

Study on Trend of Biodegradability of Phenolic Compounds During Photo-Fenton Advanced Oxidation Process

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Abstract

Phenolic acids constitute a major group of pollutants which are recalcitrant to common biological treatment. In this study synthetic wastewater containing a mixture of *p*-coumaric and *p*-hydroxybenzoic acids was evaluated for photo-Fenton pretreatment. The changes in biodegradability (ratio of biochemical oxygen demand to total organic carbon (TOC)) and mineralization (TOC removal) were monitored. While there was a significant biodegradability enhancement during the photo-Fenton process, there was little mineralization (less than 6%) taking place over the course of oxidation. Longer oxidation time did not further improve the pretreatment; rather it decreased the biodegradability of the solution through complete mineralization of the biodegradable intermediates. Resin fractionation of treated solutions indicated an increase in the hydrophilic fraction and a decrease in the hydrophobic fraction.

Indeed, there was a clear and direct correlation between the hydrophilic nature of the organics and the biodegradability of the solution, indicating that hydrophilic compounds are more biodegradable. The formation of aldehydes further supported the links between biodegradable and hydrophilic compounds

Keywords: Phenolic compounds, Advanced oxidation processes photo-Fenton, Biodegradability

Introduction

Many agro-industrial wastes and wastewaters such as olive-oil mill wastewater (OMW), wine distillery wastewaters and pulp and paper industry wastewater contain various natural phenols and their condensation products, such as tannins or lignin [1]. In the case of OMW, this problem presents severe limitations on the discharge of wastewater in rivers and the receiving environment not only

in the Mediterranean regions[2], but also in other olive producing countries such as those in the Middle East.

The amount of wastewater produced (olive oil mill wastewater, OMW) varies depending on the method used for the oil extraction: the classical press method produces 0.5-0.8 m³/ton of olives processed, although this figure for the rather recent three phase centrifugation system is 1 m³/ton of

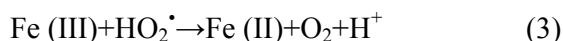
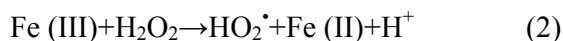
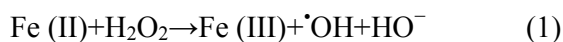
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olives[3]. The organic content of OMW consists mainly of phenols, polyphenols, polyalcohols, sugars, tannins, pectins and lipids at concentrations of up to 200 g chemical oxygen demand (COD) per L [4,5]. These values are about 200–400 times higher than those of a typical municipal sewage. Total polyphenols (TP) in the wastewater range between 2.7 g/L and 6.2 g/L depending on the olive species and the processing technique. Among the phenolic compounds commonly present in OMW are three important families: (1) cinnamic acid derivatives such as coumaric, caffeic, and ferulic acids, (2) benzoic acid derivatives such as hydroxybenzoic, gallic, vanillic, gentisic, protocatechuic, veratric acids and (3) compounds related to tyrosol such as tyrosol and hydroxytyrosol acids [6,7]. The concentration of phenolic acids in OMW may vary from as low as 0.05–0.2 g/L to as high as 10 g/L depending on the type and origin of the effluent [7,8].

The high strength of OMW, its seasonal production, and the presence of some classes of recalcitrant organic compounds such as lipids and phenolic acids [4,7] render OMW inappropriate for conventional biological treatment [9]. Hence, there are needs for alternative technologies capable of treating these wastewaters, thereby reducing the environmental and health impacts of olive oil processing.

Advanced oxidation processes (AOPs) are promising technologies that offer viable alternatives [10]. One available technique in the area of advanced oxidation process is based on the Fenton's reagent capabilities in the production of hydroxyl radicals, $\dot{\text{O}}\text{H}$. Many metals have special oxygen transfer properties which improve the usage of hydrogen peroxide in treating wastewaters. Ferrous salts catalyze the hydrogen peroxide degradation, which yields $\dot{\text{O}}\text{H}$ and OH^- (Eq.(1)). The generated Fe (III) can be reduced by reaction with the exceeding H_2O_2 to again form ferrous ion in a catalytic

mechanism (Eqs.(2) and (3)). Hydroxyl free radical is one of the most reactive chemical species known with an extremely high oxidation potential, $\dot{\text{O}}\text{H}/\text{H}_2\text{O}_2=+2.73\text{V}$ [11]. Organic substances are oxidatively and nonselectively degraded by the generated hydroxyl radicals.



Radiation can play different roles leading to increasing reaction yields so a combination of hydrogen peroxide and UV radiation with Fe(II) or Fe(III) oxalate ion, the so-called Photo-Fenton process, produces more hydroxyl radicals in comparison to the conventional Fenton's reagent (Fe(II) with hydrogen peroxide), and promoting the rates of degradation of organic pollutants. Also, the Fe (II) needed in the Fenton reaction is regenerated (Eq.(4)). The irradiated process may also involve photolysis of a Fe (III)– H_2O_2 complex to form high-valence Fe intermediates, which can directly oxidize organic pollutants [12].



AOPs have demonstrated the degradation of phenolic compounds in many wastewaters including OMW [7,12,13,14]. Various forms of AOPs have been investigated for treating synthetic wastewaters containing refractory OMW contaminants, including phenolic acids and relevant derivatives. These include the use of TiO_2 photocatalysis [15,16], Fenton and photo-Fenton oxidation [14,17,18], pyrylium-salt photo-induced oxidation [12], non-catalytic and catalytic wet oxidation [19,20], ozonation [21], and sono-chemical oxidation [22]. Fenton's reagent, a homogeneous catalytic system comprised of hydrogen peroxide and a ferrous salt, is

another common AOP applied to OMW. This process relies on the fact that iron-catalyzed hydrogen peroxide decomposition leads to the formation of $\bullet\text{OH}$ and other reactive free radicals that are capable of oxidizing many organic pollutants and converting them to lower molecular weight compounds and eventually to carbon dioxide and water [23]. The use of ultraviolet (UV) irradiation accelerates Fenton's reaction and improves the degradation rate of organic pollutants. Unfortunately, the application of either the Fenton or photo-Fenton process for the complete mineralization of organic contaminants is limited by the cost of chemical reagents (e.g. H_2O_2 and Fe^{2+}) and the production of sludge. Incomplete oxidation and improvement in the biodegradability of organic matter offers a great alternative. AOPs can be used to partially oxidize recalcitrant organics and convert them into more biodegradable compounds that can be removed completely in a downstream biological process. The combined AOP-biodegradation potentially minimizes the consumption of chemical reagents and/or energy (i.e. UV irradiation). Despite the potential benefits of such combinations, there appears to be a lack of information on the partial oxidation of organics using either the Fenton or photo-Fenton AOP and their effects on the biodegradability of the phenolic compounds present in OMW.

In the present work, photo-Fenton AOPs have been examined for degrading *p*-coumaric and *p*-hydroxybenzoic acids. Biodegradability and mineralization of the reaction mixture obtained during this process were monitored. Correlation of biodegradability with hydrophobic and hydrophilic fractions of intermediates was evaluated.

Experimental

Experiment set-up

The set-up used for the Fenton and photo-Fenton processes consisted of a 500 mL

well-mixed jacketed reactor, an annular photoreactor, and a re-circulating pump (Fig. 1). The photoreactor (custom made) was equipped with a germicidal low-pressure mercury vapor UV lamp (G10T51/2/L, Light Sources Inc., CT, USA) and a quartz sleeve protecting the lamp. The sleeve was made of diffused quartz so that it allowed the UV to penetrate through and reach the liquid solution. The effective volume and length of the photoreactor were 90 mL and 24 cm, respectively. The intensity of the UV lamp was measured at the surface of the quartz sleeve and was $73 \text{ W}\cdot\text{m}^{-2}$ (IL1700 research radiometer, International Light Inc., $\lambda=254 \text{ nm}$).

Experimental procedure

Each experiment was carried out by adding *p*-coumaric acid and *p*-hydroxybenzoic acid (Aldrich Canada) to the reactor at the desired concentration. Hydrogen peroxide (H_2O_2 , 33 %w/v, Fischer Scientific) and ferrous sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, Fluka) were added to the reactor at the beginning of the reaction. The pH was adjusted to 3.5 using hydrochloric acid. The solution was re-circulated through the photoreactor at a flow rate of 1 L/min for the photo-Fenton treatment. The temperature was controlled and maintained between 20°C and 25°C by running water through the reactor jacket. All the experiments were carried out with peroxide concentrations of 10 and 50 mg/L and Fe^{2+} concentrations of 1 and 5 mg/L. Water samples were collected at different time intervals and were analyzed for total organic carbon (TOC), peroxide concentration, pH, and biochemical oxygen demand (BOD_5).

TOC measurements for determining the extent of complete mineralization of phenolic acid were performed based on the total carbon-total inorganic carbon method using a TOC analyzer (TOC-VCPH, Shimadzu). BOD_5 measurements were according to Standard Method 5210B [24]. The

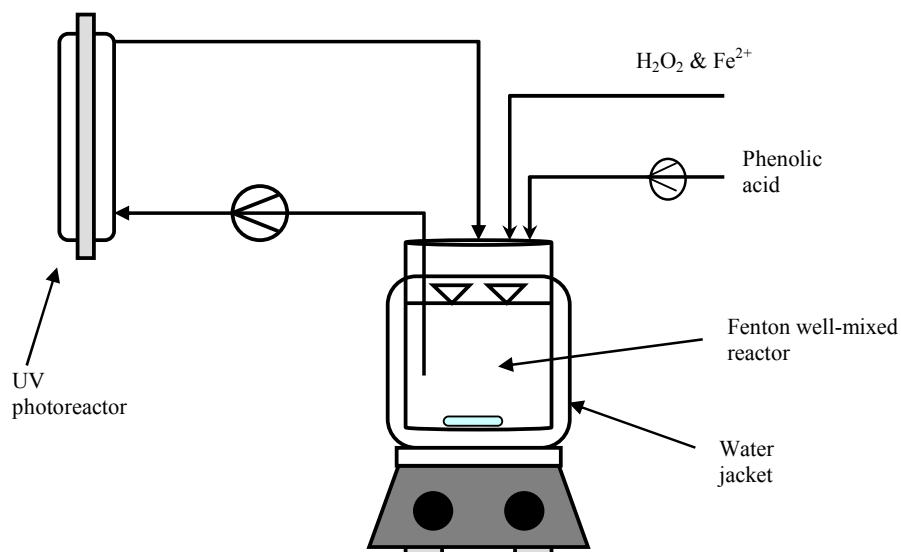


Figure 1. Schematic diagram of the experimental set-up used for Fenton and photo-Fenton treatment of phenolic acids

concentration of hydrogen peroxide was determined spectrophotometrically (UV Mini 1240 spectrophotometer, Shimadzu) using a molybdate catalyzed iodide detection method [25].

Samples were fractionated into hydrophobic and hydrophilic fractions. The fractionation procedure reported in this paper was based on the separation theory and their adsorption on resin adsorbents. However, some changes have been made and are discussed in the results section. DAX8 (Supelite DAX adsorbent resins, Sigma-Aldrich) and XAD4 (Amberlite, Rohm and Hass Ion exchange resins) resins were used to fractionate the organics according to polarity. An aliquot from each wastewater sample was mixed with 50 mL of resins and shaken (IS600 incubator/shaker, Rose Scientific) at 150 rpm and at 20°C for 3 hours. The resins were washed and wetted with distilled water and methanol before use as recommended by the manufacturers.

Results and Discussion

Effects of initial concentration of H_2O_2

An equimolar mixture of p-hydroxybenzoic

and p-coumaric acids (total concentration 100 mg/L) was used as a model for olive oil wastewater and these experiments were carried out at one ratio of initial concentration of H_2O_2 to Fe^{2+} (10:1) and the initial concentration of H_2O_2 was different (10 and 50 mg/L), while the rest of the operating variables were kept constant. Fig. 2 shows the rate of TOC removal during the oxidation at initial concentrations of 10 mg/L and 50 mg/L for hydrogen peroxide, where 5 and 15% TOC removals were achieved after 60 min of oxidation, respectively. The results clearly indicate that very little mineralization takes place over the course of treatment. 5-15% mineralization is not very significant, especially when one considers the high concentration of reagents and the energy of UV irradiation used for such treatment. In other words, the photo-Fenton process cannot be considered a viable treatment technology for the complete mineralization of phenolic compounds present in OMW. Increasing the initial concentration of H_2O_2 and Fe^{2+} increased the removal of the TOC solution [26].

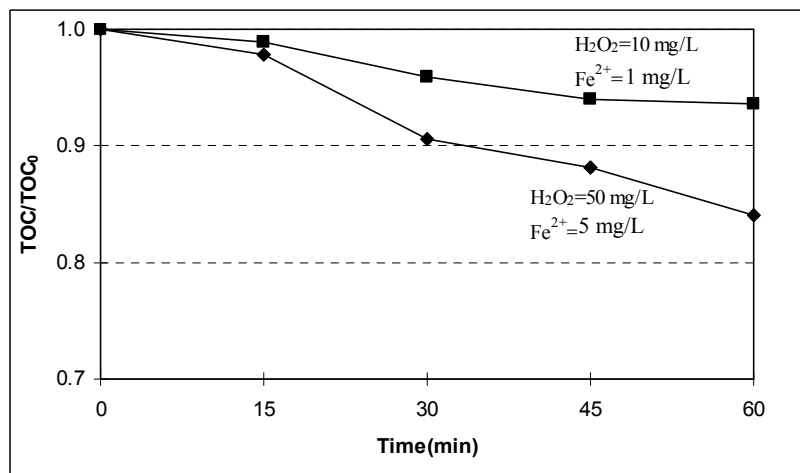


Figure 2. the degradation of phenolic compounds by photo-Fenton process at different Fenton reagent doses

Biodegradability improvement

The BOD_5/TOC ratio constitutes an appropriate measure of the biodegradability of the treated solution. Fig. 3 shows the significant increase observed in BOD_5 of the samples for different Fenton reagent doses. Indeed, a significant increase in BOD_5 was observed in the first stage of the oxidation, followed by a slow decrease after 15-20 min. This further reduction of biodegradability after an extended treatment period is likely the result of mineralization of biodegradable compounds (as demonstrated by the TOC reduction in Fig. 2). Fig. 4 indicates that such a trend is also represented by the biodegradability of the samples (ratio of BOD_5 to TOC). One important note is that the increase in biodegradability was more significant with the lower initial concentration of H_2O_2 . The BOD_5 increased by as much as three times, while little TOC removal (1%) was observed after 15 min of oxidation.

Figures 2-4 show that most of the biodegradability (BOD_5/TOC) increase was the result of the increase in BOD_5 that peaked after 15 min of oxidation. In other words, short oxidation time along with smaller

initial peroxide concentration provided the highest biodegradability increase (and perhaps most optimum oxidation). Miranda *et al.* proposed a mechanism for the degradation of cinnamic acids by ozonation and explained the trends observed in the BOD and biodegradability. This mechanism was divided into two stages. In the first stage, exocyclic double bonds are broken to get aldehydes, then with further oxidation these intermediates are oxidized to small acids. Changes in the biodegradability of the solution were explained by the abatement of recalcitrant compounds in the initial solution and the formation of more biodegradable intermediates like aldehydes [6, 27]. Hence, increasing the BOD_5 occurred during the first stage of the reaction. Chamorro *et al.* [28] found that the oxidation of formic acid, phenol, 2,4-dichlorophenol and nitrobenzene by Fenton reagent increased the biodegradability ratio (BOD_5/COD) [28]. Biodegradability (the BOD_5/COD ratio) of the Procaine Penicillin G formulation effluent by the photo-Fenton process increased and the best results were obtained at low levels of the H_2O_2 concentration [29].

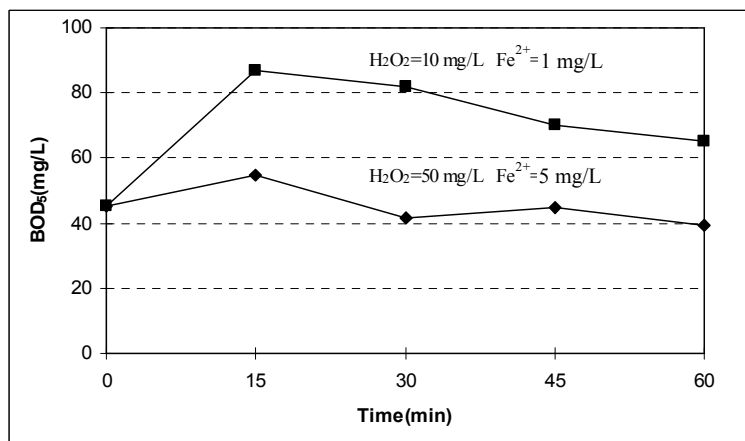


Figure 3. BOD₅ value of degradation of phenolic acid vs. irradiation time at different Fenton reagent doses

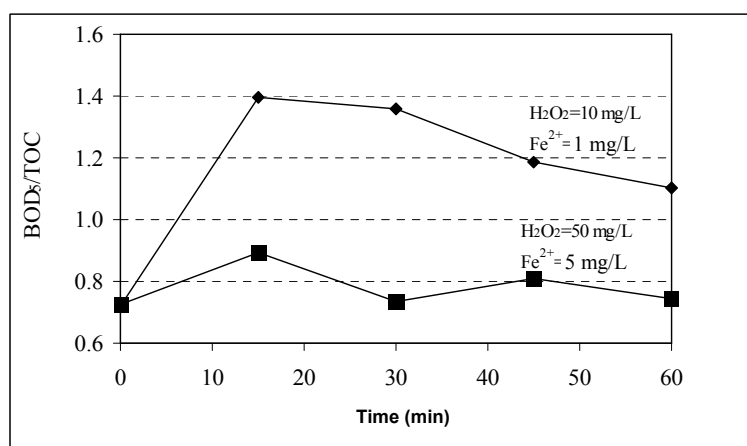


Figure 4. Evolution of BOD₅/COD ratio vs. irradiation time at different Fenton reagent

Role of the intermediates in the degradation process

Given that most of the increases in biodegradability occurred at low concentrations of H₂O₂ and during the first stage of the reaction (i.e. first 15 min), additional experiments were carried out under these conditions. The treated solutions were then fractionated using the DAX and AXD resins based on their hydrophobic and hydrophilic properties. The fractionated samples were then analyzed for TOC, BOD₅, and TOC. Figure 5 shows the results of the TOC BOD₅ value. TOC removal for the treated solution is ignored but TOC for the hydrophilic

fraction increases observed during the initial stages of the process followed the trends observed for BOD₅ and increased during the initial stages of the oxidation. On the other hand, the TOC of the hydrophobic fractions decreased significantly over the course of the experiment. Knowing that hydrophilic organic compounds are more biodegradable than the hydrophobic compounds, the results presented in Fig. 6 indicate that photo-Fenton AOP converted the recalcitrant hydrophobic fraction into a more hydrophilic and biodegradable fraction. Monitoring the formation of formaldehyde and acetaldehyde during the process further confirmed these

observations (Fig. 7). The concentration of formaldehyde increased in the early stages of oxidation, followed by a slow decrease after 15 min. Given the hydrophilic nature of aldehydes, this observation further supports the results of hydrophilic/hydrophobic data

presented in Figure 6. All these results demonstrate that there is indeed a good correlation between biodegradability and the hydrophobic and hydrophilic nature of intermediates.

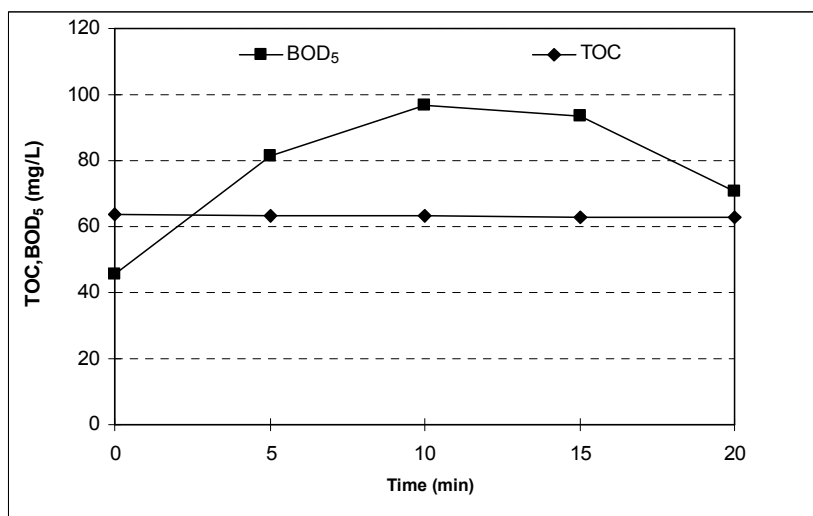


Figure 5. BOD₅ values, TOC vs. the photo-Fenton process time

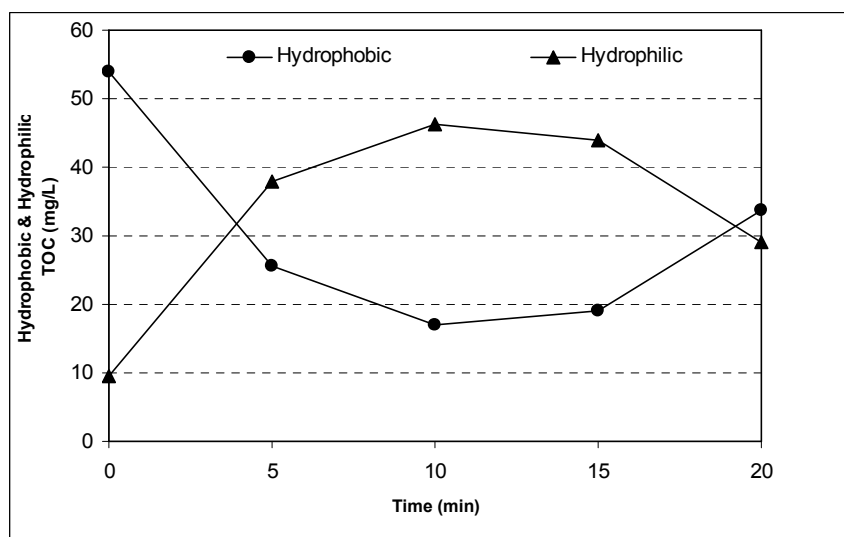


Figure 6. TOC of hydrophobic and hydrophilic intermediates vs. the photo-Fenton process time

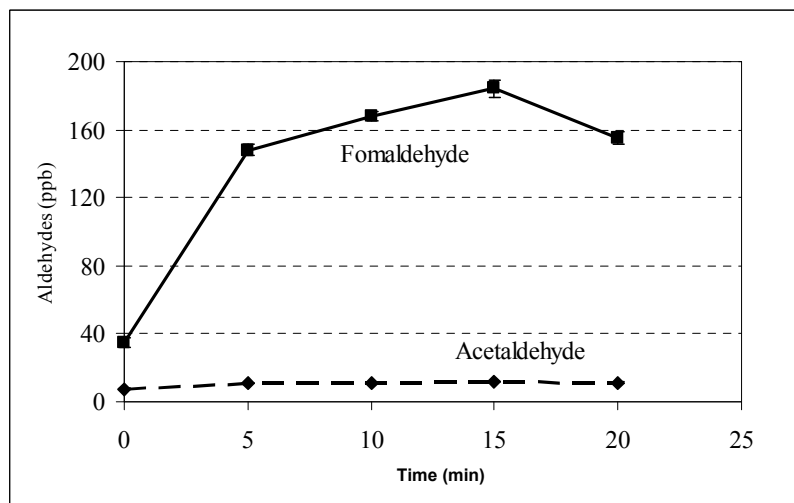


Figure 7. formaldehyde and acetaldehyde concentration vs. the photo-Fenton process time

Conclusion

In the present study the Photo-Fenton advanced oxidation process was investigated for its impacts on the biodegradability of phenolic model compounds present in olive mill wastewater. The following conclusions were reached:

- ◆ Reduction of the TOC was achieved at a high level of reagent concentration and after a long period of treatment.
- ◆ Maximum photo-Fenton process efficacy at increasing biodegradability was achieved at low concentrations of reagent and after a short treatment period (15 min). Further reagent addition and longer treatment time did not help increase the biodegradability any further.
- ◆ Increasing the biodegradability of the solution is related to the formation of hydrophilic compounds (e.g., aldehydes) and the decrease in the level of hydrophobic compounds.
- ◆ A good correlation between biodegradability and the hydrophobic and hydrophilic fraction of intermediates were observed.

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