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Effects of Electron Donors on the TiO₂ Photocatalytic Reduction of Heavy Metal Ions under Visible Light

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Abstract

The effects on TiO₂ (Degussa P25) photocatalytic reduction of Cr(VI) under visible light, using methanol, methanal and formic acid as electron donors were investigated. The results showed that the photocatalytic reduction of Cr(VI) could be encouraged by methanol, methanal and formic acid. The fastest rate of Cr(VI) photoreduction was observed in the presence of formic acid followed by methanal and methanol. Cr(VI) could hardly be reduced by TiO₂ without electron donors. The conversion percent of Cr(VI) was 100% using formic acid as electron donors after 80 min. For the methanal and methanol systems, the conversion percent of Cr(VI) were 93.62% and 22.69% after 6 h, respectively.

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Keywords: TiO₂; electron donors; visible light; photocatalytic reduction; Cr (VI)

1. Introduction

Heavy metal ions can not be degraded and they will be in environment for a long time. On the other hand, heavy metal can make creature disease through bioaccumulation and bioenrichment. So people have been trying to find method for heavy metal ions removing. Neutralization, electrolysis, chemical oxidation-reduction, extraction, adsorption, precipitation, ion exchange, membrane separation, elution, electrodialysis etc. were often used for wastewater containing heavy metal ion treatment^[1]. These techniques can play a role more or less. However, the effectiveness for wastewater containing low concentration heavy metal is reduced. Moreover, most of these technologies are simple physical separation process, and pollutants did not really change into virulent or harmless substance. It is easy to cause secondary pollution^[2].

TiO₂ is paid more attention to eliminating environmental pollutants in recent years^[3-5]. It is high oxidation power, low energy, low price, easy availability, non-toxicity. Especially using in low concentration wastewater treatment, its advantages is more outstanding^[6].

The efficiency of photocatalysis will be lowered by the recombination of photogenerated electron and hole. The recombination could be restrained when electron donors used as scavenger of hole were added into and the efficiency of photoreduction reaction would increase. On the one hand, inorganic heavy metal ions and organic pollutants together are in ctual pollution systems usually and many organic pollutants are excellent electron donors in the waste water. Therefore, it is of great importance that the combination between the reduction of toxic heavy metal ion and the oxidation of organic pollutants oxidation through TiO₂ photocatalysis technology. On the other hand, the photocatalytic reaction is a group of related oxidation reduction process in essence. If metal ions used as electron receptor and organics used as electron donor are coexistence, the reduction reaction and oxidation reaction might promote mutually^[7]. All the research about the effect of electron donors on the TiO₂ photocatalytic reduction reaction were carried out under ultraviolet light irradiation. In this paper, the effects on TiO₂ (Degussa P25) photocatalytic reduction of Cr (VI) under visible light irradiation, using methanol, methanal and formic acid as electron donors were investigated.

2. Experimental

2.1. Chemicals and instruments

Degussa TiO₂ powders (BET area 50 m²g⁻¹; anatase TiO₂ accounted for 80% and rutile TiO₂ accounted for 20%) were used as the photocatalyst. All the chemical reagents were analytical reagent and used as received. Distilled water was used throughout the experiment.

The LED (blue, wavelength range 450~475 nm, shenzhen lanbaoli photoelectric technology Co. Ltd) was used as the source of visible light. The concentration of Cr (VI) was determined by 721 spectrophotometer (shanghai precision and scientific instrument Co. Ltd). KDC-160HR high speed freeze centrifuge (Keda innovation Co. Ltd) and acidometer (HI98130, HANNA) were used through out the experiment.

2.2. Analysis and characterizations

The concentration of Cr (VI) was determined by using the diphenyl carbazide colorimetric method at 540 nm (GB 7466-87, Standards of China)

2.3. Photocatalytic reduction of Cr (VI)

The photocatalytic reduction of Cr (VI) was carried out in a cylindrical glass vessel, a 3w LED used as the source of visible light, which was positioned alongside the vessel. TiO₂ (0.04 g) was suspended into

40 mL aqueous solution of $\text{Cr}_2\text{O}_7^{2-}$ (10 mgL^{-1}) with the addition of electron donors (methanol, formaldehyde and formate). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of adsorption-desorption equilibrium of electron donors on TiO_2 surface. After equilibration, the concentration of Cr (VI) was measured and taken as the initial concentration (c_0). Then the LED was opened, 2.5 mL solutions were sampled at appropriate time intervals. The samples were centrifuged immediately at 6000 rpm for 10 min and filtered through $0.45 \mu\text{m}$ filter. The filtrates were collected and analyzed. The reaction mixture was maintained in suspension by using a magnetic stirrer. Duplicate were carried out for each test, and the relative standard deviation was generally less than 5%.

3.Results and Discussions

3.1.the Photocatalytic reduction of Cr (VI) in methanol/ TiO_2 system

Cr (VI) could not be photoreduced by TiO_2 in the absence of methanol after 6 h under visible light irradiation. The Cr (VI) conversion was raised markedly when methanol was added into system. As shown in fig.1, Cr (VI) conversion was raised gradually with the initial concentration of methanol increasing. When the initial concentration of methanol was 100 gL^{-1} , the Cr (VI) conversion could amount to be 94.71%. So the Cr (VI) conversion could be improved by increasing the concentration of methanol and it tended to increase more

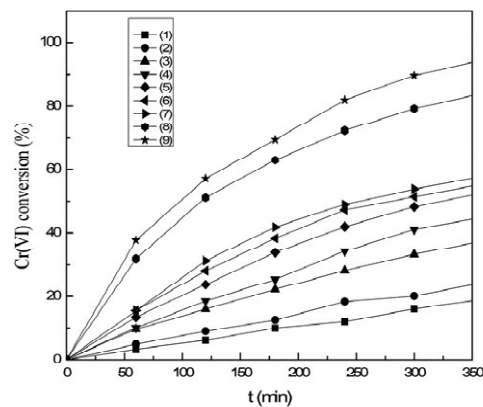


Figure 1. Effects of methanol concentration on Cr(VI) conversion $C_{0(\text{Cr(VI)})}=20 \text{ mgL}^{-1}$, $\text{TiO}_2:1 \text{ gL}^{-1}$, initial methanol concentration:(1) 0.5 gL^{-1} (2) 1 gL^{-1} (3) 5 gL^{-1} (4) 10 gL^{-1} (5) 15 gL^{-1} (6) 20 gL^{-1} (7) 25 gL^{-1} (8) 50 gL^{-1} (9) 100 gL^{-1}

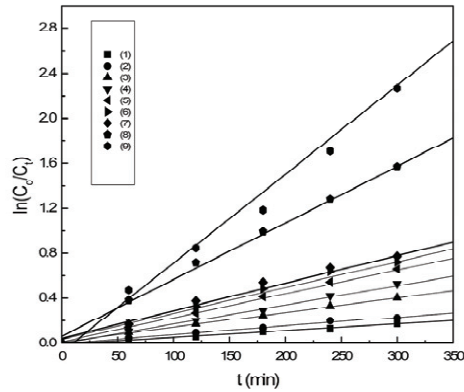


Figure 2. the photocatalytic reduction of Cr(VI) kinetics curve in different initial concentration of methanol aqueous solution
 $C_{0(\text{Cr(VI)})}=20 \text{ mgL}^{-1}$, TiO_2 : 1 gL^{-1} , initial methanol concentration: (1) 0.5 gL^{-1} (2) 1 gL^{-1} (3) 5 gL^{-1} (4) 10 gL^{-1} (5) 15 gL^{-1} (6) 20 gL^{-1} (7) 25 gL^{-1} (8) 50 gL^{-1} (9) 100 gL^{-1}

apparent when methanol concentration was lower. The trends of photocatalytic reduction of Cr (VI) were same for the different concentration curves: the initial reaction rate was faster, but as time went on, it gradually decelerated. It was most probably attributed to that Cr(VI) was reduced to Cr (III). Then Cr (III) was deposited on the surface of TiO_2 in the form of $\text{Cr}(\text{OH})_3$, which covered the surface catalytic active site and resulted to reducing the activity of TiO_2 ^[6].

The kinetics curves of the photocatalytic reduction of Cr (VI) in different concentration methanol/ TiO_2 systems could

Table 1. Kinetic parameters of reduction reaction of Cr(VI) in different concentrations of methanol aqueous solution

concentrations of methanol (gL^{-1})	k	r
0.5	0.0005	0.9961
1	0.0008	0.9971
5	0.0013	0.9986
10	0.0017	0.9984
15	0.0021	0.9981
20	0.0023	0.9923
25	0.0024	0.9969
50	0.0050	0.9983
100	0.0079	0.9937

be seen in fig.2. The photocatalytic reduction of Cr (VI) conformed to the first-order kinetic equation, which can be expressed as

$$\text{Ln} (C_0 / C_t) = kt \quad (1)$$

k : apparent reaction rate constant; C_0 : the initial concentration of methanol; C_t : the instantaneous concentration of methanol.

The parameters of the first-order kinetic equation were shown in table.1. The k value was 0.0007 when the concentration of methanol was 0.5 gL⁻¹. It was 0.0079 when the concentration of methanol was 100 gL⁻¹. The photocatalytic reduction of Cr (VI) could be enhanced through increasing the concentration of methanol. It was consistent with above.

3.2. The photocatalytic reduction of Cr (VI) in different electron donors/TiO₂ systems

The different electron donors/TiO₂ exhibited marked differences on the reduction of Cr (VI). As showed in fig.3, the Cr (VI) conversion was 100% in formate/TiO₂ system after 80 min under visible light irradiation. For the methanal and methanol systems, the Cr (VI) conversions were 93.62% and 22.69% respectively after 6 h. It was easily found that the Cr (VI) conversion in the presence of electron donors has the order of formate > methanal > methanol. On the one hand, methanol and formaldehyde were adhered to TiO₂ surface through the weak hydrogen bonding while the carboxyl of formic acid was able to form the complexes with TiO₂ and was adhered to TiO₂ surface through strong chemical adsorption [8, 9]. So formic acid was more easily absorbed on TiO₂ surface than methanol and formaldehyde. The photocatalytic reaction was carried out on TiO₂ surface, therefore only the electron donors which had already adsorbed on surface of TiO₂ were effective and the more

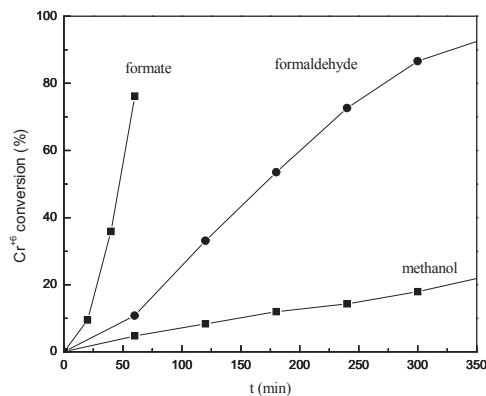
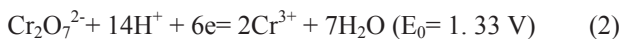


Figure 3. Effects of the same concentration of methanol and methanal, formic acid on Cr(VI) conversion

Concentration of methanol and methanal, formic acid: 0.5 gL⁻¹

adsorbance of electron donors were, the better photocatalytic reduction reaction was and the larger the Cr (VI) conversion was. On the other hand, the oxidability of Cr (VI) was very strong and its half-reaction of reduction as



Because concentration of total chromium was constant, the oxidation-reduction potential E in solution as

$$E = (E_0 + \frac{0.059 \times 14}{6} \lg[\text{H}^+]) + \frac{0.059}{6} \lg \frac{a_0 - 1/2 a_{\text{Cr(III)}}}{a_{\text{Cr(III)}}^2} \quad (3)$$

$a_{\text{Cr(III)}}$: the concentration of Cr (III), mgL⁻¹;

a_0 : the initial concentration of Cr (VI), mgL^{-1}

It could be seen that the greater the concentration of H^+ in system was, the higher the oxidation-reduction potential of Cr (VI) was and the more easily Cr (VI) was reduced. The pH values in formate/ TiO_2 , methanal/ TiO_2 and methanol/ TiO_2 systems were 2.86, 5.00 and 5.54 respectively. It was easily found that the concentration of H^+ in formate/ TiO_2 system was most, so Cr (VI) conversions was largest at the same condition.

3.3. The mechanism of photocatalytic reduction in electron donors/ TiO_2 systems under visible light irradiation

A series of control experiments were carried out. As shown in Fig. 4, the concentration of Cr (VI) was almost constant either TiO_2 or electron donors was presented alone under visible light irradiation. But Cr (VI) was significantly reduced when TiO_2 and electron donors were both presented.

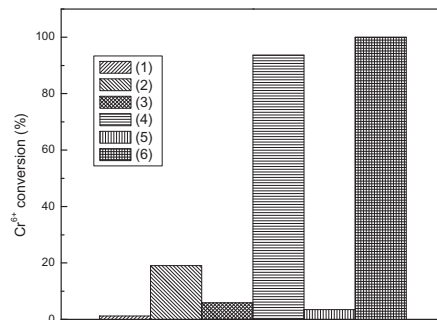


Figure 4. Effects of the same concentration of methanol and methanal, formic acid on Cr (VI) conversion at different conditions

$C_{0(\text{Cr(VI)})} = 20 \text{ mgL}^{-1}$, (1) methanol: 0.5 gL^{-1} , without TiO_2 , t: 6 h (2) methanol: 0.5 gL^{-1} , TiO_2 : 1 gL^{-1} , t: 6 h (3) methanal: 0.5 gL^{-1} , without TiO_2 , t: 6 h (4) methanal: 0.5 gL^{-1} , TiO_2 : 1 gL^{-1} , t: 6 h (5) formic acid: 0.5 gL^{-1} , without TiO_2 , t: 80 min (6) formic acid: 0.5 gL^{-1} , TiO_2 : 1 gL^{-1} , t: 80 min

It is inferred that electron donors might be excited by visible light to produce excited state with high activity. Because a part of electron donors had been absorbed on TiO_2 surface after being mixed for 30 min in darkness, electron could be injected from the excited state of electron donors to the conduction of TiO_2 and moved to TiO_2 surface. Then the Cr (VI) was reduced to Cr (III) by electron. The electron donors losing electron which was similar to hole, was a cation radical with strong oxidizing. They could oxidate water and produce a series of free radicals with strong oxidizing. But when only electron donors were present in Cr (VI) solution, Cr (VI) was hardly reduced. Maybe the reason is electron and cation radical

recombined soon, so electron could not arrive at Cr (VI) nearby. Because the energy band of TiO₂ was discontinuous and its conduction band was empty, the conditions for preservation of electron could be created when TiO₂ was in present in system.

4. Conclusion

(1) Cr (VI) could not be reduced either TiO₂ or electron donors was presented alone under visible light irradiation. The Cr (VI) conversion was 100% using formate as electron donors after 80min. For formaldehyde and methanol systems, the Cr (VI) conversion was 93.62% and 22.69% respectively after 6h.

(2) The rate of Cr (VI) reduction in the presence of electron donors has the order of formate > methanal > methanol.

(3) In the methanol/TiO₂ systems, the photocatalytic reduction of Cr (VI) conformed to the first-order kinetic equation.

Acknowledgements

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