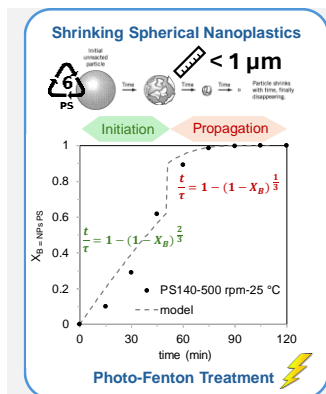


Modeling Polystyrene Nanoplastics Degradation in Water via Photo-Fenton Treatment: A Shrinking-Core Approach

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AOPs have emerged as promising treatment alternatives for the effective degradation of nanoplastics (NPs) in water. However, the research field is still in its infancy, and there are no kinetic models available to represent the advanced oxidation of micro(nano)plastics (MNP) in aqueous systems. In this study, a kinetic model based on particles with decreasing diameters is proposed for the photo-Fenton oxidation of polystyrene (PS) NPs. Various reaction parameters affecting the oxidation rate, such as particle size, agitation speed, and reaction temperature, were analyzed. From these results, the overall reaction rate can be divided into two stages following a free-radical mechanism, considering: an initiation stage followed for a propagation step. Based on the classic Shrinking Core Model (SCM), mathematical expressions were proposed and adapted to represent the conversion of PS NPs upon photo-Fenton treatment.

Introduction

Plastic debris, including micro and nano-sized particles, is considered a top environmental problem and is recognized as an emerging concern that might affect human ability to preserve the availability of safe water supplies in the future. Despite numerous scientific investigations addressing the magnitude of this issue, significant knowledge gaps persist in the development of both targeted degradation technologies for MNP in water and representative kinetic models [1]. Fluid-particle reactions are heterogeneous reactions wherein gases or liquids contact a solid, react with it, and transform into products. In the SCM, in the absence of an ash layer, the reacting particle shrinks during the reaction, gradually diminishing in size from its surface to the core until complete disappearance [2]. In this work, the main objective is to predict and describe the kinetics of the photo-Fenton oxidation process applied to PS nanospheres in water.

Material and Methods

Four commercial PS NPs were purchased from MicroParticles GmbH (140, 252, 460, 909 nm, 5% w/v), labeled as: PS140, PS252, PS460, and PS909. Oxidation tests were performed in an immersion-wall batch jacketed photoreactor (0.7 L) equipped with a 150 W medium pressure Hg lamp (UV-Vis Nova Light TQ-150, Peschl Ultraviolet). The experimental set-up was detailed in a previous contribution [3]. The tests were carried out using $[PS\ NPs]_0 = 100\ mg\ L^{-1}$, $[Fe^{3+}]_0 = 1\ mg\ L^{-1}$, and at $pH_0 = 3$. Various reaction parameters were considered, including particle size (140–909 nm), agitation speed (250, 500 and 1000 rpm), and reactor temperature ($T = 25$ and $60\ ^\circ C$). Under the studied conditions, H_2O_2

degraded rapidly. To ensure its excess in the reaction medium, a multiple-step oxidant addition strategy was implemented adding $[H_2O_2]_0 = 1000\ mg\ L^{-1}$, and dosing $500\ mg\ L^{-1}$ every 30 min. Turbidity measurements (HI88713, Hanna) were conducted to monitor NPs conversion ($X_{NPs\ PS}$). Alternatively, $X_{NPs\ PS}$ was determined from TEM images (JEOL JEM 2100) considering particle geometry (not shown here). PS mineralization was evaluated by TOC measurements (Shimadzu TOC VSCH). FTIR spectroscopy (Spectrum Two, Perkin Elmer) was employed for calculating the carbonyl index (CI). Pyr-GC/MS (7890B, Agilent Techn.) allowed for the identification of intermediate compounds and ionic chromatography (790 IC, Metrohm) for the quantification of short-chain acids. GPC (GPC 2414, Waters) was used to determine the molecular weight (M_w) and polydispersity index (PI).

Results and Discussion

Fig. 1A displays the complete and fast oxidation of PS NPs upon photo-Fenton treatment carried out under a wide range of operating conditions. It can be observed that significant changes in reactor temperature, agitation speed, and particle size led to slight modifications in the oxidation rate of PS NPs, achieving complete conversion of the solids within 60–90 min reaction time.

The SCM is the best simple representation for the majority of reacting fluid-solid systems. This model proposes conversion-time equations considering three steps occurring in succession (Eq. 1): i) Diffusion of fluid reactant from the bulk solution throughout the film to the solid surface ($n = 2/3$, small particles in Stokes regime); ii) Reaction on the surface ($n = 1/3$); and iii) Diffusion of the products

from the solid surface through the film back to the solution [2]. Where τ is the time for complete conversion and X_B the conversion of the solids.

$$\frac{t}{\tau} = 1 - (1 - X_B)^n \quad \text{Eq. 1}$$

The SCM considers particles with homogeneous composition and a single reaction occurring at the solid surface. Because of this, it fails to accurately predict the conversion of PS NPs with different particle sizes. In the SCM, the τ should be ideally proportional to the particle size in the order of R^{1-2} [2], resulting in much longer degradation times for larger particles, such as PS909 compared to PS140. In the case of PS NPs, the complex degradation mechanism is influenced by the nature and properties of the polymeric particles (M_w and PI), as well as the free-radical mechanism of the photo-Fenton process. Additionally, the conversion profiles are S-shaped, indicating that the reaction rate is governed by two processes: an initial slower phase characterized by minor changes in particle size, followed by a faster degradation phase (Figs. 1A and B).

The photo-Fenton oxidation of NPs is likely initiated within the phenolic rings through $\text{HO}\cdot$ attack, leading to electronically excited states and the formation of polymer macro radicals, thereby facilitating the breakdown of polymeric chains, and its crosslinking and/or re-polymerization, favoring particle agglomeration Fig.1B [3]. Once the PS surface undergoes radical activation, the reactivity of the solids increases, and the oxidation propagates to the unreacted core. This results in the incorporation of oxygen-functional groups, such as C=O (evidenced by CI increase), significant reduction in particle size, and the release of leached by-products such as polycyclic and monocyclic aromatic hydrocarbons (Pyr-GC-MS), and short-chain acids (IC), finally mineralizing to CO_2 and H_2O (TOC measurements). Despite the differences with the classic SCM, the experimental data fits well to the rate expressions proposed by the model (see graphical abstract and Fig.1C). In this context, it is suggested that the advanced oxidation of NPs follow a typical free-radical mechanism, including initiation, propagation, and termination steps, and it is proposed to adopt an

exponent value of $n = 2/3$ for the initiation phase, and $n = 1/3$ for the propagation phase (graphical abstract and Fig.1C).

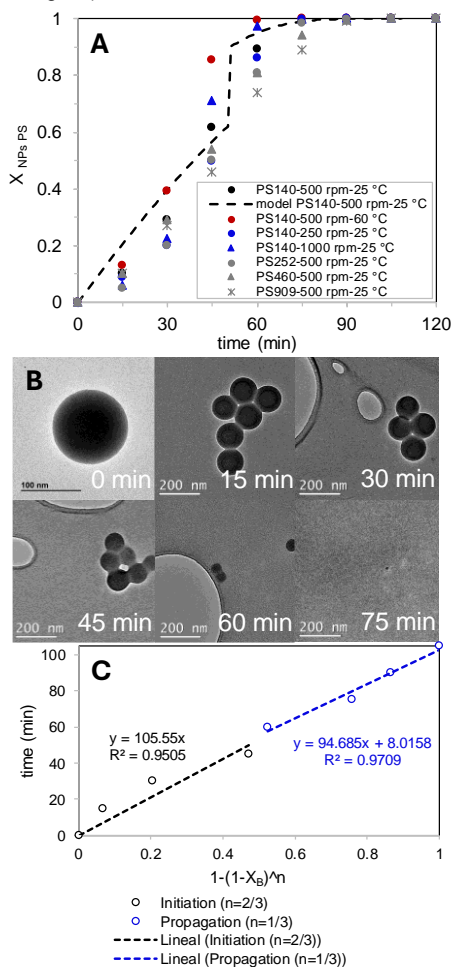


Figure 1. Photo-Fenton oxidation of PS NPs: A) Conversion-time profiles, B) TEM results for PS140-500 rpm-25 °C, and C) Fitting of the model for PS140-500 rpm-25 °C, where the slope represents the time for complete conversion (τ) for the initiation and propagation stages.

Conclusions

The kinetics of the photo-Fenton process, applied to the oxidation of PS NPs in water, was successfully adapted to the simple mathematical expressions proposed by the SCM. The photo-oxidation of NPs involves a complex free-radical mechanism initiated by the formation of electronically excited states at the polymer surface, followed by a fast propagation stage to the unreacted core, consequently reducing the particle size until complete disappearance.

Acknowledgments

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