Relationship between reaction rate constants of organic pollutants and their molecular descriptors during Fenton oxidation and *in situ* formed ferric-oxyhydroxides

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ABSTRACT

Fenton oxidation is a promising water treatment method to degrade organic pollutants. In this study, 30 different organic compounds were selected and their reaction rate constants (k) were determined for the Fenton oxidation process. Gaussian09 and Material Studio software sets were used to carry out calculations and obtain values of 10 different molecular descriptors for each studied compound. Ferric-oxyhydroxide coagulation experiments were conducted to determine the coagulation percentage. Based upon the adsorption capacity, all of the investigated organic compounds were divided into two groups (Group A and Group B). The percentage adsorption of organic compounds in Group A was less than 15% (wt./wt.) and that in the Group B was higher than 15% (wt./wt.). For Group A, removal of the compounds by oxidation was the dominant process while for Group B, removal by both oxidation and coagulation (as a synergistic process) took place. Results showed that the relationship between the rate constants (k values) and the molecular descriptors of Group A was more pronounced than for Group B compounds. For the oxidation-dominated process, E_{HOMO} and Fukui indices ($f(0)_x$, $f(-)_x$, $f(+)_x$) were the most significant factors. The influence of bond order was more significant for the synergistic process of oxidation and coagulation than for the oxidation-dominated process. The influences of all other molecular descriptors on the synergistic process were weaker than on the oxidation-dominated process.

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Introduction

Fenton (1894) reported as early as 1894 that ferrous ions strongly promote the oxidation of malic acid by hydrogen peroxide. Subsequent work has shown that the combination of H_2O_2 and a ferrous salt, "Fenton's reagent," is an effective oxidant for a wide variety of organic substrates, such as chlorophenols (Barbeni et al., 1987; Potter and Roth, 1993), chlorobenzene (Sedlak and Andren, 1991), nitrophenols (Kang et al., 1999) and dye pollutants (Kuo, 1992; Solozhenko et al., 1995). Due to its high oxidation potential and fast reaction kinetics, the Fenton reaction has gained much attention for its capability of degrading organics into harmless low molecular weight compounds. Examples of such compounds (degradation products) include carbon dioxide, water and organic acids such as formic acid, acetic and oxalic acid (Muruganandham and Swaminathan, 2004; Sun et al., 2007). The effectiveness of the Fenton process is mainly controlled by the generation of

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hydroxyl radicals, but also can be enhanced by other physico-chemical methods (Pignatello et al., 2006). For instance, Lucas et al. (2007) reported that the decolorization of Reactive Black 5 could reach 91% by a Fenton process enhanced by an aerobic biological treatment. Combination with ultrasound could enhance the decolorization of Acid Orange 7 (Zhang et al., 2009) and improve the COD removal of Reactive Black 8 from aqueous solutions by the Fenton process (Torrades et al., 2004). Yang et al. (2009) presented a microwave-enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater, which removed more than 55% COD and enhanced the 5-day biochemical oxygen demand (BOD5)/COD ratios. Besides these chemical treatments, photo-assisted Fenton-like reactions as a source of hydroxyl radicals have been shown to be effective in the environmental detoxification and photo-degradation of non-biodegradable contaminants, including textile dyes (Herrera et al., 1999; Nadtochenko and Kiwi, 1998; Ruppert et al., 1993; Sawyer et al., 1996).

Based upon our previous research, the choice of appropriate quantum-chemical descriptors is of great importance and can also easily be obtained by computation. Therefore, quantum-chemical descriptors have been applied to develop quantitative structure-activity relationship (QSAR) models to study the relationship between removal and the molecular descriptors of organic pollutants in Fenton oxidation (Jia et al., 2015).

Generally, the Fenton process is composed of the following stages: pH adjustment, oxidation reaction, neutralization, coagulation and solid–liquid separation (Kang and Hwang, 2000). According to Walling and Kato (1971), the basic mechanism of the Fenton process consists of chemical oxidation and coagulation of organic compounds. However, for Fenton precipitation processes, the coagulation step has not yet been completely understood. Therefore, in the present study, focus has been given to the coagulation of ferric-oxyhydroxides formed in the Fenton process. Based upon the adsorption capacity, 30 organic pollutants have been divided into two groups. The relationship between the reaction rate constants (k) of the organic pollutants in both groups and their molecular descriptors during Fenton oxidation have been studied. In order to better understand the coagulation of ferric-oxyhydroxides, coagulation experiments for different compounds were conducted. Finally, considering the removal rate constants of the compounds, the effect of the molecular descriptors on the removal rates was discussed.

1. Experiments

1.1. Materials

The 30 organic compounds studied and the hydrogen peroxide solution (30%, W/W) were supplied by Alfa Aesar Pty. Ltd., USA. Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was obtained from Sigma-Aldrich Pty. Ltd., USA. Sodium hydroxide and concentrated sulfuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All the chemicals were of analytical grade and were used directly without further purification. Water used for chemical solutions was purified by using a Milli-Q® Integral system provided by EMD Millipore Pty. Ltd., USA.

1.2. Fenton oxidation experiments

The initial concentration of highly soluble organic compounds was 100 mg/L. The concentration of the insoluble organic compounds was such that they formed a saturated solution. Fenton oxidation experiments were carried out at room temperature (20 ± 2°C) with a H_2O_2: Fe(II) molar ratio of 10:1. Since the pH of each compound's solution was different, before further treatment pH was adjusted for all solutions to a value of 3.0 by using a 1 mol/L solution of sulfuric acid. While mixing the reaction mixtures, the solutions were stirred continuously using a magnetic stirrer. In each experiment, the ferrous sulfate solution was added to the pH-adjusted solution. H_2O_2 (30%) was added to each solution and the recording of the reaction time was started. 1 mL of 1 mol/L sodium hydroxide solution was added to terminate the reactions at 0.25, 1.0, 2.0, 5.0, 10.0, 20.0, 40.0 and 60.0 min respectively (Pontes et al., 2010). Later, the samples were filtered through 0.45 μm membrane filters to separate the formed precipitates. The concentrations of organic compounds in the supernatant were measured at their maximum absorption wavelengths using a spectrophotometer (HACH DR4000).

1.3. Ferric-oxyhydroxide coagulation experiments

Ferric-oxyhydroxide coagulation experiments were also conducted using the same experimental conditions as were used for the Fenton oxidation experiments. The initial concentration for each organic compound's solution was 100 mg/L, pH was maintained at 3.0 and the temperature was kept constant at 20 ± 2°C. The concentrations of ferrous ion and sodium hydroxide solutions were also the same as for the Fenton oxidation experiments. However, in the coagulation experiments, the H_2O_2 was not added to the reaction systems. Instead, in these experiments, an equivalent dosage of sodium hydroxide was added in order to generate in situ flocs of ferric-oxyhydroxides. Later, the samples were filtered through 0.45 μm membrane filters to separate the precipitates formed. The concentrations of organic compounds were determined by using a spectropho-tometer (DR4000, HACH Company, USA).

1.4. Computational details

The initial geometries of all the investigated compounds were optimized using density functional theory (DFT) calculations using the DFT/B3LYP model with the 6–311++G(d,p) basis set of the GAUSSIAN09W package (Frisch et al., 2009). The vibrational frequency analysis was done by using HF and B3LYP methods, which also determined the nature of stationary points found by the optimization of geometries. Vibrational frequency analysis revealed that there was no virtual frequency for the optimized structures that would correspond to the minimum points on the potential energy surface. This showed that all of the optimized structures were stable. The energy value for the highest occupied molecular orbital (E_{HOMO}) and that for the lowest unoccupied molecular orbital (E_{LUMO}) was obtained from GAUSSIAN09. The HOMO-LUMO analysis was carried out to explain the charge transfer within the molecule.

Bond order (BO) and Fukui indices ($f(+)$, $f(-)$ and $f(0)$) (Famini et al., 1992; Parr and Yang, 1984) were specifically analyzed by

using Accelry Material Studio 6.1. All of the calculations and the localized double numerical basis set with polarization (DNP) were adopted as implemented in DMol^3 code in Material Studio 6.1. The self-consistent field procedure having a convergence criterion of 10^{-6} a.u was carried out for both energy and electron densities. Density mixing was set at 0.2 charge and 0.5 spin. The smearing of the electronic occupations was set to 0.005 Ha. Bond order (BO) was defined as the number of chemical bonds formed between pairs of atoms and gave information about the stability of the bonds. Within a BO value of four, the molecules of all the studied compounds tend to be more stable if their BO is increased. In the present study, BO_n refers to the minimum while BO_x refers to the maximum value of the carbon–carbon bond order in a molecule. Similarly, $f(+)_x$, $f(-)_x$ and $f(0)_x$ stand for the maximum values of nucleophilic, electrophilic and .OH attacks respectively. $f(+)_n$, $f(-)_n$ and $f(0)_n$ represent their corresponding minimum values for the main-chain carbon atom.

2. Results and discussion

The degradation of 30 different organic pollutants was investigated during the Fenton process. Degradation kinetic comparison was performed using an initial rate technique to eliminate any interferences from competition by intermediate products. The initial reaction rate constants of the organic compounds (k) were determined and presented in Table 1. Fenton oxidation is a pseudo first-order reaction with respect to the concentration of organic substrate (Huang et al., 1993; Sedlak and Andren, 1991). According to the pseudo first-order kinetic model, the k values of the studied organic compounds were calculated from the linear regression of $\ln(C_0/C_t)$ *versus* the reaction time. These values for the rate constants ranged between 0.031 min^{-1} (for bis(2-methoxyethyl) phthalate) and 2.934 min^{-1} (for Malachite Green) with a mean value of 0.636 min^{-1}. All these k values are shown in Fig. 1, and the degradation curves obtained *versus* reaction time suggest that a first-order kinetics model approaches the real kinetics of this Fenton oxidation process. Degradation of different kinds of organic pollutants by the Fenton process, sono-Fenton process, electro-Fenton process, photo-Fenton process, *etc.* has been studied previously (Alshamsi et al., 2007; Lucas et al., 2007; Pignatello et al., 2006; Torrades et al., 2004; Yang et al., 2009; Zhang et al., 2009). Zhang et al. (2009) investigated the degradation of Acid Orange 7 (AO7) by the Fenton process in combination with ultrasonic irradiation (Zhang et al., 2009). The results showed that the rate constant of AO7 was determined to be 0.71 min^{-1} under these conditions (AO7 = 200 mg/L, Fe = 0.5 g/L, H$_2$O$_2$ = 5 mmol/L, pH = 2). Alshamsi et al. (2007)conducted a study on the degradation of Crystal Violet (CV) using UV/hydrogen peroxide and Fenton's reagent (Alshamsi et al., 2007). The results showed that the rate constant of CV was 0.54 min^{-1} under these experimental conditions (CV = 0.027 mmol/L, Fe = 0.333 mmol/L, H$_2$O$_2$ = 0.333 mmol/L, pH = 2). Under the experimental conditions of the current study, AO7 and CV were also degraded, and the corresponding rate constants were found to be 0.787 min^{-1} and 0.446 min^{-1}, which are in agreement with those reported in the above study.

Previous studies have mentioned that the chemical structure of the molecules (pollutants) has a significant influence on the removal rate of these molecules. Different structural units would result in different removal rates. Fig. 1 shows that the largest reaction rate constant among the studied compounds is almost 95 times greater than that of the smallest. This difference in rate constant values ensures that the chosen compounds actually represent a wide range of structures. This also highlights the importance of analyzing the relationship between the removal of organic compounds and the molecular descriptors of the organic compounds. Theoretical molecular descriptors relating to the structural, electronic and thermodynamic parameters were selected to describe the organic compounds. These descriptors play an important role in Fenton oxidation. The organic compounds chosen for the present study and their corresponding 10 molecular descriptors are listed in Table 1.

In this study, sodium hydroxide solution was used as a quenching agent to terminate the reaction. Subsequently flocs of ferric-oxyhydroxides were generated and the color of the aqueous solution changed to yellow-brown at the end of the experiments. The *in situ* formed ferric-oxyhydroxides, having large surface area and adsorption capacity, adsorbed the organic compounds, as has already been reported in the literature (Julien et al., 1994).

There are two possible routes for the removal of organic pollutants during the Fenton process. They can either be adsorbed on the ferric-oxyhydroxides or can be degraded by the oxidation process. In order to determine the coagulation percentage of organic compounds on ferric-oxyhydroxides, the coagulation experiments were performed for all chosen organic compounds, and the adsorption percentages (AP) are summarized in Table 1. The results showed that 14 (out of 30) organic compounds were significantly adsorbed on ferric-oxyhydroxides and had AP values of more than 15%. However, AP values for the remaining 16 organic compounds were less than 15% (wt./wt.). Based on AP values, all organic compounds were divided into two groups. The organic compounds having AP values less than 15% were placed in Group A while compounds having AP values higher than 15% were placed in Group B. For Group A, the adsorption was negligible and therefore the removal of pollutants was dominated by the oxidation process. However, for Group B compounds, both coagulation and oxidation proceeded side by side. Therefore, for this group both the coagulation and oxidation were responsible for the removal of the organic compounds. Due to the significant contribution of both coagulation and oxidation processes to the removal of the organic pollutants, it is reasonable to say that the removal mechanism of Group B organic substances is more complicated than that of the Group A compounds.

Analysis of the correlation between k values and the molecular descriptors of the organic compounds shows that the E_{HOMO} variable is positively correlated to k values and the correlation coefficient (r) is 0.528 (Table 2). A closer look at the correlation coefficient (r) values presented in Table 2 also reveal that these (r values) decreased significantly for the Group B compounds. However, such a decreasing trend was not observed for BO_n and BO_x values for the Group B compounds. Maximum values for the correlation coefficient

Table 1 – Reaction rate constants (k), adsorption percentages (AP) and the structural descriptors of the studied organic compounds.

| No.	Group	Organic compounds	CAS No.	k (min⁻¹)	AP (%)	E_{LUMO} (eV)	E_{HOMO} (eV)	BO_n (-)	BO_x (-)	$f(+)_x$ (e)	$f(+)_n$ (e)	$f(-)_x$ (e)	$f(-)_n$ (e)	$f(0)_x$ (e)	$f(0)_n$ (e)
1	Group A	P-chlorophenol	106-48-9	0.217	-1.61	-0.028	-0.233	1.318	1.4	0.116	0.045	0.087	0.06	0.096	0.066
2		2-Nitroso-1-naphthol	132-53-6	0.356	-0.97	-0.106	-0.226	1.169	1.547	0.068	0.020	0.052	0.013	0.060	0.021
3		Methyl Blue	28631-66-5	2.090	-0.43	0.033	-0.036	1.089	1.501	0.024	-0.001	0.024	0.000	0.024	0.000
4		Eriochrome Black T	1787-61-7	2.133	0.11	-0.122	-0.214	1.098	1.513	0.050	-0.010	0.024	-0.002	0.035	-0.002
5		4-Bromobenzaldehyde	1122-91-4	0.450	0.14	-0.0819	-0.266	1.024	1.931	0.143	0.045	0.095	0.030	0.119	0.040
6		2,4-Dichlorophenoxyacetic acid	94-75-7	0.781	0.22	-0.046	-0.265	0.912	1.949	0.102	0.014	0.086	0.014	0.089	0.014
7		2,4,5-7-Tetrabromofluorescein disodium salt	17372-87-1	0.203	0.24	-0.092	-0.200	0.963	1.805	0.054	-0.021	0.028	-0.019	0.041	-0.020
8		4-Dimethylaminobenzaldehyde	100-10-7	0.472	0.35	-0.047	-0.21	1.055	1.457	0.143	0.018	0.080	0.029	0.095	0.023
9		9H-Fluoren-9-ylmethyl carbonochloridate	28920-43-6	0.129	1.07	-0.048	-0.231	0.967	1.409	0.076	0.008	0.087	0.005	0.082	0.006
10		2,6-Dinitrotoluene	606-20-2	0.172	1.15	-0.111	-0.298	1.015	1.373	0.079	0.015	0.039	0.011	0.057	0.017
11		3,5-Dichlorophenol	591-35-5	0.229	3.24	-0.039	-0.253	1.313	1.344	0.104	0.052	0.110	0.043	0.092	0.060
12		Bisphenol A	80/05/7	0.266	3.87	-0.014	-0.215	0.953	1.416	0.064	0.000	0.050	0.004	0.056	0.002
13		3,4-Dichloroaniline	95-76-1	0.185	4.45	-0.029	-0.222	1.272	1.425	0.113	0.035	0.081	0.038	0.090	0.050
14		p-Nitroaniline	100-01-6	0.863	8.01	-0.079	-0.237	1.266	1.439	0.050	-0.013	0.056	0.012	0.036	0.031
15		4-Methyl-2-nitroaniline	89-62-3	0.506	10.6	-0.085	-0.224	0.989	1.476	0.078	0.023	0.092	0.045	0.067	0.037
16		N-Benzoyl-N-phenylhydroxylamine	304-88-1	0.303	13.9	-0.049	-0.236	0.982	1.398	0.070	-0.014	0.058	-0.027	0.059	-0.021
17	Group B	Acid Red 73	5413-75-2	1.204	31.6	-0.138	-0.236	1.186	1.503	0.031	-0.006	0.033	-0.002	0.031	-0.004
18		Acid Orange 7	633-96-5	0.787	34.7	-0.089	-0.208	1.162	1.522	0.042	-0.023	0.041	-0.007	0.041	-0.015
19		Ethidium bromide	1239-45-8	0.534	43.3	-0.108	-0.158	0.984	1.496	0.017	-0.008	0.018	-0.009	0.019	-0.010
20		Bis(2-methoxyethyl) phthalate	117-82-8	0.031	46.2	-0.065	-0.257	0.962	1.386	0.091	0.002	0.046	-0.001	0.056	0.008
21		Basic fuchsin	632-99-5	0.089	49.9	-0.205	-0.311	1.006	1.620	0.073	0.006	0.046	0.008	0.056	0.008
22		m-Toluic acid	99-04-7	0.123	50.6	-0.053	-0.26	1.011	1.414	0.105	0.052	0.081	0.042	0.085	0.063
23		Methylene Blue	61-73-4	0.931	59.9	-0.127	-0.173	1.038	1.418	0.037	0.009	0.037	0.010	0.036	0.012
24		Bromocresol Green	76-60-8	1.132	70.6	-0.069	-0.245	1.016	1.409	0.071	-0.012	0.035	-0.009	0.056	0.002
25		Basic Red 2	477-73-6	0.422	72.5	-0.115	-0.179	1.003	1.450	0.027	-0.024	0.029	-0.023	0.026	-0.024
26		Phthalic anhydride	85-44-9	0.075	72.8	-0.103	-0.299	0.996	1.388	0.084	0.050	0.066	0.021	0.074	0.038
27		Bromophenol Blue	115-39-9	0.281	76.4	-0.068	-0.252	0.950	1.405	0.095	-0.008	0.039	-0.010	0.053	0.002
28		Isatin	91-56-5	0.747	88.2	-0.105	-0.246	0.878	1.392	0.119	0.026	0.076	0.017	0.096	0.025
29		Crystal Violet	548-62-9	0.446	88.6	-0.101	-0.151	1.103	1.503	0.053	0.002	0.050	0.007	0.051	0.007
30		Malachite Green	569-64-2	2.934	97.5	-0.108	-0.173	1.068	1.514	0.056	0.002	0.056	0.003	0.056	0.002
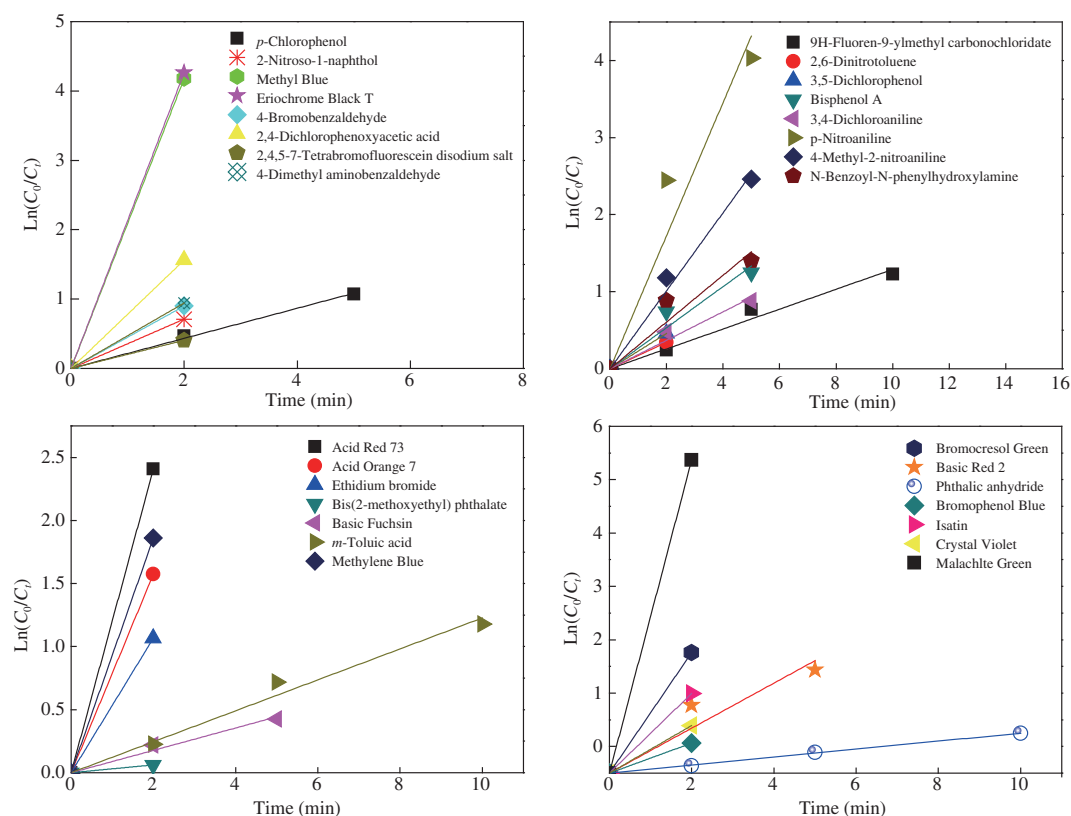
Fig. 1 – Reaction rate constants of studied organic compounds for the Fenton process.

(r) for BO_n and BO_x in Group B were observed to be 0.355 and 0.213 respectively. On the contrary, for Group A compounds, the 'r' values for E_{HOMO}, $f(+)_x$, $f(-)_x$ and $f(0)_x$ increased for all compounds, while no significant change was observed for other descriptors. These results highlight the difference in 'r' values for compounds present in both the groups.

For Group A compounds, the values of correlation coefficients between the rate constant values and values of various other descriptors were found to be in the following order: E_{HOMO} (0.625) > $f(0)_x$ (−0.557) > $f(-)_x$ (−0.524) > $f(+)_x$ (−0.504). Similarly, for Group B compounds, the correlation coefficient values between rate constant values and two other descriptors were found vary in the following order: E_{HOMO} (0.443) > BO_n (0.355). It is evident from the results that E_{HOMO} has the highest correlation coefficient values among all the compounds present in Group A and Group B. Furthermore, absolute r values of five of the descriptors are higher than 0.5 in Group A, while the largest absolute r value in Group B is 0.443. It can be concluded that the

relationship between k values and molecular descriptors of Group A is more apparent than that of Group B. According to the correlation analysis, E_{HOMO} plays a key role in both Group A and Group B. The standout results of BO_n in Group B can possibly be attributed to its close association with the adsorption. Since the compounds in Group A are difficult to adsorb, the effects of BO are not so obvious for this group. However, the effects of Fukui indices, especially $f(0)_x$, are quite obvious in Group A. Therefore, for the synergistic process of oxidation and coagulation (Group B), the influence of BO is more obvious than that for the oxidation-dominated process (Group A). The influences of all other molecular descriptors are weaker in the oxidation-dominated process. In general, molecular orbital energy, bond order (BO) and Fukui indices ($f(+)$, $f(-)$ and $f(0)$) are three descriptors that have showed the largest influence on the removal rates of the studied organic compounds.

To study various mechanisms of organic compounds, such as pharmacological activities, toxicity and degradability, the

Table 2 – Values of correlation coefficient (r) between k values of organic compounds and their molecular descriptors.

Group	E_{LUMO}	E_{HOMO}	BO_n	BO_x	$f(+)_x$	$f(+)_n$	$f(-)_x$	$f(-)_n$	$f(0)_x$	$f(0)_n$
Overall[a]	−0.026	0.528	0.102	0.093	−0.400	−0.316	−0.331	−0.225	−0.363	−0.283
Group A	0.089	0.625	0.194	0.101	−0.504	−0.369	−0.524	−0.253	−0.557	−0.283
Group B	−0.056	0.443	0.355	0.213	−0.287	−0.251	−0.065	−0.169	−0.131	−0.268

[a] Representing complete set of studied organic compounds.

electronic energy of the highest occupied molecular orbital (E_{HOMO}) has widely been used in developing QSAR models (Güsten, 1999; Gramatica et al., 2004; Isayev et al., 2006; Rasulev et al., 2007; Turabekova et al., 2008). It is well-known that the E_{HOMO} parameter determines the nucleophilic ability of a compound and hence can determine the possibility of a reaction due to the attack of a strong electrophile such as the .OH radical. E_{HOMO} governs many chemical reactions and characterizes the susceptibility of a molecule towards an attack by an electrophile (Karelson et al., 1996). It is shown in Table 1 that the average value for E_{HOMO} is −0.224 eV. The smallest and largest values for E_{HOMO} were observed to be −0.311 eV (basic fuchsin) and −0.036 eV (Methyl Blue) respectively. It is also worth mentioning here that basic fuchsin has comparatively slower kinetics (k value of 0.089 min^{-1}) while Methyl Blue shows faster kinetics (k value of 2.09 min^{-1}). .OH is an electrophilic radical. The ability of a molecule to lose an electron increases as its E_{HOMO} value increases. This in turn leads to an increase in susceptibility to .OH attack and consequently results in a higher k value for the compound. Thus, the descriptor E_{HOMO} is positively correlated with the k values of the compounds present in both the groups. This correlation is in accordance with the chemical reactivity rules and explains why Methyl Blue has faster kinetics than basic fuchsin. According to the frontier molecular orbital theory, a higher value of E_{HOMO} facilitates the oxidation and hence increases the degradation rate of the chemicals. Furthermore, the analysis of the structure–activity relationship of the representative compounds also confirmed the correlation of degradation rate with chemical reactivity rules.

Bond order (BO) is one of the electron density-based descriptors, which satisfies the need of structural chemistry for a compact characteristic of electron distribution in molecules. This intuitive property is described by the popular quantum chemical index called the Mayer bond order (Mayer, 1986; Mayer 2003). Bond order carries complementary information about the electronic structure and is able to indicate the presence or absence of electron delocalization between a pair of the atoms. Obviously, the absence of electron delocalization (very small bond order) makes electron flow improbable, which reflects the strongly ionic character of these interactions. Table 1 shows that BO_n and BO_x have the average values of 1.058 and 1.493 respectively for Group B compounds. The maximum values for BO_n and BO_x are observed to be 1.318 (for P-chlorophenol) and 1.949 (for 2,4-dichlorophenoxyacetic acid) respectively. The minimum values for BO_n and BO_x were observed to be 0.878 (for isatin) and 1.344 (for 3,5-dichlorophenol) respectively. Table 2 also shows that for Group B, both BO_n and BO_x are positively correlated to k values. This means the higher the values of BO_n and BO_x, the faster the reaction rate would be. For example, basic fuchsin, Eriochrome Black T and Malachite Green all have high values for BO_n and BO_x and also exhibit fast reaction rates (k values of 2.090, 2.133 and 2.934 respectively). It is also observed that the influence of BO in Group B is more obvious than that in Group A. The coagulation and adsorption on ferric-oxyhydroxides may be associated with BO and may belong to the category of static electronic adsorption.

Fukui indices are one of the key concepts to portray the decomposition sequence of organic structures in Fenton oxidation. Fukui indices are defined as the derivatives of the electron density with respect to the number of electrons at constant molecular geometry (De Proft et al., 2002; Parr and Yang, 1984). Eqs. (3)–(5) represent three important concepts of nucleophilic attack, electrophilic attack and radical attack.

$$f(+) = \rho N+1(r) - \rho N(r) \qquad (3)$$

$$f(-) = \rho N(r) - \rho N-1(r) \qquad (4)$$

$$f(0) = 1/2[\rho N+1(r) - \rho N-1(r)] \qquad (5)$$

where, $\rho N + 1(r)$, $\rho N(r)$ and $\rho N − 1(r)$ are the electron densities of the $N + 1$, N, and $N − 1$ electron systems respectively.

The average values of parameters $f(+)_x$, $f(–)_x$ and $f(0)_x$ are 0.075 e, 0.057 e and 0.061 e respectively, while those of $f(+)_n$, $f(–)_n$ and $f(0)_n$ are 0.009 e, 0.010 e and 0.015 e respectively. The variation of each Fukui Index was highly significant. The largest values for $f(+)_x$, $f(–)_x$ and $f(0)_x$ were observed to be 0.143 e, 0.110 e, and 0.119 e respectively while the smallest values for $f(+)_x$, $f(–)_x$ and $f(0)_x$ were 0.017 e, 0.018 e and 0.019 e respectively. Similarly, the largest values for $f(+)_n$, $f(–)_n$ and $f(0)_n$ were 0.052 e, 0.060 e and 0.066 e respectively, while the smallest values for $f(+)_n$, $f(–)_n$ and $f(0)_n$ were −0.024 e, −0.027 e and −0.024 e respectively. The r values changed in Group A in the order: $f(0)_x$ (−0.557) > $f(–)_x$ (−0.524) > $f(+)_x$ (−0.504) > $f(+)_n$ (−0.369) > $f(0)_n$ (−0.283) > $f(–)_n$ (−0.253). Among these, the largest absolute value for r is observed for $f(0)_x$, which is approximately equal to 0.6. Moreover, after E_{HOMO}, $f(0)_x$ is the second most significant molecular descriptor which had the most influence on the removal of the organic compounds in Group A. Table 2 shows that increasing the values of Fukui indices leads to a drop in the values of the rate constant k in Group A. However, no such significant correlation was observed for compounds in Group B. Therefore, it can safely be proposed that the compounds in Group A, which have low $f(0)_x$ values, have stronger susceptibility to .OH radical attack. For example, Methyl Blue shows a low $f(0)_x$ value (0.024) and hence, leads to a faster reaction rate ($k = 2.09$ min^{-1}). Similarly, 4-Bromobenzaldehyde has a higher $f(0)_x$ value (of 0.119), however it shows very slow kinetics (k value of 0.450 min^{-1}). Therefore, for compounds that are weakly adsorbed on the ferric oxyhydroxides, a higher value of Fukui indices results in slower removal kinetics and *vice versa*.

3. Conclusions

In this work, focus has been given to the coagulation of ferric-oxyhydroxides formed in the Fenton process. Based upon the adsorption capacity, the investigated organic compounds were divided into two groups (Group A and Group B). The percentage adsorption of organic compounds in Group A was less than 15% while in Group B the value was higher than 15%. In Group A, removal by oxidation plays a dominant role during the Fenton process. For Group B, in addition to the removal by

oxidation, removal by coagulation also plays a significant role. Based upon the analysis of the correlation coefficient between the k values and the molecular descriptors of the compounds present in the two groups, it is concluded that the molecular orbital energy (E_{HOMO}) plays an important role in the removal of the organic compounds. In addition, Fukui indices ($f(0)_x$, $f(-)_x$ and $f(+)_x$) and bond order (BO_n) are of significance for removing organic compounds. For the oxidation-dominated process, E_{HOMO} and Fukui indices ($f(0)_x$, $f(-)_x$, $f(+)_x$) have a more significant effect on k values. Meanwhile, for the synergistic process of oxidation and coagulation, the influence of bond order is more pronounced than that in the oxidation-dominated process. The influences of the other molecular descriptors are weaker for the synergistic process than the oxidation-dominated process. Therefore, the grouping of organic compounds is of great importance in studying the relationship between k values of organic compounds and their molecular descriptors during Fenton oxidation and *in situ* formed ferric-oxyhydroxides. Meanwhile, it also helps to better understand degradation of organic compounds during the Fenton process.

Acknowledgments

REFERENCES

Alshamsi, F.A., Albadwawi, A.S., Alnuaimi, M.M., Rauf, M.A., Ashraf, S.S., 2007. Comparative efficiencies of the degradation of crystal violet using UV/hydrogen peroxide and Fenton's reagent. Dyes Pigments 74 (2), 283–287.

Barbeni, M., Minero, C., Pelizzetti, E., Borgarello, E., Serpone, N., 1987. Chemical degradation of chlorophenols with Fenton's reagent (Fe^{2+} + H$_2$O$_2$). Chemosphere 16 (10), 2225–2237.

De Proft, F., Van Alsenoy, C., Peeters, A., Langenaeker, W., Geerlings, P., 2002. Atomic charges, dipole moments, and Fukui functions using the Hirshfeld partitioning of the electron density. J. Comput. Chem. 23 (12), 1198–1209.

Famini, G.R., Penski, C.A., Wilson, L., 1992. Using theoretical descriptors in quantitative structure activity relationships: some physicochemical properties. J. Phys. Org. Chem. 5 (7), 395–408.

Fenton, H.J.H., 1894. Oxidation of tartaric acid in presence of iron. J. Chem. Soc. Trans. 65, 899–910.

Frisch, M.J. et al. (2009). Gaussian, Inc., Wallingford CT

Gramatica, P., Pilutti, P., Papa, E., 2004. A tool for the assessment of VOC degradability by tropospheric oxidants starting from chemical structure. Atmos. Environ. 38 (36), 6167–6175.

Güsten, H., 1999. Predicting the abiotic degradability of organic pollutants in the troposphere. Chemosphere 38 (6), 1361–1370.

Herrera, F., Kiwi, J., Lopez, A., Nadtochenko, V., 1999. Photochemical decoloration of Remazol Brilliant Blue and Uniblue A in the presence of Fe3+ and H2O2. Environ. Sci. Technol. 33 (18), 3145–3151.

Huang, C., Dong, C., Tang, Z., 1993. Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. Waste Manag. 13 (5), 361–377.

Isayev, O., Rasulev, B.F., Gorb, L., J., L, 2006. Structure–toxicity relationships of nitroaromatic compounds. Mol. Divers. 10 (2), 233–245.

Jia, L., Shen, Z., Guo, W., Zhang, Y., Zhu, H., Ji, W., Fan, M., 2015. QSAR models for oxidative degradation of organic pollutants in the Fenton process. J. Taiwan Inst. Chem. Eng. 46 (0), 140–147.

Julien, F., Güeroux, B., Mazet, M., 1994. Comparaison de l'élimination de molecules organiques par coagulation-floculation et par adsorption sur flocs d'hydroxyde metallique preformes. Water Res. 28 (12), 2567–2574.

Kang, Y.W., Hwang, K.-Y., 2000. Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Res. 34 (10), 2786–2790.

Kang, S.F., Wang, T.H., Lin, Y.H., 1999. Decolorization and degradation of 2,4-dinitrophenol by Fenton's reagent. J. Environ. Sci. Health A 34 (4), 935–950.

Karelson, M., Lobanov, V.S., Katritzky, A.R., 1996. Quantum-chemical descriptors in QSAR–QSPR studies. Chem. Rev. 96 (3), 1027–1043.

Kuo, W., 1992. Decolorizing dye wastewater with Fenton's reagent. Water Res. 26 (7), 881–886.

Lucas, M.S., Dias, A.A., Sampaio, A., Amaral, C., Peres, J.A., 2007. Degradation of a textile reactive azo dye by a combined chemical–biological process: Fenton's reagent-yeast. Water Res. 41 (5), 1103–1109.

Mayer, I., 1986. Bond orders and valences from ab initio wave functions. Int. J. Quantum Chem. 29 (3), 477–483.

Mayer, I., 2003. Simple Theorems, Proofs, and Derivations in Quantum Chemistry. Kluwer/Plenum, NewYork.

Muruganandham, M., Swaminathan, M., 2004. Decolourisation of reactive Orange 4 by Fenton and photo-Fenton oxidation technology. Dyes Pigments 63 (3), 315–321.

Nadtochenko, V., Kiwi, J., 1998. Primary photochemical reactions in the photo-Fenton system with ferric chloride. 1. A case study of xylidine oxidation as a model compound. Environ. Sci. Technol. 32 (21), 3273–3281.

Parr, R.G., Yang, W., 1984. Density functional approach to the frontier-electron theory of chemical reactivity. J. Am. Chem. Soc. 106 (14), 4049–4050.

Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Environ. Sci. Technol. 36 (1), 1–84.

Pontes, R.F., Moraes, J.E., Machulek, A., Pinto, J.M., 2010. A mechanistic kinetic model for phenol degradation by the Fenton process. J. Hazard. Mater. 176 (1), 402–413.

Potter, F.J., Roth, J.A., 1993. Oxidation of chlorinated phenols using Fenton's reagent. Hazard Waste Hazard. Mater. 10 (2), 151–170.

Rasulev, B.F., Saidkhodzhaev, A.I., Nazrullaev, S.S., Akhmedkhodzhaeva, K.S., Khushbaktova, Z.A., Leszczynski, J., 2007. Molecular modelling and QSAR analysis of the estrogenic activity of terpenoids isolated from Ferula plants. SAR QSAR Environ. Res. 18 (7–8), 663–673.

Ruppert, G., Bauer, R., Heisler, G., 1993. The photo-Fenton reaction — an effective photochemical wastewater treatment process. J. Photochem. Photobiol. A Chem. 73 (1), 75–78.

Sawyer, D.T., Sobkowiak, A., Matsushita, T., 1996. Metal [MLx; M = Fe, Cu, Co, Mn]/hydroperoxide-induced activation of dioxygen for the oxygenation of hydrocarbons: oxygenated Fenton chemistry. Acc. Chem. Res. 29 (9), 409–416.

Sedlak, D.L., Andren, A.W., 1991. Oxidation of chlorobenzene with Fenton's reagent. Environ. Sci. Technol. 25 (4), 777–782.

Solozhenko, E., Soboleva, N., Goncharuk, V., 1995. Decolourization of azodye solutions by Fenton's oxidation. Water Res. 29 (9), 2206–2210.

Sun, J.H., Sun, S.P., Fan, M.H., Guo, H.Q., Qiao, L.P., Sun, R.X., 2007. A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process. J. Hazard. Mater. 148 (1), 172–177.

Torrades, F., García-Montaño, J., García-Hortal, J.A., Núñez, L., Domènech, X., Peral, J., 2004. Decolorisation and mineralisation of homo- and hetero-bireactive dyes under Fenton and photo-Fenton conditions. Color. Technol. 120 (4), 188–194.

Turabekova, M.A., Rasulev, B.F., Levkovich, M.G., Abdullaev, N.D., Leszczynski, J., 2008. *Aconitum* and *Delphinium* sp. alkaloids as antagonist modulators of voltage-gated Na+ channels: AM1/DFT electronic structure investigations and QSAR studies. Comput. Biol. Chem. 32 (2), 88–101.

Walling, C., Kato, S., 1971. Oxidation of alcohols by Fenton's reagent. Effect of copper ion. J. Am. Chem. Soc. 93 (17), 4275–4281.

Yang, Y., Wang, P., Shi, S., Liu, Y., 2009. Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater. J. Hazard. Mater. 168 (1), 238–245.

Zhang, H., Zhang, J., Zhang, C., Liu, F., Zhang, D., 2009. Degradation of C.I. Acid Orange 7 by the advanced Fenton process in combination with ultrasonic irradiation. Ultrason. Sonochem. 16 (3), 325–330.