Hp-β-Cyclodextrin assisted ozonation

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Keywords: Ozone, Hp-β-cyclodextrin, ozonation, ABTS, spectra,inclusion complex

Abstract. The purpose of this paper is to introduce hydroxypropyl-β-cyclodextrin(Hp-β-cyclodextrin) into ozonation, and investigate the oxidation properties of Hp-β-cyclodextrin after ozonation. In this study, Potassium indigo trisulfonate, (Indigo) and 2.2'-azino-bis (3-ethylbenzothiazoline-6-sulfonate, (ABTS) were used as indicative contaminants. During our observation, the oxidizing ability of Hp-β-cyclodextrin solution increased significantly after ozonation. The kinetic curves of ABTS and ozone/Hp-β-cyclodextrin inclusion complex solution shows that the reaction between two compounds are mixed reactions with muti-steps. On the basis of these results, it appears that ozone/Hp-β-cyclodextrin inclusion complex solution may be useful as a combination with ozoantion or applied after ozonation for sustained oxidation.

Introduction

Cyclodextrins(CDs) are supramoleculars which extract from starch, and comprised of glucopyranose units[1]. The typical feature of CDs is to combine some molecules to form a coordination compound or accommodate one or more molecules to form a inclusion complex[2]. 2-hydroxypropyl-β-cyclodextrin (Hp-β-CD)is the most important cyclodextrin derivative due to its high water solubility. Hp-β-CD has been employed in the enhanced fenton degradation of hydrophobic organic compounds(HOC) by forming ternary HOC-CD-iron inclusion complexes[3,4]. The ternary structure HOCs-CD-iron has been assessed and observed with NMR and fluorescence detection[5,6]. In this study, we tried to introduce 2-hydroxypropyl-β-cyclodextrin in ozonation and analysis its oxidatizing performance.

Experimental materials and procedures

All chemical reagents were purchased from Sigma Aldrich Co, with high purity.Ozone/CD inclusion complex solution are prepared by bubbling ozone gas through a 1 liter volume glass reactor with a diffuser cover. In our study, various Hp-β-CD solutions were used for studying the kinetics of ABTS decay, the transferred ozone dose were calculated by the integrated difference of the absorbance of ozone gas from inlet and outlet of the reactor, recorded by two UV-vis spectrophotometer, respectively. the spectra of the indicators change will be measured by an UV-vis spectrophotometer with time and then the changes will be plotted.

Results and discussing

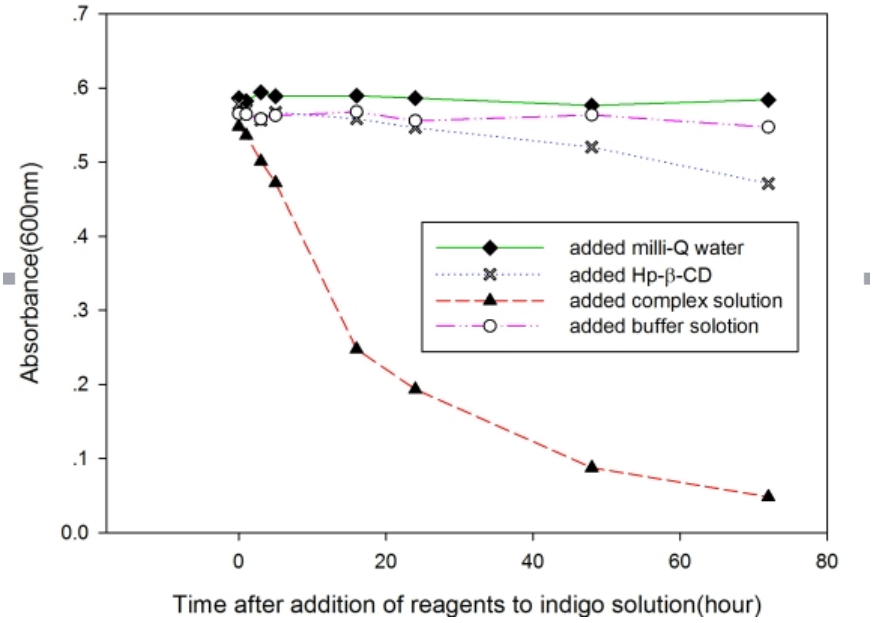

Fig. 1 Comparison of indigo decay rate in different solutions

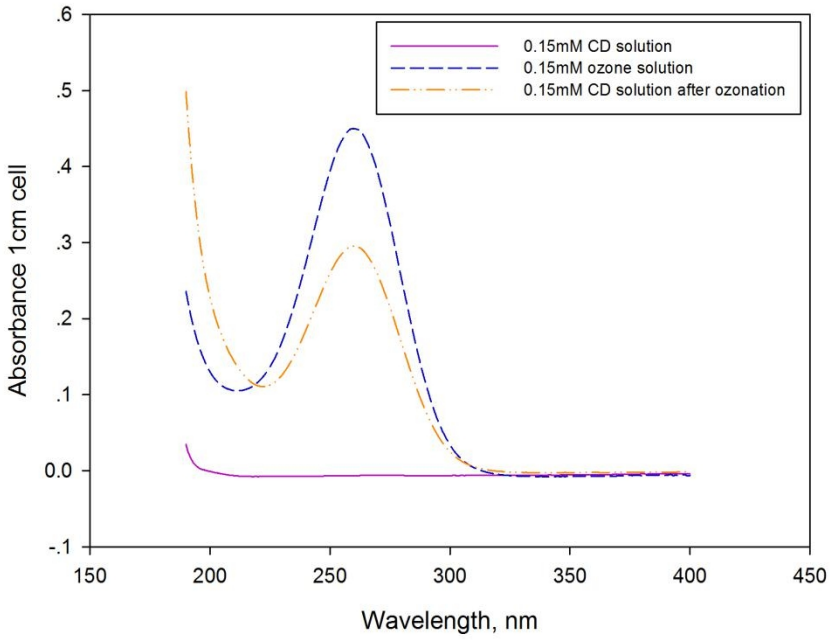

Fig. 2 Comparison of the Spectra among pure CD, ozone and ozone/CD solution

As seen in Fig.1, the flask added ozone/CD solution is the only one that indigo color decrease obviously,the only reason for the degradation of indigo is the addition of ozone/CD solution, which means the ozone/CD solution is able to oxidize indigo for more than one week. .During the contrast experiment, the flask added ozone/CD solution is the only one that indigo color decrease obviously, which means Milli-Q water, Hp-β-CD solution, and buffer solution do not affect the indigo degradation much. The only reason for the degradation of indigo is the addition of ozone/CD solution. In figure 1, the absorbance of the flasks added with various reagents at 600 nm were presented. After 72 hrs, the absorbance of the Indigo stock with the addition of Milli-Q water, pure

Hp-β-CD solution and buffer solution almost had no changes, while the flask added with ozone/CD solution decrease at a slow rate[4,5].

From the comparison of spectra of ozone, ozone/CD and pure CD solution, we know that the pure CD solution has no obvious absorbance at 190-400 nm, however, after ozonation, the spectra of ozone/CD solution has a significant increase in 190-400 nm. This phenomenon confirms the formation of ozone/CD inclusion complex in another aspect[6]

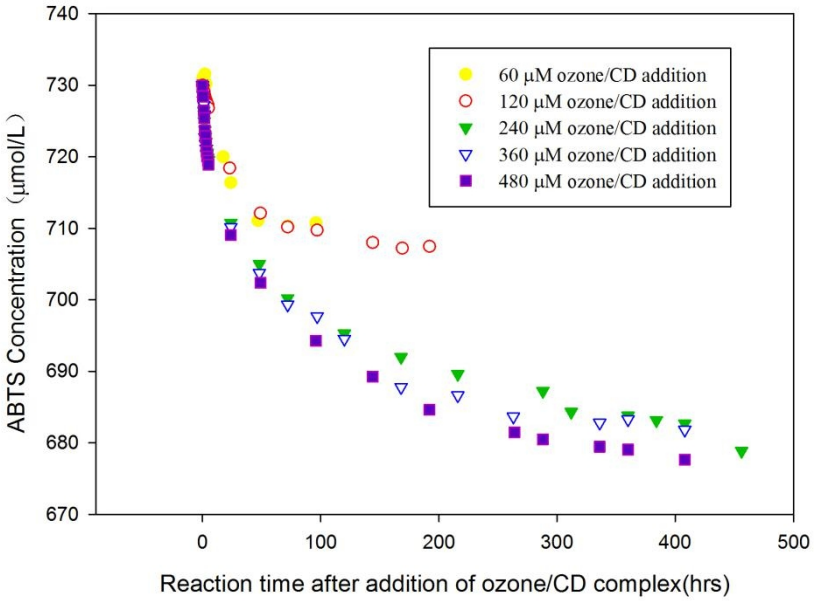

Fig. 3 ABTS decay curves with respect to the addition of various dose of ozone/CD solution

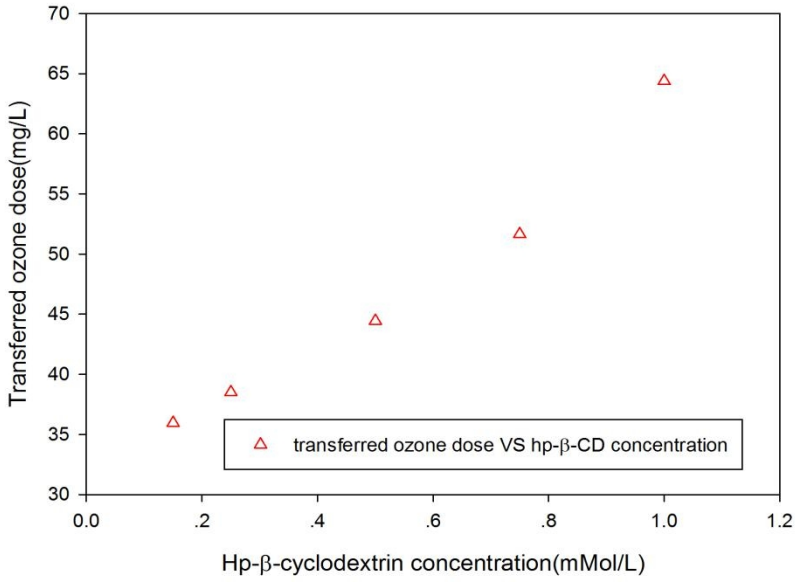

Fig. 4 The transferred ozone dose with the ozonation of Hp-β-CD solution in one hour

The kinetics of various concentration of ozone/CD solution with ABTS are neither fit for first order reaction rate nor for the second order reaction rate, there, we consider it a mixed reaction.

The kinetic curves shown in fig. 3 was clearly give a mixed reaction rate combined by a fast raction and slow reaction. The CSR(chemical stochiomtric ration) numberis a parameter used in calculating of the ratio of guest and host molecule in cyclodextrin chemistry. Based on the theory of cyclodextrin, one host molecule generally able to include one guest molecule. In view of the molecule size of ozone, the most possible form of ozone/CD inclusion complex is one ozone molecule accommodated in one cyclodextrin. In fig. 4 the relationship between transferred ozone dose and CD dose a generally give a CSR number of 1:1 of ozone and CD[7-10].

Conclusions

A new material based on the ozonation of cyclodextrin was presented. This ozone/CD solution as proved to be a powerful and sustainable oxidant, and this new oxidant could be used in contaminant remediation in many fields.

Acknowledgements

This work was supported by China scholarship council (file NO: 201207000022).

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