



# Breakdown of plastic waste into economically valuable carbon resources: Rapid and effective chemical treatment of polyvinylchloride with the Fenton catalyst



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## ABSTRACT

Polyvinylchloride (PVC) is a typical non-biodegradable plastic that is resistant to chemicals, sunlight, and weathering. These properties make its disposal problematic, as items made from PVC retain their form for decades. The objective of this study is to provide an effective waste management method for the degradation of huge amounts of the robust plastic waste. In this work, a rapid chemical treatment method has been developed by utilizing the Fenton catalyst to break down PVC plastic wastes into recoverable high-value organic compounds. During this chemical process, surface activation of PVC takes place to generate coordinating sulfonate groups that get tagged with iron(III) chloride. The iron(III)-tagged PVC is a highly active Fenton catalyst that breaks down the entire bulk polymer into a number of valued organic acids selectively using hydrogen peroxide as a green oxidant. By using this procedure, all treated PVC plastic wastes were completely degraded into water soluble organic compounds and CO<sub>2</sub> under ambient dark conditions within 10 min. The dissolved organic compounds were identified mainly as mono- and dicarboxylic acids. The formation of these products indicates that the reaction is selective, which is not expected from the classical Fenton-type radical oxidation reactions. A detailed study was conducted to probe the possible mechanism of degradation that takes place during the chemical treatment process. It was found that the temperature conditions for PVC activation significantly affect the number of activated sites (sulfonated groups) generated on the polymer backbone, in which the carbon-to-sulphur atom (C/S) ratio can vary from 8:1 to 29:1. The degradation efficiency, which is typically defined in terms of the bulk mass of the treated PVC plastics, was found to be greater than 98% in all cases. This also included the real samples of rigid PVC pipe. The recovered amount of the characteristic compound butanedioic acid, which is formed during the PVC plastic breakdown process, was found to consistently vary from 9.8% to 61.3% with respect to the C/S ratio. The results of this study are also helpful for the further development of similarly fast and effective plastic waste treatment and management protocols in lieu of landfill disposal, which is particularly important for polymers such as polyethylene (PE), and polypropylene (PP).

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## 1. Introduction

Global plastic consumption has dramatically increased over the last few decades because of the benefits derived from the low cost, versatility, resistance to degradation, and durability of plastics. In fact, it can be said that we are living in the “Age of Plastic”, as nearly every object contains this material. Plastics show a high resistance towards degradation, and while this feature may be considered as a

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merit for their utility, it is very problematic in waste treatment or management. Plastic wastes are now recognized globally as a serious threat to our environment. Polyvinylchloride (PVC) is an inert and rigid polymer that was discovered in the early 20th century [1] and later plasticized by blending with various additives [2]. It has been widely used for a variety of applications such as production of water pipes, for electrical cable insulation, posters, and flip-flops. It is the third-most widely produced synthetic plastic polymer after polyethylene (PE) and polypropylene (PP). PVC waste is projected to be 7.2 million tons per year by 2020 [3a], and therefore there is an urgent need to find a proper solution for PVC waste management [3b]. However, there are a lot of limitations encountered during PVC waste treatment and management as this is a particularly difficult material to recycle owing to the presence of heavy metal additives such as lead and cadmium, which are contaminants in other recycling streams [3c]. At present, less than 1% of PVC is being recycled, and its disposal in landfills is also not a feasible solution because it is durable and resistant to natural degradation processes [4]. Waste-to-energy conversion of PVC via incineration is prone to secondary pollution, such as the emission of dioxins, and pyrolysis is not an appropriate recovery technique for PVC waste streams due to the emission of toxic secondary pollutants that contain chlorine [5,6]. Therefore, an effective protocol for PVC plastic waste treatment and management is urgently needed. The objective of this study is to develop a fast, effective, and feasible method for the chemical degradation of PVC plastic waste under ambient conditions and subsequent recovery of high-value organic products.

Fenton's reagent has been widely used for the treatment of different pollutants [7,8] because it generates powerful and active hydroxyl radicals that break down and/or mineralize organic substances. However, this chemical reaction has not been applied for the treatment of PVC plastic waste [9,10]. It is known that the degradation processes with Fenton's reagent are usually uncontrollable because the reaction involves radical initiated bond cleavage. In order to break down PVC plastic waste into specific small molecules by Fenton's reaction, it is necessary to develop a method that allows control of its reactivity and enhances its selectivity towards the desired valuable end-products. Thus, it is crucial to understand and establish a thermodynamically controllable Fenton reaction in order to break down and convert synthetic polymers selectively into useful chemicals. This technique is perhaps one of the best options for the preservation and recycling of otherwise limited fossil fuel resources.

PVC is significantly different in its structure from the other inert plastic materials such as PE or PP, as it has a heteroatom (Cl) in its polymer backbone. The activation of C–Cl bond is more feasible compared to either C–C or C–H bond activation for PE or PP.

Physical activation by plasma and laser treatments that utilize high energy and UV radiation is a plausible approach towards polymer degradation. These techniques usually provide means for more precise surface modification of the polymer without changing its bulk properties, and do not involve caustic chemicals [10]. However, such physical surface treatment methods cannot effectively handle the bulk volume of polymer wastes and are limited in their use because they often require costly equipment. On the other hand, chemical activation is a more practical alternative. Bulk PVC polymer can be activated by utilizing strong oxidative agents such as  $\text{SO}_2/\text{O}_2$  acids [12], ozone [13,14], and hydrogen peroxide [15] to generate functional groups on the polymer surface [11]. These treatments are relatively economical and are able to generate high densities of active functional groups on the surface for further degradation reactions. In this study, an active iron(III) catalyst has been introduced onto the PVC polymer at a position specifically replacing the Cl atom of the polymer backbone. In the present study, a practical chemical degradation method has been developed that involves the activation of PVC via the replacement of chlorine atoms with iron(III) sulfonate groups ( $\text{SO}_3\text{FeCl}_2$ ) and the proceeding of the Fenton reaction to the activated PVC ( $\text{PVC}\text{SO}_3\text{-Fe}$ ) with a green oxidant ( $\text{H}_2\text{O}_2$ ). Additionally, it is important that the number of tags ( $\text{SO}_3\text{FeCl}_2$ ) in the activated PVC polymer can be used as a tool to control the thermodynamic and kinetic parameters of the degradation reaction. This chemical treatment method is very effective in breaking down PVC plastics into valuable organic acids with good selectivity and high yield under ambient and mild conditions. To the best of our knowledge, a similar method for the recovery of valuable chemicals from PVC has not been reported before. The method developed in this work provides a possible waste treatment protocol to solve the generic plastic waste problem.

## 2. Experimental

**Materials and methods.** PVC (average  $M_w$  ~43000 and average  $M_n$  ~22000) was purchased from Sigma-Aldrich. Chlorosulfuric acid (98%) was obtained from International Laboratory. 1,1,2,2-Tetrachloroethane (Sigma-Aldrich), ferric chloride (Acros), hydrochloric acid (ACS), dichloromethane (ACS), and 30 wt% hydrogen peroxide (BDH) were used without further purification. Characterization of the activated PVC materials ( $\text{PVC}\text{SO}_3\text{-Fe}$ ) by infrared spectroscopy, elemental analysis, and examination of surface morphology, as well as characterization and quantification of the dissolved organic matter in the degradation studies by determination of the dissolved organic carbon (DOC) content and liquid chromatographic analyses were performed using the protocols and instrumental procedures reported in the literature [9b].

**Table 1**

Degradation product distribution for the activated polymers prepared at different reaction temperatures (50–140 °C) during sulfonation.

PVC Samples	Activated temp. (°C)	Degradation efficiency (DOC (mg/L))	C/S Ratio	Degradation product yields							
				CO <sub>2</sub>	Monocarboxylic acids		Dicarboxylic acids			Other carboxylic acids	Total
					C1 <sup>a</sup>	C2 <sup>b</sup>	C2' <sup>c</sup>	C3 <sup>d</sup>	C4 <sup>e</sup>		
Virgin PVC	50	98.1% (292.7)	8.0	29.3%	7.3%	4.0%	3.8%	8.8%	61.3%	14.8%	100%
	65	99.8% (302.2)	8.3	24.5%	6.1%	3.9%	4.7%	9.3%	52.6%	23.3%	100%
	80	99.1% (331.6)	8.5	25.4%	6.0%	6.7%	4.1%	5.8%	41.8%	35.6%	100%
	140	99.9% (401.6)	28.7	31.0%	8.0%	6.7%	5.8%	13.6%	9.8%	56.3%	100%
Water pipe	50	99.8% (385.7)	8.7	9.75%	7.9%	5.9%	4.1%	4.8%	60.8%	16.5%	100%

<sup>a</sup> Formic acid.

<sup>b</sup> Acetic acid.

<sup>c</sup> Oxalic acid.

<sup>d</sup> Propanedioic acid.

<sup>e</sup> Butanedioic acid.

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