Removal of emerging contaminants from water via peroxymonosulfate activation with various iron sources (Fe^{2+}, Fe^{3+}, ZVI)

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Abstract This project studied the conversion of caffeine (stimulant), ibuprofen (analgesic), and diuron (herbicide) with novel Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs). Chemical oxidation was achieved through electron transfer activation of peroxymonosulfate (PMS), from different iron sources including the ferrous ion (Fe^{2+}), the ferric ion (Fe^{3+}) and zero-valent iron (ZVI) in different size particles. The in-situ generated radical species mainly included sulfate radicals (SO$_4^{\bullet-}$), which have high redox potential for electron abstraction (2.5-3.1 V). Among the iron sources tested, ZVI was the most efficient and reactive form because of the slow and continuous release of Fe^{2+} and electrons that favors the production of a greater percentage SO$_4^{\bullet-}$. Controlled Fe^{2+} release, minimizes undesirable quenching (consumption) of SO$_4^{\bullet-}$ by the Fe^{2+}, making ZVI the preferred method for PMS activation. Overall, the contaminant with the highest removal percentage, irrespectively of the oxidizing system used, was ibuprofen because of its aromatic ring and lack of electron withdrawal groups in its structure.

Keywords: peroxymonosulfate, zero-valent iron, caffeine, diuron, ibuprofen

1. Introduction

The increasing use of pesticides, pharmaceuticals and personal care products in modern societies has resulted in the need for application of additional treatment of water and wastewater mainly due to the recalcitrant nature of these compounds. Since, conventional treatment processes are found to be inefficient in removing these contaminants or produce additional hazardous waste (Petrovic *et al*, 2003 & Halling-Sorensen *et al*, 1998), current research activities are focusing on their complete destruction through advanced chemical oxidation processes (Rodriguez *et al.*, 2011 & Lee *et al.*, 2011).

In general, AOPs utilize oxidants, catalysts, heat and/or radiation for the formation of reactive species, known as free radicals. Fenton Reagent (FR) is one of the most known AOPs that utilizes iron for the activation of hydrogen peroxide through electron transfer mechanisms.

FR results in the formation of many different ROS including hydroxyl radicals (HO$^{\bullet}$) which are highly selective species with high second order rate constants for most of the contaminants (Antoniou *et al*, 2009).

Though FR has been applied for the removal of a wide range of contaminants from water and wastewater, its wide-spread application is limited due to the short application pH range and limited iron solubility. To overcome these, researchers have focused on utilizing various iron sources (iron in different oxidation states and zero-valent iron-ZVI) and chelating agents (such as citric acid) to increase iron solubility. In addition, Fenton like processes have been also tested, where hydrogen peroxide is substituted by the sulfate radicals (SRs) generating oxidants persulfate (PS) and peroxymonosulfate (PMS) (Rastogi eta al, 2009a and 2009b). The in-situ generated radical species from SR-AOPs mainly include sulfate radicals (SO$_4^{\bullet-}$), which have high redox potential for electron abstraction (2.5-3.1 V). Side reactions can cause the formation of additional radical species such hydroxyl radicals (HO$^{\bullet}$) and peroxymonosulfate radicals (SO$_5^{\bullet-}$).
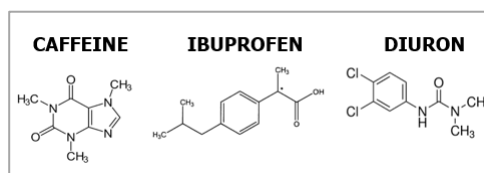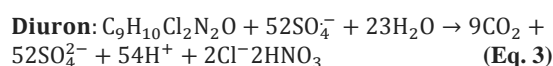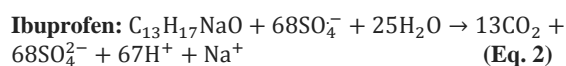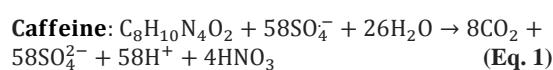

Figure 1. Tested compounds

In this study, the sulfate radical generating oxidant peroxymonosulfate (HSO$_5^-$, PMS) was chosen to be activated by various iron sources (Fe^{2+}, Fe^{3+}, and ZVI), since sulfate radicals have higher redox potential for electron abstraction than hydroxyl radicals and can cause selective oxidation. The above-mentioned oxidizing species where used for the removal of a mixture of emerging contaminants with varying chemical structures (Fig 1).

To the best of our knowledge, this is the first study that compared the efficiency of the iron/PMS oxidation system activated by different iron sources for the removal of a mixture of persistent organic compounds under the same experimental conditions.

2. Materials and Methods

Stock solutions of the model contaminants were initially prepared in Milli-Q water. All the experiments were conducted in open reactor vessels with a treated volume of 500 mL, under continues stirring conditions at room temperature (T = 20°C). The initial contaminant concentration was 0.1 mM, and treated solution pH=3.5. The added oxidant and iron concentration was based on the stoichiometric reactions listed below (Eq. 1-3). The remaining contaminant concentration was quantified in an Agilent 1100 HPLC equipped with PDA. The column used was an Agilent ZORBAX Eclipse Plus-C18 (4.6 x 100 mm, 3,5μm) and the mobile phase consisted of 92.5 % of 0.02% v/v H_2SO_4 and 7.5 % acetonitrile (ACN). The remaining PMS concentration was quantified with KI and $Na_2S_2O_3$ titration.

Caffeine: $C_8H_{10}N_4O_2 + 58SO_4^- + 26H_2O \rightarrow 8CO_2 + 58SO_4^{2-} + 58H^+ + 4HNO_3$ **(Eq. 1)**

Ibuprofen: $C_{13}H_{17}NaO + 68SO_4^- + 25H_2O \rightarrow 13CO_2 + 68SO_4^{2-} + 67H^+ + Na^+$ **(Eq. 2)**

Diuron: $C_9H_{10}Cl_2N_2O + 52SO_4^- + 23H_2O \rightarrow 9CO_2 + 52SO_4^{2-} + 54H^+ + 2Cl^- 2HNO_3$ **(Eq. 3)**

3. Results and Discussion

The obtained results of this study were compared with a previous study by Rodríguez *et al*. (2012), where all the above mentioned iron sources where used for PS activation. To enable comparison between the two studies, all the experimental conditions were kept the same as in Rodríguez *et al*. (2012), including initial contaminant concentration (0,1mM), temperature (T= 20ºC), initial solution pH (pH= 3.5), and estimation of the added oxidant concentrations for each model contaminant. Initially, the objective was to find the optimum molar ratio between Fe^{2+} / PMS (1:100, 1:10, 1:5 and 1:1) that results in the highest contaminant removal. Among the tested molar ratios (Fe^{2+}/PMS=1:100, 1:10, 1:5 and 1:1), Fe^{2+} / PMS=1:5 was found to be the optimum one and was further tested for the remaining iron sources (Fig 2).

Between the iron sources tested, ZVI was the most efficient and reactive form because of the slow and continuous release of Fe(II) and electrons that favor the production of a greater percentage $SO_4^{\bullet-}$. The reaction between ZVI and PMS takes place on the outer surface of the ZVI particles, where the diameter of each ZVI particle used, determines the release of Fe(II). Controlled Fe(II) release, is believed to have minimized undesirable quenching (consumption) of $SO_4^{\bullet-}$ by the Fe(II), making ZVI the preferred method for PMS activation.
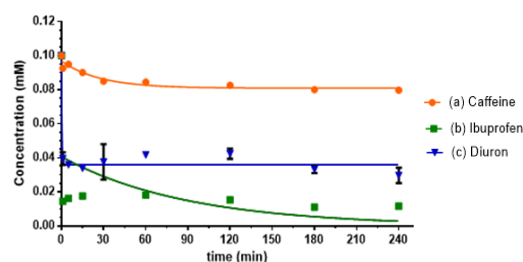

Figure 2. Degradation of pollutants in Fe^{2+} / PMS oxidation system at a ratio of 1: 5

Conditions: (a) [Caf]$_0$ = 0.1mM, [PMS$_C$]$_0$ = 5.8mM, [Fe(II)]$_0$ = 1,16mM
(b) [Ibu]$_0$ = 0.1mM, [PMS$_I$]$_0$ = 6,8mM, [Fe(II)]$_0$ = 1,36mM
(c) [Diu]$_0$ = 0.1mM, [PMS$_D$]$_0$ = 5,2mM, [Fe(II)]$_0$ = 1,04mM

Overall, the contaminant with the highest removal percentage, irrespectively of the oxidizing system used, was ibuprofen because of its aromatic ring and lack of electron withdrawal groups in its structure. The least degradable was caffeine, due to heteroatoms (N) in its structure that has reduced second order kinetic constants with radical species compared to carbon groups. Diuron appeared to have a significant decrease in its concentration due to dechloronization caused by radical attack (Fig 3).
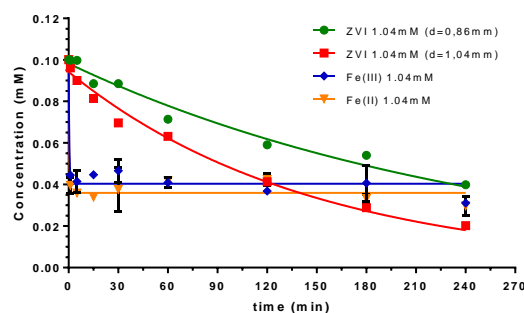

Figure 3. Activation of PMS with different iron sources for the degradation of the algecide diuron

4. Conclusions

The oxidation of caffeine, ibuprofen and diuron (emerging pollutants) was carried out through electron transfer activation of peroxymonosulfate (PMS) from different iron sources (Fe^{2+}, Fe^{3+}, ZVI) in order to assess the effect of its valence. Apart from the effect of the iron source, it was also important to optimize iron addition because excess amounts can result in the quenching of the radical species generated and result in the reduction of the system's efficiency. The ZVI / PMS system was proved to be the most effective to completely remove caffeine, ibuprofen and diuron from aqueous solutions. It was found that, peroxymonosulfate plays a dual role in its activation reactions, both as oxidizing and as reducing agent. The heterogeneous catalysis of PMS with ZVI takes place on the outer surface of the ZVI particles and allows for the controlled release of Fe^{2+}. The latter one reacts with PMS for the continuous production of free radicals resulting in the reduction of the pollutants. It was also proven that the higher the specific surface area of the ZVI particles, the more effective the pollutants' degradation was. Ibuprofen

was the most susceptible compound for oxidation, while caffeine the most persistent one as its chemical structure contains heteroatoms, which affect the kinetics of free radicals reactions. However, when ZVI / PMS system was used the pollutants completely degraded when 24 hours of reaction period was allowed.

Acknowledgments

References

Antoniou M.G., de la Cruz A.A., and Dionysiou D.D. (2010), Intermediates and Reaction Pathways from the Degradation of Microcystin-LR with Sulfate Radicals, Environmental Science & Technology, **44**, 7238-7244.

Antoniou, M.G., Cruz, A.A., Dionysiou, D.D. (2009). Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis and etransfer mechanisms. Applied Catalysis B Environment, 96, 290–298.

Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lutzhoft, H.C.H., Jorgensen S.E. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere, 36 (2), 357–394.

Lee, J., Hong S., Mackeyev Y., Lee C., Chung E., Wilson L.J., Kim J.H., Alvarez P.J.J. (2011). Photosensitized oxidation of emerging organic pollutants by tetrakis C60 aminofullerene-derivatized silica under visible light irradiation, Journal of Environmental Science Technology, 45, 10598–10604.

Petrovic, M., Diaz A., Ventura F., Barcelo D. (2003). Occurrence and removal of estrogenic short chain ethoxy nonylphenolic compound and their halogenated derivatives during drinking water production. Journal of Environmental Science Technology, 27, 4442–4448.

Rastogi, A., Al-Abed, S. R., & Dionysiou, D. D. (2009a). Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols. Water Research, 43(3), 684–94.

Rastogi, A., Al-Abed, S. R., & Dionysiou, D. D. (2009b). Sulfate radical-based ferrous–peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems. Applied Catalysis B: Environmental, 85(3-4), 171–179.

Rodriguez, S., Santos, A., Romero, A. (2011). Effectiveness of AOP's on abatement of emerging pollutants and their oxidation intermediates: nicotine removal with Fenton's reagent. Desalination, 20 (1–3), 108–113.

Rodriguez, S., Santos A., Romero A., Vicente F. (2012). Kinetic of oxidation and mineralization of priority and emerging pollutants by activated persulfate. Chemical Engineering Journal, 213, 225–234.