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Characteristics and difference of oxidation and coagulation mechanisms for the removal of organic compounds by quantum parameter analysis

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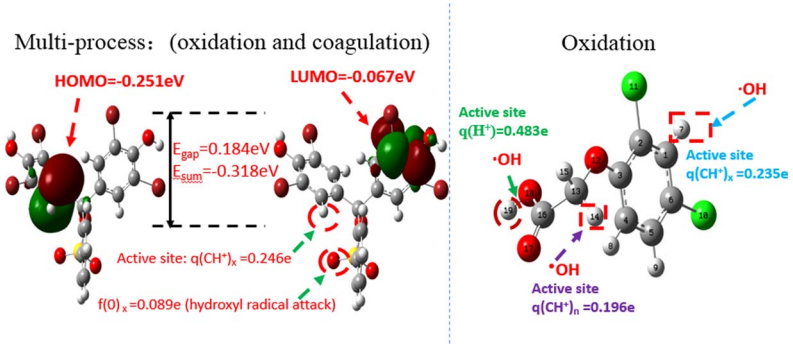
GRAPHICAL ABSTRACT



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ABSTRACT

Oxidation and coagulation are two basic processes in removing organic pollutants from water. In this study, reaction rate constants and adsorption ability of twenty-eight organic compounds with different structures were implemented by Fenton experiments and Ferric-oxyhydroxides coagulation experiments. Based on the adsorption percentage, twenty-eight compounds were divided into two groups (group L, low adsorptive and group H, High adsorptive). Fifteen compounds with the adsorption percentage less than 15% were set as group L and the rest thirteen compounds with the adsorption percentage higher than 15% were set as group H. As for group L, the removal of fifteen compounds were mainly degraded by oxidation. While as for group H, the removal of thirteen compounds attributed to both oxidation and coagulation. According to the grouping, classified Quantitative Structure Activity Relationship (QSAR) models were subsequently developed by reaction rate constants and quantum chemical descriptors using multivariable linear regression. Results in this work showed that classification QSAR models exhibited different predictive ability for reaction rates. The classification models proposed the different mechanisms and characteristics of oxidation-dominated process and multi-process. The main factors governing reaction rate in oxidation process are $q(CH^+)_x$, $q(CH^+)_n$ and $q(H^+)$, they are relevant to the active site and hydroxide radical attack. While the frontier molecule orbital (E_{gap} (E_{LUMO} − E_{HOMO}) and E_{sum} (E_{LUMO} + E_{HOMO})) and active sites ($q(CH^+)_x$ and $f(0)_x$) play the important roles in multi-process. Furthermore, the quantum parameter analysis also provide a preliminary assessment of oxidation and coagulation in multi-process.

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Nomenclature

k	Reaction rate constants
AP	Adsorption percentages
μ	Dipole moment
$E_{(B3LYP)}$	The total energy of a molecule
E_{HOMO}	Energy of the highest occupied molecular orbital
E_{LUMO}	Energy of the lowest unoccupied molecular orbital
E_{gap}	The gap energy ($E_{LUMO} - E_{HOMO}$)
E_{sum}	The sum energy ($E_{LUMO} + E_{HOMO}$)
qH^+	Most positive partial charge on a hydrogen atom
$q(C^-)_n/q(C^-)_x$	Minimum and maximum negative partial charge on a carbon atom
$q(CH^+)_n/q(CH^+)_x$	Minimum and maximum positive partial charge on a hydrogen atom linked with a carbon atom
BO	Bond order
f(+), f(−), f(0)	Fukui indices
$QSAR_{FENTON}$	QSAR model for Fenton process
$QSAR_{OX}$	QSAR model for oxidation in Fenton process
$QSAR_{AD}$	QSAR model for adsorption in Fenton process
DFT	Density functional theory

1. Introduction

The amount of organic pollutions has emerged increasingly in water due to the industrial production and lives as well as the leaks of harmful agricultural production. These organic pollutions are always chemically stable, having a great variety, being highly toxic in water. For example, the rat oral median lethal doses (LD50) of 2,6-dinitrotoluene, 2,4-dichlorophenoxyacetic acid and 3,4-dichloroaniline in this study are 177 ppm, 375 ppm and 545 ppm, respectively [1–5]. These contaminants once released into the ecosystem will cause various environmental problems, such as increasing chemical oxygen, adversely affecting aquatic biota and clogging sewage treatment plants, *etc.* [6]. Since global regulations have restricted the release of organic pollutants in wastewater [7], it is imperious to develop some effective and economical techniques to eliminate the organic pollutions into less toxic organic compounds or inorganic like CO_2, H_2O, NO_3^-, *etc.* [8].

Among various traditional degradation methods, chemical oxidation and adsorption/coagulation are two main methods in removing organic compounds, including O_3 [9], H_2O_2 [10], $OClO^-$ [11], Cl_2 [12], $SO_4^{2-}/S_2O_8^{2-}$ [13,14], Ferric and manganese binary oxide adsorption [15], iron and aluminum oxides adsorption [16], metal-organic framework adsorption [17], monolithic carbon cryogel [18], *etc.*. However, Fenton/Fenton-like oxidation process is an effective treatment method which combines both oxidation and coagulation in removing organic compounds. It is increasing adopted in recent years owing to the highly efficiency, simplicity, better reproducibility and easy handling [19–21]. Generally, Fenton process mainly involves *in situ* generation of chemical oxidants like $^{\cdot}OH$ and $^{\cdot}O_2^-$ which have highly reactive and nonselective [19]. And many researchers reported that Fenton process showed a good performance in removing organic pollutants in the past decade [22–26]. For example, Sun et al. (2007) studied the degradation of azo organic compounds by Fenton process, they found that the removal efficiency of dye in aqueous solution could be achieve 99.25% [24]. Bautista et al. (2007) researched the removal of TOC and COD in cosmetic wastewater using Fenton process, and demonstrated that TOC and COD had significant decrease in their optimized operating conditions [25]. Tekin et al. (2006) observed that Fenton oxidation could obviously improve the biodegradability of pharmaceutical [26]. However, according to former researchers, Fenton process contained four stages: oxidation, neutralization, coagulation/flocculation and solid-liquid separation [27–29]. The generation of $^{\cdot}OH$ in Fenton reaction is the determining factor in oxidation process. After neutralization stage, ferri-oxyhydroxides will be generated, and the coagulation will influence the removal of organics as well [30,31]. Specifically, Guo et al. (2016) found that in Fenton process, the COD removal mainly resulted from a combination of oxidation ($^{\cdot}OH$) and coagulating sedimentation (Fe^{2+}/Fe^{3+}) in desizing wastewater [32]. By Ivan et al. (2001) reported that 70% COD of leachate was removed by Fenton process and of which 56% was removed by coagulation, only 14% by free radical oxidation [33]. Yoon et al. (1998) found that coagulation determined the effect in removing organic pollutants from leachate [34]. Therefore, coagulation process also plays an important role in eliminating organic pollutants, and as a result, it is meaningful to carry out some further researches to confirm the mechanisms of oxidation and coagulation in terms of the removal of organics and investigate the difference between oxidation and coagulation by Fenton process.

The reaction rate constant of organic compounds in Fenton system has prominent relevance to their degradation [35]. Quantitative Structure Activity Relationship (QSAR) analysis as a theoretical predicted method has the advantages of rapid and cost-effective in evaluating reaction rate [36]. And it could imply some physicochemical properties of the respective chemicals [37]. It is usually applied to alternate to traditional analytical methods and has a broad application prospect in recent years [38,39]. In fact, QSAR analysis about Fenton process have been reported recently. Jia et al. (2015) developed some QSAR models in Fenton process, and found that the reaction rate constants had positive correlation with SAG (surface area grid) and $f(0)_n$, while had negative correlation with E_{gap} [40]. Li et al. (2013) also established a QSPR model equation for the decoloration and mineralization of azo dyes in Fenton system, they discovered that MW/S and $N_{N=N}$ were the most important factors for the degradation of azo dyes [41]. However, they focused primarily on the whole effects by using QSAR analysis, the efficiency by coagulation were not considered and the relationship between quantum descriptors and different processes (oxidation and coagulation) is still limited and have not been clear in Fenton process. Consequently, it is of significance to carry out some QSAR analysis for the classification discussion in Fenton process.

In this paper, Fenton experiments were performed on 28 widely used organic compounds for the reaction rate constants firstly, then Ferri-oxyhydroxide coagulation experiments were carried out on the 28 compounds for the classification in Fenton process. Based on the adsorption capacity and adsorption percentages (AP), 28 organic compounds were divided into two groups (group L and group H). Meanwhile, two softwares (Gaussian 09 and Material Studio7.0) were used to calculate the chemical descriptors used in this study. They were widely used in computational chemistry for calculating the electronic structure parameters of molecules and simulating the characters and properties of molecular frontier orbital, *etc* [42,43]. Later, QSAR models were established for Fenton process, at the same time, classification QSAR models were also developed for the two groups respectively. It is our primary purpose to have a better understanding of the difference for oxidation and coagulation in multi-process by quantum parameter analysis. Besides, we also aim to establish some accurate and robust classification models for predicting the reaction rate and explore the roles of oxidation and coagulation during Fenton process.

2. Materials and methods

2.1. Materials

In the present work, 28 kinds of organic compounds were selected as experimental materials, including p-Chlorophenol, Methyl blue, Bisphenol A and other organic compounds. These chemicals covered