a 100 W LED lamp (Guangdong Ant Illumination Co., China). In a typical procedure, 1.0 g Fe-EDTA-Cotton was dispersed in each of 100 mL Cr(VI) solution (0.04 mmol L^{-1}) and 100 mL RR195 (0.05 mmol L^{-1}), the latter including SPS (1.5 mmol L^{-1}). The test solution was sampled at fixed time intervals and the sub-sample separated by centrifugation. The Cr(VI) concentration was determined with a UV-2401 Shimadzu spectrophotometer using a colorimetric method based on the 1,5-diphenylcarbazide reaction at 540 nm (maximum absorption wavelength). The total concentration of the remaining Cr species in the test solution was measured using a PinAAcle 900H atomic absorption spectrometer (Perkin-Elmer Inc., USA). The proportional removal of Cr(VI) ($R\%$) was calculated using Equation (1). Total Cr species removal efficiency ($\eta\%$) was expressed using Equation (2). The concentration of RR195 remaining in solution was measured during the reaction by a method reported in Dong *et al.* (2010).

$$R\% = (1 - C_{t6}/C_{06}) \times 100\% \quad (1)$$

$$\eta\% = (1 - C_{tt}/C_{0t}) \times 100\% \quad (2)$$

where C_{06} and C_{t6} were the initial and residual concentrations of Cr(VI), respectively, and C_{0t} and C_{tt} the initial and residual concentrations of total Cr species during the reaction.

RESULTS AND DISCUSSION

Preparation of EDTA-Cotton

To investigate the effect of reaction conditions on the EDTA-Cotton surface Q_{COOH} , the concentrations of EDTA and SHP and the hydrothermal reaction temperature were changed respectively, and the cotton fabrics were modified by the method noted above to obtain EDTA-Cotton with different Q_{COOH} values. The results – that is, reaction conditions vs Q_{COOH} value – are shown in Figure 1.

Figure 1(a) shows clearly that the Q_{COOH} value on the EDTA-Cotton surface increases significantly with increasing Na_2EDTA concentration, indicating that raising the Na_2EDTA concentration can significantly promote cross-linking with the cotton fiber. In part, this is because a pair of adjacent carboxyl groups in Na_2EDTA 's molecular structure will dehydrate to form cyclic anhydride, with high reaction activity, when the temperature and pressure are high, which reduces the esterification reaction activation energy between Na_2EDTA and hydroxyl groups in the cellulose molecular structure and promotes esterification between them, introducing carboxyl groups onto the fabric surface (Júnior *et al.* 2009; Gan & Dong 2019) – see Equation (3). The probability of contact between Na_2EDTA molecules and hydroxyl groups in the cellulose molecular structure and the diffusion rate of Na_2EDTA into the cotton fiber also increase, increasing the number of molecules involved in cross-linking, which increases Q_{COOH} . It is noted that, during the cross-linking reaction between polycarboxylic acid and cellulose, NaH_2PO_4 can significantly promote the reaction between carboxyl and hydroxyl groups.

Figure 1(b) shows a gradual rise in the Q_{COOH} value as the SHP concentration increases, which means that increasing the SHP concentration can promote the esterification reaction. This is mainly because SHP can promote the dehydration of adjacent carboxyl groups in the Na_2EDTA molecular structure to form cyclic anhydride (Mao *et al.* 2012), which is conducive to esterification. It is noted that when the SHP concentration exceeds

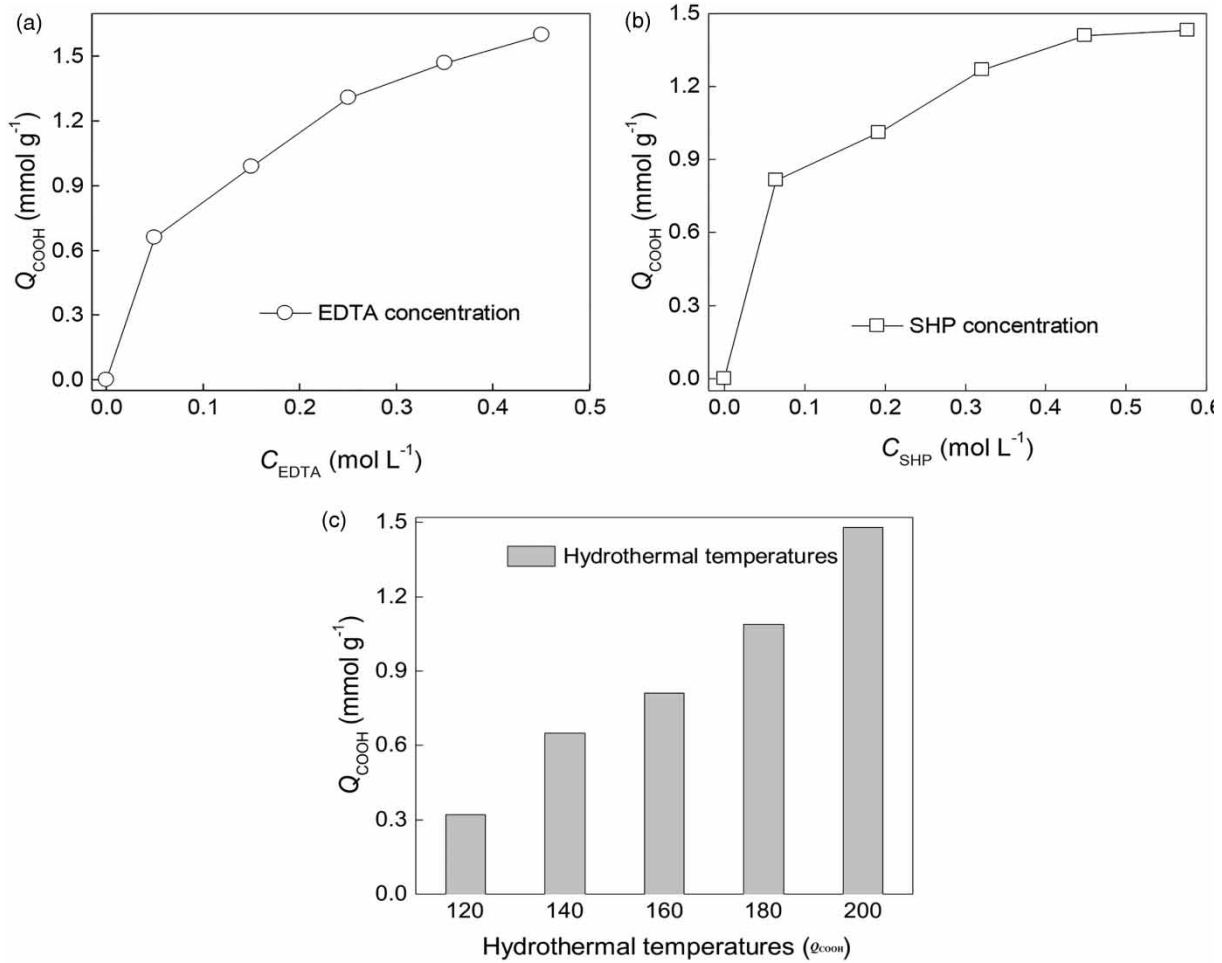
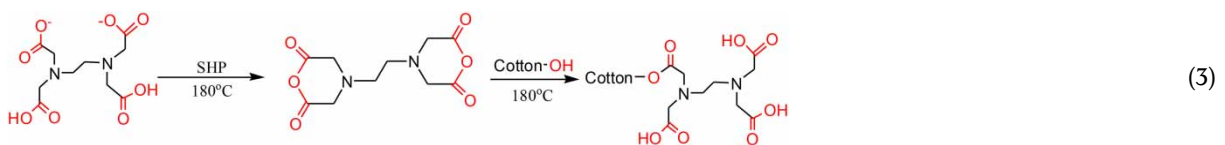


Figure 1 | Relationship between C_{EDTA} , C_{SHP} , hydrothermal temperature and Q_{COOH} value.

0.32 mol L⁻¹, the EDTA-Cotton surface's Q_{COOH} value no longer increases significantly, and the modification reaction tends to be balanced. There are two reasons: (1) high concentrations of SHP will cause the ester bond generated during esterification to break and reduce the amount of Na₂EDTA esterified with the fiber macromolecules; and (2) the increase in SHP concentration will promote the esterification of more carboxyl groups in the EDTA-Cotton molecular structure to form ester bonds, reducing the number of free carboxyl groups and preventing the EDTA-Cotton surface's Q_{COOH} value from increasing. Therefore, it can be considered that the optimal SHP concentration for EDTA-Cotton preparation is 0.32 mol L⁻¹.

Figure 1(c) shows that increasing the hydrothermal temperature also increases the Q_{COOH} value – that is, increasing the temperature can promote modification significantly. This is mainly because increasing the hydrothermal temperature promotes the dehydration of the adjacent carboxyl group pairs in EDTA's molecular structure to form anhydride (Júnior *et al.* 2009), accelerating the esterification rate between EDTA and the cotton fiber, so that the fabric surface contains more carboxyl groups. The temperature increase also increases the degree of swelling and wetting of the cotton fiber, so that EDTA molecules immerse more easily in the fiber (Júnior *et al.* 2009). However, although the Q_{COOH} value of the EDTA-Cotton surface at 200 ° is high, the fiber's mechanical properties are reduced severely due to the high temperature and pressure conditions. Therefore, it is considered that the best hydrothermal temperature for preparing EDTA-Cotton is 180 °C.



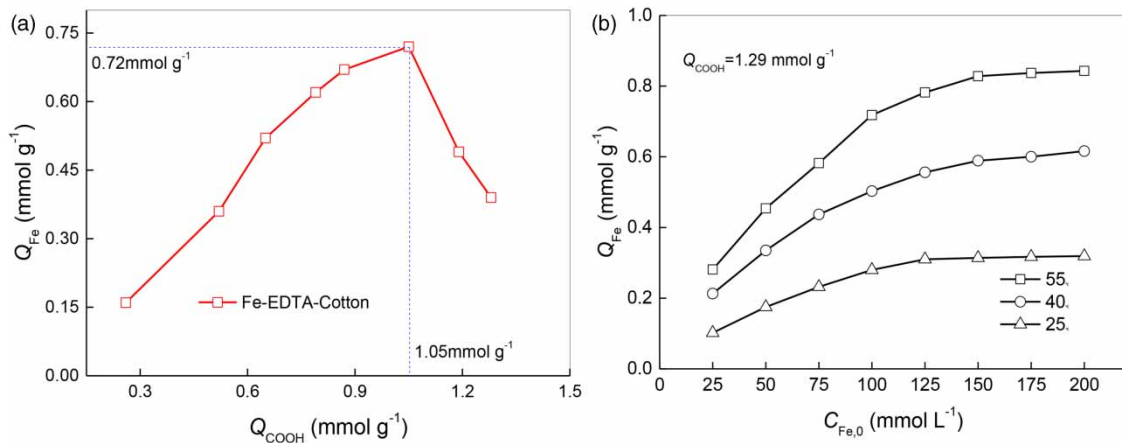


Figure 2 | Coordination reaction between Fe(III) and EDTA-Cotton under various conditions.

Preparation of Fe-EDTA-Cotton

EDTA-Cotton was coordinated with Fe(III) under specific conditions and, after the reaction was complete, the Q_{Fe} values on the Fe-EDTA-Cotton surface were measured – see Figure 2.

Figure 2(a) shows that Q_{Fe} increases initially but then decreases with increasing Q_{COOH} , indicating that increasing Q_{COOH} is a benefit and increases Q_{Fe} . However, strong concentrations lower the Fe(III)/cotton coordination. The mechanism is that higher Q_{COOH} concentration on the EDTA-Cotton surface improves coordination with Fe(III), yielding higher Fe(III) concentrations on the cotton fiber surface. However, excess coordination tightens the cotton fiber surface structure. The resulting steric effect blocks the carboxyl/Fe(III) coordination reaction and lowers the cotton surface's hydrophilicity (Liu *et al.* 2018), which also blocks Fe(III) permeation. Temperature and Fe(III) concentration were the two main factors in the coordination reaction – see Figure 2(b). Obviously, Q_{Fe} generally increases with $C_{Fe,0}$ at the same temperature, so $C_{Fe,0}$ increases the coordination reaction, mainly because increasing $C_{Fe,0}$ enhances Fe(III) expansion on the cotton fiber surface and its permeability, benefiting the coordination reaction between them. Equally, Q_{Fe} increases with reaction temperature at the same $C_{Fe,0}$, indicating that raising the reaction temperature enhances Fe(III)/EDTA-Cotton coordination. The increased temperature accelerates the swelling of the cotton fiber, exposing more internal carboxyl groups, which enhances coordination. With the temperature increase, however, the Brownian movement of the liquid molecules will also increase, leading the spreading of Fe(III) internally and externally to the cotton fiber surface, which is good for coordination with the cotton fiber. While a higher reaction temperature will increase Q_{Fe} , it will also cause explosive hydrolysis to generate $FeOOH$, so it should not be too high.

Catalyzer characterization

SEM images (Figure 3(a)–3(c)) show that folds on the cotton surface are covered by heterogeneous, raised, soil-like material, which is thought to be caused by the Fe(III) on the cotton fiber surface (Liu *et al.* 2018; Dong *et al.* 2019). This indicates that the cotton fiber surface is the main location of the coordination reaction between EDTA-Cotton and Fe(III). It is noted that no obvious change is detected and the fiber appearance is preserved, after the EDTA modification and Fe(III) coordination reactions.

Figure 3(d) shows that the characteristic spectral line peaks of cotton fiber all migrate after EDTA modification. More importantly, a new peak has appeared at around $1,745\text{ cm}^{-1}$. This might be a carboxyl and ester characteristic peak after EDTA-Cotton modification. This indicates that esterification happened between the hydroxyl in the cotton-fiber-molecule structure and carboxyl in the EDTA-molecule structure (Dong *et al.* 2019). The migration and lower magnitude of the characteristic spectral line peaks for Fe-EDTA-Cotton also mean that the coordination reaction between EDTA-Cotton and Fe(III) and its complex has shown up.

Figure 3(e) shows a strong characteristic peak in the EDTA-Cotton UV area, arising from π - π transition of the unsaturated bond in its macro-molecular structure. Fe-EDTA-Cotton has higher absorption capability than EDTA-Cotton in the UV and Vis spectral region, and higher Q_{Fe} can improve this further. In other words, introducing Fe(III) will promote the light absorption properties of cotton fiber significantly. The strong visible light

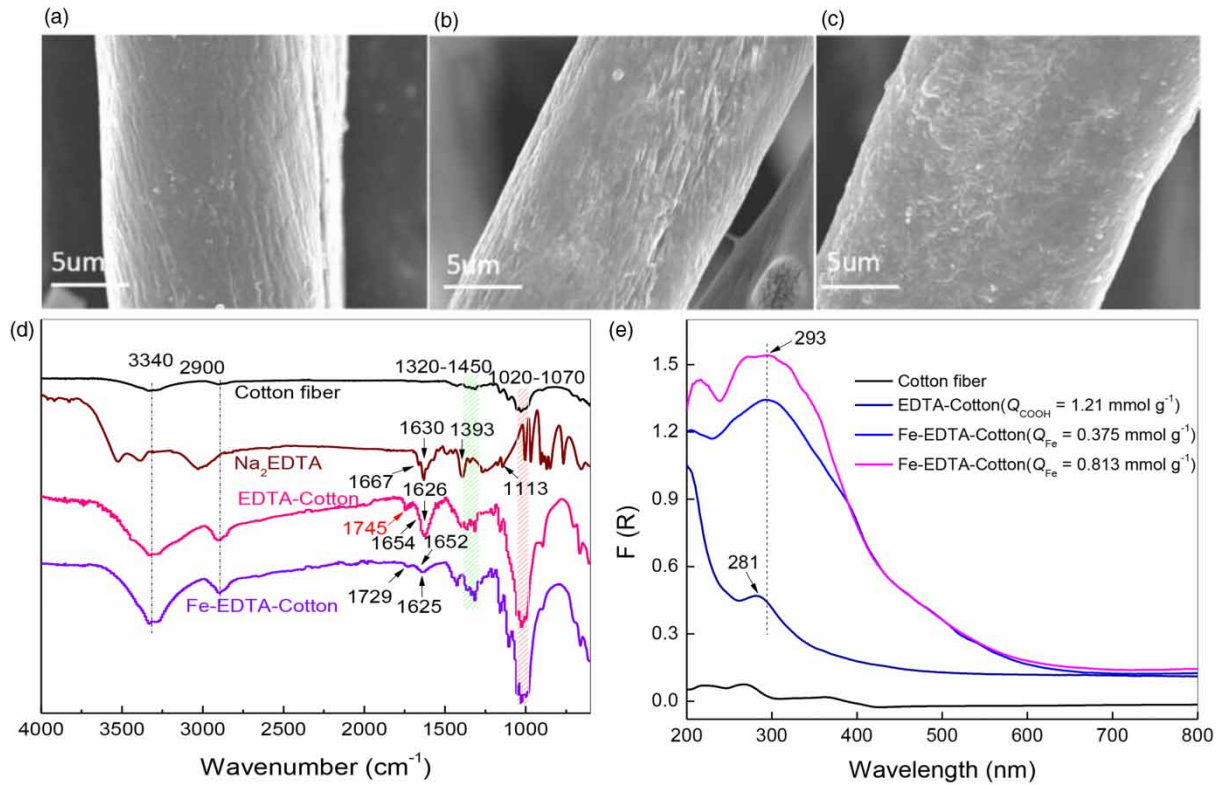


Figure 3 | SEM (a) Cotton fiber, (b) EDTA-Cotton, (c) Fe-EDTA-Cotton, and (d) FTIR and (e) DRS spectra of cotton fiber, EDTA-Cotton and Fe-EDTA-Cotton.

absorption performance of Fe-EDTA-Cotton indicates that the utilization rate of solar or LED light can be improved, accelerating the reduction of Cr(VI) and/or the oxidation removal of dyes.

Heterogeneous photocatalytic reduction of aqueous Cr(VI)

Several different reaction systems containing 100 ml 0.04 mmol L⁻¹ Cr(VI) solution were set up at pH 6.0 and 25 °C. The results – Figure 4 – show that *R*% values within the first 60 minutes were below 5% when the original cotton fiber or EDTA-Cotton were used, with or without irradiation (curves i to iii), indicating that Cr(VI) is reduced very little under these conditions. The *R*% value increased gradually to 13.75% at 60 minutes for

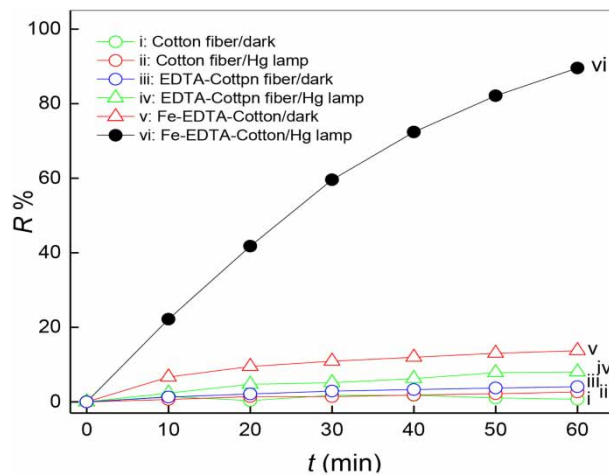


Figure 4 | Reduction efficiency of Fe-EDTA-Cotton for Cr(VI).

EDTA-Cotton with irradiation (curve iv), which may be due to the weak light absorption properties of EDTA-Cotton in the UV and Vis regions (Figure 3(e)).

Light irradiation can promote reduction by the reducing groups C-H and C = O on the EDTA-Cotton surface with Cr(VI) in aqueous solution (Deng *et al.* 2017), causing some Cr(VI) reduction – Equations (4) and (5). $R\%$ is only 8.03 after 60 minutes in the dark (curve v). When irradiation is introduced into the system, however, (curve vi), $R\%$ increases sharply to 89.53 at 60 minutes – i.e., the catalytic reduction of Cr(VI) by Fe-EDTA-Cotton is highly dependent on light irradiation. Several similar results have been reported for the homogeneous photocatalytic reduction of Cr(VI) in the presence of Fe(III) and organic acids – for example, oxalic and citric – in water (Marinho *et al.* 2016; Ye *et al.* 2017). The main reason is that Fe(III) on the Fe-EDTA-Cotton surface absorbs incident photons and is converted to Fe(II) due to LMCT (ligand to metal charge transfer) effects under light radiation. The Fe(II) generated on the Fe-EDTA-Cotton surface can act as an effective reducing agent to convert Cr(VI) to Cr(III) through a series of single electron transfer processes (Luo *et al.* 2017). At the same time, Fe(II) is oxidized to Fe(III), and the cyclic Fe(III)/Fe(II) reaction is realized – Equations (6) and (7).

Usually, reaction conditions have the greatest impact on catalytic performance, so the reaction conditions were optimized and $R\%$ under different conditions obtained. The data generated were used in the pseudo-first-order reaction kinetics equation and the results showed that it could be used to describe the Cr(VI) reduction reaction. The reduction reaction rate constants (k) are shown in Figure 5.



Figure 5(a) shows that k increases significantly with increases in Q_{Fe} , indicating that the increase in Q_{Fe} can significantly accelerate the Cr(VI) reduction reaction, when catalyzed by Fe-EDTA-Cotton. This is because the number of active sites on the catalyst surface increases, so that more Cr(VI) ions are adsorbed on the catalyst surface where reduction occurs, which is conducive to the conversion of Cr(VI) to Cr(III).

Figure 5(b) shows the effect of pH on k . As can be seen, k is significantly higher at pH 3 and 6 than at pH 9 – that is, acidic and neutral conditions are favorable for the reduction reaction. Generally, Cr(VI) exists mainly in aqueous media in the forms of H_2CrO_4 , CrO_4^- and CrO_4^{2-} , while $HCrO_4^-$ is its principal form in the pH range 1.0 to 6.8 (Deng *et al.* 2017). The -N= functional group on the Fe-EDTA-Cotton surface is also protonated at low pH levels, promoting the adsorption of negatively charged Cr(VI) through electrostatic attraction. This is conducive to the rapid reduction of Cr(VI) species, as shown in Equation (8) (Li *et al.* 2009). Equations (9) and (10), however, show that high H^+ concentrations in solution can also promote rapid Cr(VI) reduction (Marinho *et al.* 2016; Luo *et al.* 2017).

As pH levels increase in the reaction system, the concentration of H^+ falls, making the Fe(III) at the active site interact easily with OH^- in the solution to form an insoluble precipitate, thus reducing the number of active sites and reducing the catalyst performance for Cr(VI). Figure 5(c) shows that k increases significantly with increasing reaction temperature, indicating that higher reaction temperatures are beneficial to the catalytic reduction reaction. With the temperature increase, the Brownian motion of the molecules in solution intensifies, and the average kinetic energy increases, intensifying the thermal motion of Cr(VI) in the solution. The fibers also swell to a greater extent, helping to improve contact probability between Cr(VI) and the catalyst, thus enhancing Cr(VI) reduction.

The Arrhenius equation (Zhang *et al.* 2018) shows that the apparent activation energy of the Cr(VI) reduction reaction in this system is $25.45 \text{ kJ mol}^{-1}$. As can be seen in Figure 4, irradiation is necessary for catalytic reduction reaction. Figure 5(d) shows that k under the Hg lamp is significantly higher than with the other three LED light sources. In other words, although the intensity of visible light from the Hg lamp is lower than that of LED-h, the former can improve the catalytic reduction performance of Fe-EDTA-Cotton for Cr(VI) more effectively. It is important that the increase in LED light radiation intensity is conducive to the increase in k , as it means that the increase in visible light intensity from LEDs can promote the Cr(VI) reduction reaction,

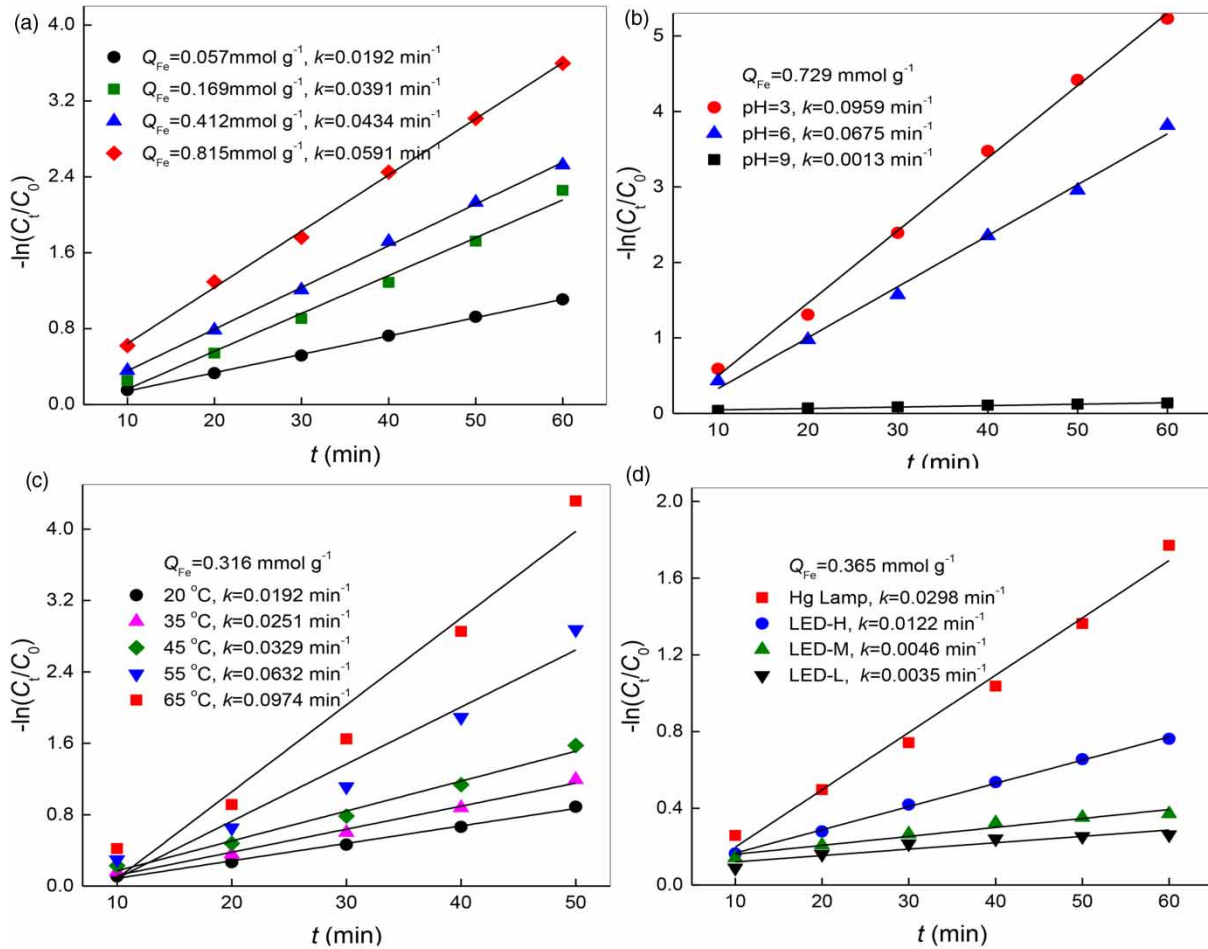
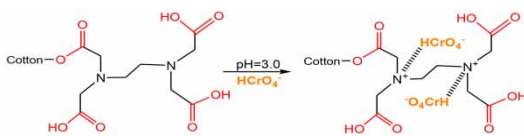
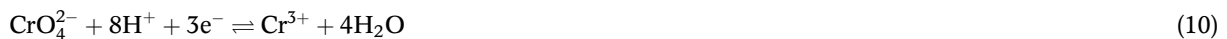


Figure 5 | Photocatalytic reduction of Cr(VI) with Fe-EDTA-Cotton under various conditions (LED-L: 1.87 mW cm^{-2} , LED-M: 5.10 mW cm^{-2} and LED-H: 14.95 mW cm^{-2} at 400–1,000 nm).

and that LEDs with high light radiation intensity can replace Hg lamps, which consume more energy, in the context of the catalytic reduction of Cr(VI) by Fe-EDTA-Cotton.



(8)



Heterogeneous photocatalytic oxidation of RR195

Figure 6(a) shows the effect of Q_{Fe} on the catalytic oxidation performance of Fe-EDTA-Cotton. It is obvious that the dye decolorization rate ($D\%$) is only about 14% after 90 minutes, when $Q_{Fe} = 0 \text{ mmol L}^{-1}$. This is mainly due to the limited adsorption of dyes on cotton fibers, and the weak and slow oxidation of dyes by SPS. When $Q_{Fe} > 0 \text{ mmol L}^{-1}$, $D\%$ increases significantly with increasing reaction time, indicating that Fe(III) on the fiber surfaces is the key factor in Fe-EDTA-Cotton's photocatalytic oxidation activity, mainly because the dye molecules in aqueous solution are excited when exposed to visible light radiation (Equation (11)). The excited dye molecules transfer their own electrons to Fe(III) ions on the catalyst surface, reducing them to Fe(II) (Equation (12)) (Gao *et al.* 2016), and then reacting with $\text{S}_2\text{O}_8^{2-}$ adsorbed onto the surface active site, or dissolved oxygen in

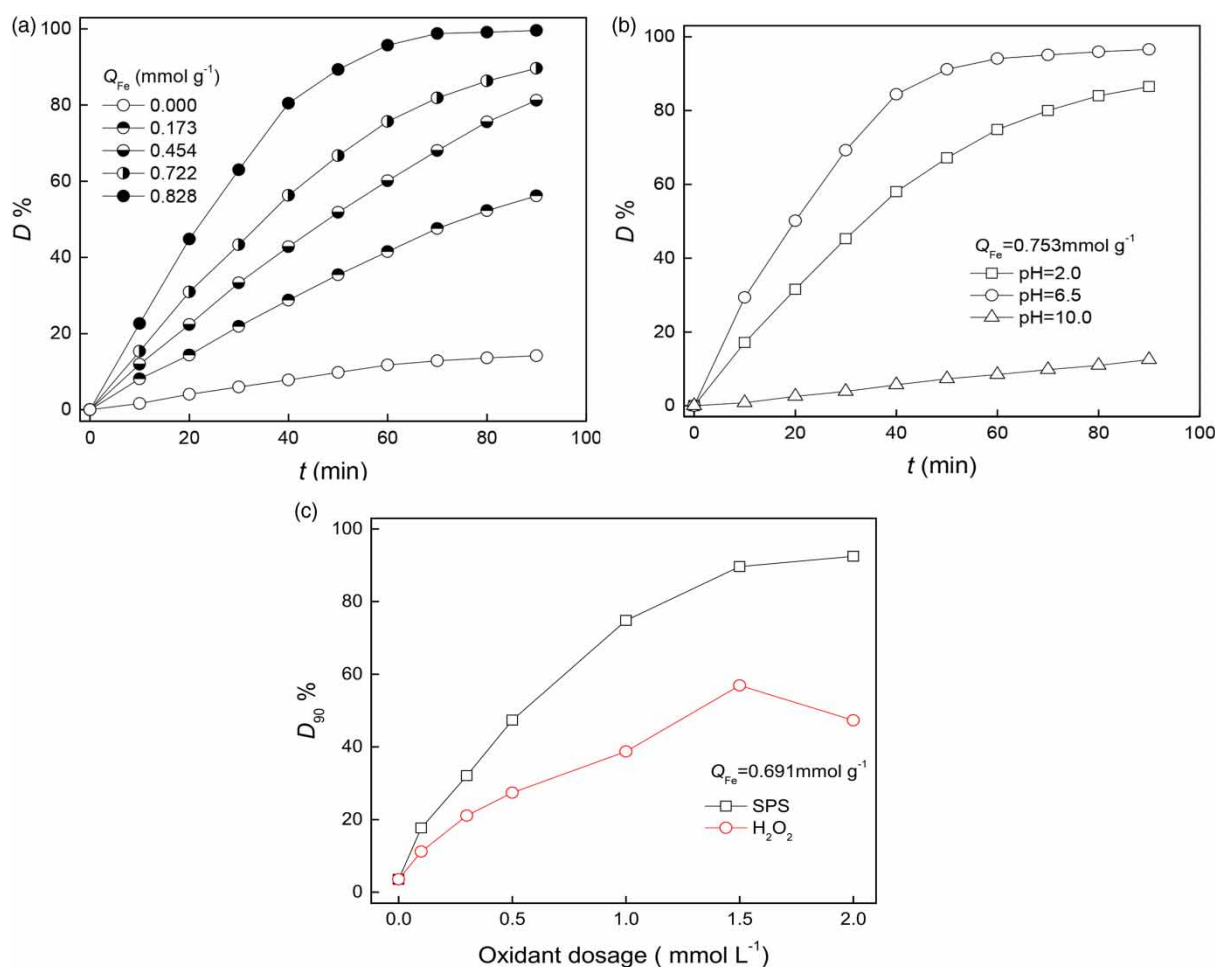


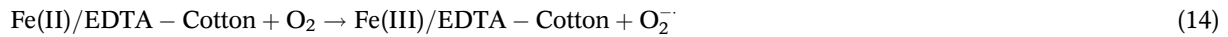
Figure 6 | Catalysis of Fe-EDTA-Cotton during dye degradation under differing conditions.

the water, to produce SO_4^- and O_2^- , which are used for oxidative dye degradation (Equations (13) and (14)) (Leng *et al.* 2014). At the same time, the SO_4^- generated can interact with OH^- to produce OH^\cdot (Equation (15)). The synergistic effect of the three free radicals (OH^\cdot , SO_4^- and O_2^-) leads to the degradation of dye molecules in the aqueous solution. In addition, Fe(II) ions on the catalyst surface can react with $S_2O_8^{2-}$ in the system to be oxidized to Fe(III), thus promoting the Fe(III)/Fe(II) cyclic reaction (Equation (16)) (Leng *et al.* 2014), and accelerating the production of active species, thereby improving catalytic oxidation performance significantly.

Figure 6(b) shows that the photocatalytic oxidation activity of Fe-EDTA-Cotton is significant under acidic and neutral conditions, but is reduced significantly under alkaline conditions. On the one hand, the reaction of $S_2O_8^{2-}$ with water to form SO_4^- and O_2^- (Equation (17)) can be promoted under alkaline conditions (Matzek & Carter 2016; Huang *et al.* 2017), generating further OH^\cdot to oxidize dyes (Equation (18)) (Furman *et al.* 2010). However, the system's H^+ concentration decreases and the Fe(III) ions in the active sites interact easily with the OH^- in solution to form insoluble precipitates, while the formation rate of active free radicals is reduced. On the other hand, the dye molecule adsorption on the catalyst surface decreases under alkaline conditions.

Figure 6(c) shows that the oxidation effect of SPS is significantly better than that of H_2O_2 . This may be due to the fact that SPS system not only contains $S_2O_8^{2-}$ with oxidation ability, but can also produce OH^\cdot with stronger oxidation ability and SO_4^- with longer half-life, after being activated by Fe-EDTA-Cotton (Vicente *et al.* 2011). SPS is thus a safe alternative oxidant, replacing H_2O_2 in environmental remediation.





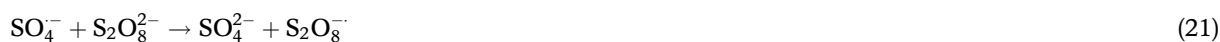
Heterogeneous photocatalytic treatment of wastewater contain Cr(VI) and RR195

Previous research has shown that Fe-EDTA-Cotton has both a catalytic effect on the oxidative degradation of organic dyes in water and excellent catalytic reduction performance for Cr(VI) in aqueous solution (Dong *et al.* 2020). However, wastewater composition is often complex, containing both organic dyes and inorganic heavy metal ions. There is thus great practical significance in investigating the removal performance of Fe-EDTA-Cotton for mixed pollutants. On this basis, a mixed solution containing Cr(VI) and RR195 was simulated, at natural pH level and 20 °C, to assess Fe-EDTA-Cotton's photocatalytic performance of ($Q_{\text{Fe}} = 0.83 \text{ mmol g}^{-1}$) in treating different pollutant categories simultaneously under Hg lamp radiation. As shown in Table 1, the values of $R_{120\%}$ and $\eta_{120\%}$ decrease significantly with increasing initial SPS concentration. In other words, SPS has a significant inhibitory effect on the Cr(VI) reduction reaction in mixed solution. This is mainly because $\text{S}_2\text{O}_8^{2-}$ in aqueous solution can react with Fe(II) to form OH^- and SO_4^- (Equations (13) and (15)), which will react with the dissolved dye molecules via oxidative degradation reactions and, at the same time, react with Cr(III) in the system to produce Cr(VI) (Equations (19) and (20)). This leads to a significant decrease in $R_{120\%}$, which affects the adsorption and removal of Cr(III) on the catalyst surface (Dong *et al.* 2019), and causes $\eta_{120\%}$ to decrease slowly. The competitive adsorption of dye molecules and Cr(VI) on the catalyst surface also reduce $R_{120\%}$. It is noted in this context that $R_{120\%}$ increases gradually when the SPS concentration exceeds 2.0 mmol L^{-1} . So, the increase in the $\text{S}_2\text{O}_8^{2-}$ concentration in the system can promote the Fe(III)/Fe(II) cyclic reaction (Equation (16)), which accelerates the Cr(VI) reduction reaction in the system, and increases $R_{120\%}$. On the other hand, excess SPS will become a radical quencher and capture the active radicals (Equations (21) and (22)) generated in the reaction system (Li *et al.* 2017), reducing the free radical content in solution, and thus the occurrence of reactions (19) and (20). Further, both Equation (15) and Gao *et al.*'s (2016) research results show that as the SPS concentration increases in the system, the pH of the solution falls gradually. The acidic condition is conducive to Cr(VI) photoreduction (Equations (9) and (10)). Despite this, a literature survey (Gao *et al.* 2016) has shown that acidic conditions are not conducive to Cr ion removal, which is the main reason that $\eta_{120\%}$ decreases with increasing SPS concentration. $D_{60\%}$ increased significantly, after 60 minutes, in the mixed pollutants, with the increased SPS concentration in the system. This is mainly because the SPS concentration increase raises the number of reactive radicals generated, oxidizing more dye molecules. Azo dyes and Cr(VI) can still be removed by redox in the mixed pollutant system, which means that Fe-EDTA-Cotton, as a heterogeneous catalyst, can be applied not only to the removal of a single pollutant in water, but also in the treatment of wastewater containing

Table 1 | $D_{60\%}$, $R_{120\%}$ and $\eta_{120\%}$ in the presence of Fe-EDTA-Cotton

SPS conc. (mmol L^{-1})	0	0.2	1	2	3	4.5
$R_{120\%}$	95.43	86.35	60.57	47.27	52.71	58.57
$\eta_{120\%}$	73.28	53.77	39.51	30.22	24.79	1.65
$D_{60\%}$	2.01	12.92	42.05	63.43	70.56	89.39

organic dyes, Cr(VI) and other pollutants, and still achieve the desired effect.



CONCLUSIONS

Fe-EDTA-Cotton can be prepared by modification of Na₂EDTA with cotton fiber and an Fe(III) coordination reaction. The carboxylic acid content of the EDTA-Cotton surface can be increased significantly by increasing the Na₂EDTA and NHP concentrations, and the hydrothermal reaction temperature. Increasing the Fe(III) concentration and the coordination reaction's temperature can increase the Fe(III) content on the surface of the complex.

SEM and FTIR analysis showed that EDTA could react successfully with hydroxyl groups on a cotton fiber surface. Carboxyl groups can be introduced onto cotton fiber surfaces, and Fe-EDTA-Cotton can be prepared by coordination reaction with Fe(III).

Fe-EDTA-Cotton, a heterogeneous catalyst, has a significant catalytic effect on Cr(VI) reduction and the reaction can be described by the pseudo first-order kinetic model.

Increasing Q_{Fe} , reaction temperature and/or light radiation intensity, and/or lowering pH can increase the reduction rate significantly. The complexes obtained can remove Cr(VI) and organic dyes from aqueous solution in one stage, with strong photocatalytic effects on both processes. Although the increase in oxidant concentration is beneficial to dye degradation, it is not conducive to Cr(VI) reduction.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Bei yuan, J., Tsang, D. C. W., Valix, M., Baek, K., Ok, Y. S., Zhang, W. H., Bolan, N. S., Rinklebe, J. & Li, X. D. 2018 Combined application of EDDS and EDTA for removal of potentially toxic elements under multiple soil washing schemes. *Chemosphere* **205**(8), 178–187.
- Deng, L., Shi, Z., Wang, L. & Zhou, S. 2017 Fabrication of a novel NiFe₂O₄/Zn-Al layered double hydroxide intercalated with EDTA composite and its adsorption behavior for Cr(VI) from aqueous solution. *Journal of Physics and Chemistry of Solids* **104**(5), 79–90.
- Dong, Y., Han, Z., Liu, C. & Du, F. 2010 Preparation and photocatalytic performance of Fe(III)-amidoximated PAN fiber complex for oxidative degradation of azo dye under visible light irradiation. *Science of the Total Environment* **408**(4), 2245–2253.
- Dong, Y., Wang, P., Gan, L., Li, B. & Wen, H. 2019 Enhanced removal of aqueous Cr(VI) using optimized Fe complex on EDTA modified cotton fiber via photocatalytic reduction and adsorption hybrid functions. *Cellulose* **26**(12), 7383–7397.
- Dong, Y., Wen, H., Bian, L. & Wang, P. 2020 Optimized synthesis of CA/EDTA modified cotton fiber Fe complex as a sustainable hybrid photocatalyst for accelerating simultaneous removal of Cr(VI) and azo dye. *Cellulose* **27**(12), 2293–2308.
- Furman, O. S., Teel, A. L., Ahmad, M., Merker, M. C. R. & Watts, J. 2010 Effect of basicity on persulfate reactivity. *Journal of Environmental Engineering* **137**(4), 241–247.
- Gan, L. & Dong, Y. 2019 Photocatalytic performance of Fe-complexes prepared using cotton fiber modified with different dicarboxylic acids. *Chemical Journal of Chinese Universities* **40**(10), 2205–2213.

- Gao, Y., Zhang, Z., Li, S., Liu, J., Yao, L., Li, Y. & Zhang, H. 2016 Insights into the mechanism of heterogeneous activation of persulfate with a clay/iron-based catalyst under visible LED light irradiation. *Applied Catalysis B: Environmental* **185**(5), 22–30.
- Huang, X., An, D., Song, J., Gao, W. & Shen, Y. 2017 Persulfate/electrochemical/FeCl₂ system for the degradation of phenol adsorbed on granular activated carbon and adsorbent regeneration. *Journal of Cleaner Production* **165**(11), 637–644.
- Jing, F., Liang, R., Xiong, J., Chen, R., Zhang, S., Li, Y. & Wu, L. 2017 MIL-68(Fe) as an efficient visible-light-driven photocatalyst for the treatment of a simulated waste-water contain Cr(VI) and Malachite green. *Applied Catalysis B: Environmental* **206**(5), 9–15.
- Júnior, O. K., Gurgel, L. V. A., Freitas, R. P. & Gil, L. F. 2009 Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD). *Carbohydrate Polymers* **77**(3), 643–650.
- Kim, D., Lee, D., Monllor-Satoca, D., Kim, K., Lee, W. & Choi, W. 2019 Homogeneous photocatalytic Fe³⁺/Fe²⁺ redox cycle for simultaneous Cr(VI) reduction and organic pollutant oxidation: roles of hydroxyl radical and degradation intermediates. *Journal of Hazardous Materials* **372**(6), 121–128.
- Klüner, T., Hempel, D. C. & Nörtemann, B. 1998 Metabolism of EDTA and its metal chelates by whole cells and cell-free extracts of strain BNC1. *Applied Microbiology and Biotechnology* **49**(2), 194–201.
- Lakshminathiraj, P., Raju, G. B., Basariya, M. R., Parvathy, S. & Prabhakar, S. 2008 Removal of Cr(VI) by electrochemical reduction. *Separation and Purification Technology* **60**(1), 96–102.
- Leng, Y., Guo, W., Shi, X., Li, Y., Wang, A. & Hao, F. 2014 Degradation of rhodamine B by persulfate activated with Fe₃O₄: effect of polyhydroquinone serving as an electron shuttle. *Chemical Engineering Journal* **240**(3), 338–343.
- Li, Y., Gao, B., Wu, T., Sun, D., Li, X., Wang, B. & Lu, F. 2009 Hexavalent chromium removal from aqueous solution by adsorption on aluminum magnesium mixed hydroxide. *Water Research* **43**(12), 3067–3075.
- Li, J., Ren, Y., Ji, F. & Lai, B. 2017 Heterogeneous catalytic oxidation for the degradation of p-nitrophenol in aqueous solution by persulfate activated with CuFe₂O₄ magnetic nano-particles. *Chemical Engineering Journal* **324**(9), 63–73.
- Liu, G., Dong, Y., Wang, P. & Bian, L. 2018 Activation of Na₂S₂O₈ for dye degradation by Fe complexes fixed on polycarboxylic acids modified waste cotton. *Carbohydrate Polymers* **181**(2), 103–110.
- Luo, Z., Wang, J., Qu, L., Jia, J., Jiang, S., Zhou, X., Wu, X. & Wu, Z. 2017 Visible-light-driven photocatalytic reduction of Cr(VI) on magnetite/carboxylate-rich carbon sheets. *New Journal of Chemistry* **41**(21), 12596–12603.
- Mao, N., Yang, L. Q., Zhao, G. H., Li, X. L. & Li, Y. F. 2012 Adsorption performance and mechanism of Cr(VI) using magnetic PS-EDTA resin from micro-polluted waters. *Chemical Engineering Journal* **200**(8), 480–490.
- Marinho, B. A., Cristóvão, R. O., Loureiro, J. M., Boaventura, R. A. R. & Vilar, V. J. P. 2016 Solar photocatalytic reduction of Cr(VI) over Fe(III) in the presence of organic sacrificial agents. *Applied Catalysis B: Environmental* **192**(9), 208–219.
- Marinho, B. A., Djellabi, R., Cristóvão, R. O., Loureiro, J. M., Boaventura, R. A. R., Dias, M. M., Lopes, J. C. B. & Vilar, V. J. P. 2017 Intensification of heterogeneous TiO₂ photocatalysis using an innovative micro-meso-structured-reactor for Cr(VI) reduction under simulated solar light. *Chemical Engineering Journal* **318**(6), 76–88.
- Matzek, L. W. & Carter, K. E. 2016 Activated persulfate for organic chemical degradation: a review. *Chemosphere* **151**(5), 178–188.
- Palmer, C. D. & Wittbrodt, P. R. 1991 Processes affecting the remediation of chromium-contaminated sites. *Environmental Health Perspectives* **92**(5), 25–40.
- Petruzzelli, D., Passino, R. & Tiravanti, G. 1995 Ion exchange process for chromium removal and recovery from tannery wastes. *Industrial & Engineering Chemistry Research* **34**(8), 2612–2617.
- Vicente, F., Santos, A., Romero, A. & Rodriguez, S. 2011 Kinetic study of diuron oxidation and mineralization by persulfate: effects of temperature, oxidant concentration and iron dosage method. *Chemical Engineering Journal* **170**(1), 127–135.
- Wang, Z., Yang, J., Li, Y. S., Zhuang, Q. X. & Gu, J. L. 2017 Simultaneous degradation and removal of Cr(VI) from aqueous solution with Zr-based metal-organic frameworks bearing inherent reductive sites. *Chemistry-A European Journal* **23**(61), 15415–15423.
- Yang, B., Zhang, J. X., Zhang, Y. F., Deng, S. B., Yu, G., Wu, J. H., Zhang, H. & Liu, J. H. 2014 Promoting effect of EDTA on catalytic activity of highly stable Al-Ni bimetal alloy for dechlorination of 2-chlorophenol. *Chemical Engineering Journal* **250**(8), 222–229.
- Ye, Y., Jiang, Z., Xu, Z., Zhang, X. L., Wang, D. D., Lv, L. & Pan, B. C. 2017 Efficient removal of Cr(III)-organic complexes from water using UV/Fe(III) system: negligible Cr(VI) accumulation and mechanism. *Water Research* **126**(1), 172–178.
- Zhang, C., Dong, Y., Li, B. & Li, F. 2018 Comparative study of three solid oxidants as substitutes of H₂O₂ used in Fe(III)-oxalate complex mediated Fenton system for photocatalytic elimination of reactive azo dye. *Journal of Cleaner Production* **177**(10), 245–253.

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