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Ultraviolet-H₂O₂ oxidation of surfactants

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Abstract This paper describes a study of the treatment of surfactant synthetic solutions by chemical and photolytic oxidation. Synthetic solutions of linear alkylbenzene sulfonates (LAS) are treated in this work as this is a model compound commonly used in the formulation of detergents, with a great presence in urban and industrial waste-waters. The application of ultraviolet (UV) radiation combined with hydrogen peroxide to oxidize linear alkylbenzene sulfonates (LAS) is shown to be suitable as a primary oxidation step since conversions of about 50% of the original compounds are achieved in the most favorable cases. Initially, the influence of the operating variables on the degradation levels is analyzed in this work. A kinetic model that considers the contributions of both direct photolysis and radical attack is also worked out. Direct photolysis is performed to determine the quantum yield in the single photodecomposition reaction. In addition, the rate constant of the reaction between hydroxyl radicals and linear alkylbenzene sulfonates in the oxidizing system H₂O₂/UV is determined for different operational conditions. Finally, the contribution of each oxidation pathway is quantified, resulting in a higher contribution of the radical reaction than of photolysis in all cases.

Keywords Advanced oxidation process (AOP) · H₂O₂/UV · Pollutants at high load · Linear alkylbenzene sulfonates (LAS) · Direct photolysis · Hydroxyl radicals · Quantum yield · Degradation levels · Influence of variables

Introduction

Surfactants are the major compounds used in the formulation of synthetic detergents world-wide for both

domestic and industrial applications. They are a group of organic compounds characterized by having both a hydrophobic group, e.g. an alkyl chain, and a hydrophilic group (e.g. sodium sulfate). Surfactants used in the formulation of commercial detergents are mixtures of homologues, i.e. with different lengths of the alkyl chain. According to their nature, surfactants are classified as anionic, cationic or non-ionic. In this study, linear alkylbenzene sulfonates (LAS) have been chosen as a model of anionic surfactants. Indeed, LAS are one of the major ingredients of synthetic detergents and surfactants used world-wide due to their acceptable biodegradability. It is estimated that approximately 1.8 million metric tons year⁻¹ is used (Perales et al. 1999). As their aerobic biodegradability is proven, the problem of removing LAS from wastewater has been solved with conventional aerobic biological treatments at low concentrations (Cavalli et al. 1996). They have shown some inhibitory behaviour in some types of biological treatment processes, in both aerobic and anaerobic processes at concentrations above 50 ppm (García-Morales et al. 2001).

In this paper, we report the oxidation of an LAS synthetic effluent at high load (2,500 mg L⁻¹). At high concentrations, biological treatment does not seem suitable because problems such as foaming, necessity for neutralization and long retention times may occur. Therefore we studied the photochemical oxidation of surfactants in combination with hydrogen peroxide. This is one of the advanced oxidation processes (AOP) very commonly used in wastewater treatment. These processes are based on the generation of the very oxidative hydroxyl radicals. In this paper the effect of some operating variables on the oxidation of LAS has been studied. As a second step, a kinetic mechanism based on the contribution of both photolysis and radical reactions has been proposed in the oxidation of LAS.

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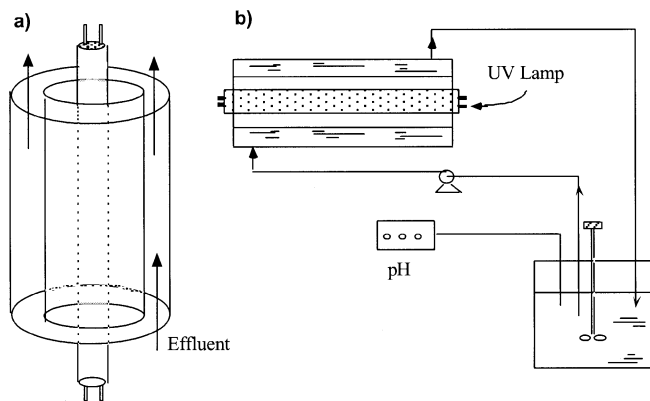


Fig. 1 Schematic diagram of the ultraviolet reactor. **a** The reactor consists of two concentric tubes (the UV lamp is located in the inner tube); **b** the whole reaction system for the recirculation to the homogenization tank of the $\text{H}_2\text{O}_2/\text{UV}$ system

Experimental

Ultraviolet (UV) reactor

The reaction setup is shown in Fig. 1. Experiments were carried out at room temperature in a 750-cm^3 photolytic steel reactor, consisting of two concentric tubes, the inner one of quartz where the UV lamp is located. A Hannau T44/NN15 low-pressure 19-W mercury lamp was used (8 W L^{-1} power output, 254 nm). The solution circulates through the annular space where it is irradiated and is continuously recirculated with a peristaltic pump (flow rate 0.7 L min^{-1}) to a homogenization tank where the pH is measured and samples are extracted. Actinometry experiments to characterize the lamp were carried out using the potassium ferrioxalate method (Hatchard and Parker 1956) in order to determine the incident flux radiation (I_0). Hydrogen peroxide was used as an actinometer for the calculation of the effective path (L) of the radiation in the reactor. Consequently, values of $0.21 \times 10^{-6}\text{ Einstein L}^{-1}\text{ s}^{-1}$ and 6.9 cm respectively were obtained.

Analysis of linear alkylbenzene sulfonates

In the experiments, synthetic solution of LAS were prepared from the commercial product supplied by Reckitt and Benckiser. This commercial product formed by a mixture of homologues with the formula $\text{C}_n\text{H}_{2n+1}\text{C}_6\text{H}_4\text{SO}_3\text{H}$, with n ranging from 10 to 13 (12, 38, 31, 19 wt%). The total amount of LAS quantified in these experiments is the sum of these four homologue groups. LAS were determined by high performance liquid chromatography (HPLC) with a Waters 2690 separation module and a 2487 absorbance detector, using a KROMASIL 100 C4 5-cm 15×0.46 reverse phase column and a pre-column. Deionized water and acetonitrile (50:50 v/v) with 0.1 M sodium perchlorate were used as the mobile phase.

UV detection was at 220 nm. Retention times were from 5 min for the C_{10} -isomers to 13 min for the C_{13} -isomers. Synthetic LAS solutions of $2,500\text{ mg L}^{-1}$ were used in all experiments (96% purity; Reckitt and Benckiser). The extinction coefficient for LAS (ϵ_{LAS}) was determined using a Perkin Elmer Lambda 10 spectrometer obtaining a value of $641.5\text{ M}^{-1}\text{ cm}^{-1}$ at 254 nm.

Oxidation

Thirty per cent (w/v) hydrogen peroxide (Panreac) was used as the oxidant. The pH was adjusted before the experiment (sulfuric acid or phosphate buffer). The rate of disappearance of the H_2O_2 was followed colorimetrically (Eisenberg 1943) for concentrations lower than 0.02 M and iodometrically for higher concentrations (Kolthoff and Medalia 1949).

Experiments were carried out under different conditions to analyze the influence of the pH and the concentration of oxidant on the removal of sulfonates. For pH values between 2.2, the value of the natural solution, and 7, different values of the molar ratio oxidant to pollutant (r_M) were studied, from $r_M=2$ to $r_M=40$. The operational sequence was as follows: 1 L of synthetic solution sample, with an initial concentration of approximately $2,500\text{ mg L}^{-1}$ of LAS, was prepared and the initial pH previously adjusted for each experiment, once the oxidant had been added. The reactor was filled with the solution and the lamp was switched on to start the reaction.

Results and discussion

Introduction

In this paper, the oxidation of an effluent of linear alkylbenzene sulfonates (LAS) at high load is reported with a physical-chemical process of the advanced oxidation process (AOP) type. AOPs have shown to effectively modify the molecular structures of a variety of surfactants and related compounds, resulting in dissolved organic carbon (DOC) and chemical oxygen demand (COD) reductions, loss of surface-active properties (e.g., foaming, hydrophobicity), and enhanced biodegradability.

The synthetic solutions of LAS in acid form used in this work are a mixture of four homologues with between 10 and 13 carbons in the alkyl chain. The disappearance of LAS is quantified by the sum of these four homologue groups. In the experiments performed, no difference was observed in the removal of each homologue group, with the disappearance being proportional to the amount of each one. The relative composition of each homologue is practically constant throughout the oxidation reaction.

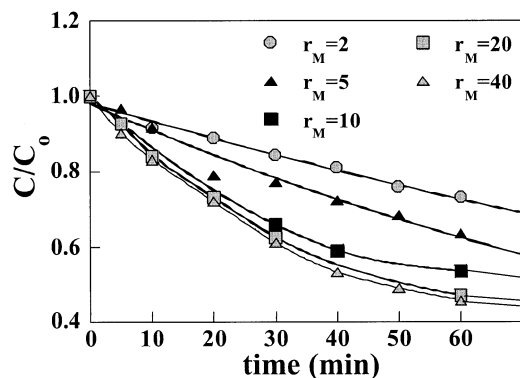


Fig. 2 Oxidation of linear alkylbenzene sulfonates (LAS), conversion vs. time. Effect of oxidant concentration on rate of disappearance of LAS: increasing hydrogen peroxide concentration enhances the oxidation rate up to an optimum H_2O_2/LAS molar ratio (r_M) of around 20, when hydrogen peroxide starts to inhibit the oxidation process. Conditions of experiments: pH=3, initial LAS concentration $C_0=2,500 \text{ mg L}^{-1}$

Effect of oxidant concentration

This paper is related to the treatment of wastewater with an AOP, based on the generation of hydroxyl radicals derived from the usage of hydrogen peroxide as an oxidant. The highly reactive and oxidizing hydroxyl radicals (OH) are generated by the combination of hydrogen peroxide and UV radiation. Thus, it is important to study the effect of the amount of hydrogen peroxide as it will be the limiting variable of the extent of oxidation of LAS.

Figure 2 shows that the amount of hydrogen peroxide significantly influences the decomposition rate, which increases to a value close to a hydrogen peroxide/LAS molar ratio (r_M) of 20. At higher values of oxidant no enhancement in the removal of LAS is observed. We are always working below the stoichiometric molar ratio, $r_M=50$.

The maximum oxidation is achieved with a molar ratio of approximately $r_M=40$, close to the stoichiometric value of 50. Nevertheless, around 90% of this conversion is already obtained using a molar ratio of only $r_M=15$ at pH=3. Consequently, oxidation efficiency is reduced drastically when the r_M is increased above this value. This value is thus considered the *critical* amount of oxidant for an initial pH of 3. The knowledge of this limiting value allows us to optimize the efficiency of oxidant use.

Effect of initial pH

The pH was selected as another important operating variable in wastewater treatment due to the frequent necessity of adjusting the pH and the additional cost involving this operation; thus it is important to determine the optimal pH for oxidation.

Experiments were conducted by varying the initial pH between 2.2 and 7. The initial level is the natural pH value of the solution of $2,500 \text{ mg L}^{-1}$ of LAS, close to the pKa of alkylbenzene sulfonic acids (2.142). Two tests were performed. First, the solution was buffered to maintain the pH at a constant throughout the reaction; these experiments were performed at pH values of 3, 5 and 7. Second, the pH of the solution was adjusted only initially. During oxidation the pH fell to values close to 2, which is the usual tendency, due to the formation of carboxylic acids.

It can be concluded from the results of the experiments that the pH has no remarkable effect on the rate of LAS oxidation. Also, it can be deduced that degradation rates are slightly higher at acidic values (pH=2.2 and 3), close to the pKa of LAS. This could be explained by the higher reactivity of the dissociated LAS species, which are more abundant at this pH.

Kinetic study

The second objective of this work was to carry out a kinetic study of the disappearance of LAS in order to assess of effect of direct photolysis and radical oxidation on the degradation of the pollutant. AOPs have very complex mechanisms, but in this case a simple mechanism has been proposed, schematized in the following three elementary steps, described as follows: LAS degradation is basically due to direct photolysis as given by Eq. (1) and by the hydroxyl radical attack (Eq. 3). These radicals are generated in the photodecomposition of peroxide by Eq. (2). Equation (3) is the most characteristic and important reaction of AOPs, being the pathway responsible for most of the degradation of organic pollutants (Glaze et al. 1987).



According to the mechanism proposed, the global decomposition rate can be assumed to be the sum of the contributions of both direct photolysis (r_P) and the radical reaction (r_R) between LAS and the hydroxyl radicals (Benítez et al. 2001):

$$-r_T = -\frac{dC_{LAS}}{dt} = -(r_P + r_R) \quad (4)$$

The kinetic of oxidation with this AOP can be conveniently described through the disappearance of LAS by Eq. (5), derived from Eq. (4). The first term of the equation, based on the Lambert-Beer law, corresponds to the contribution of direct photolysis to the decomposition of LAS. The term on the right represents the contribution of oxidation due to the radical reaction:

$$-\frac{dC_{LAS}}{dt} = I_0\phi_{LAS}F_{LAS}[1 - \exp(-2.303L\epsilon_{LAS}C_{LAS})] + k_{OH}C_{OH}C_{LAS} \quad (5)$$

This complex equation leads to the calculation of the kinetic parameters of each oxidation pathway: the quantum yield of LAS (ϕ_{LAS}) for the photodecomposition and the rate constant for the radical reaction.

The kinetic of photoreaction is defined by the radiation flux of the UV source (I_0) and the quantum yield of the radiated compound (ϕ_i). The quantum yield is the most fundamental kinetic parameter of a photolytic reaction, defined as the number of molecules decomposed photochemically per photon absorbed. In Eq. (5), the term F_{LAS} is the fraction of the total light absorbed by LAS (μ_{LAS}) with respect to the total absorbance of the whole solution. The absorbance of the radiated compound (cm^{-1}) is the product of the extinction coefficient for LAS ($\text{M}^{-1} \text{cm}^{-1}$) and the concentration of LAS at any determined time [C_{LAS} (M)].

To model the process suitably it is necessary to determine the main kinetic parameters for each contribution. To achieve this, two different sets of experiments are performed, with hydrogen peroxide for the determination of the rate constant of the radical reaction and without hydrogen peroxide (direct photolysis) for the calculation of the LAS quantum yield.

Direct photolysis: determination of quantum yield

In this first stage, the acid is photodegraded by UV radiation in the absence of peroxide with the main objective of determining the quantum yield of LAS in the photochemical reaction (ϕ_{LAS}). This is the main kinetic parameter for the analysis and design of a photoreactor. Nevertheless, the estimation of the quantum yield (ϕ_{LAS}) in a photolytic reaction is complex because the effect of lowering of LAS concentration is not known, as the factors involved in the degradation mechanism of LAS are not accurately known.

As well as the photodecomposition of LAS, and in spite of the absence of hydroxyl radicals in solution, some organic radicals may be generated from LAS in the form of oxidation intermediates. These radicals can react with LAS in chain reactions, contributing to the removal of the pollutant. So, the calculated value of ϕ_{LAS} is an effective quantum yield that covers the contribution of two mechanisms to the degradation of LAS: direct photolysis and decomposition due to radical reactions.

In these direct photolysis experiments it is assumed that LAS are the only compounds liable to absorb radiation. In many cases it is assumed that oxidation intermediates do not absorb UV radiation (Beltrán et al. 1993). Thus the fraction of light absorbed by this compound is $F_{LAS}=1$. The calculation of ϕ_{LAS} for different initial pH values is performed by Eq. (5), neglecting in this equation the contribution of the radical reaction ($k_{OH}C_{OH}C_{LAS}$) as experiments are performed in the

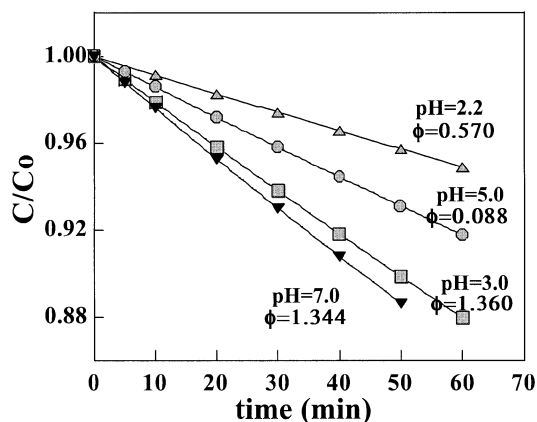


Fig. 3 Determination of quantum yield by the zero-order kinetic equation derived from simplification of Eq. (5) using high LAS concentrations for different pH values. Integrating this equation and representing the conversion vs. time gives us the slope that is $I_0\phi_{LAS}$. From this value, as we know the value of the intensity of flux radiation (I_0) by actinometry experiments, we can ascertain the values of quantum yield for different pH values

absence of peroxide. With the direct mathematical integration of the equation, the kinetic of the degradation of LAS turns out as follows:

$$C_{LASO} - C_{LAS} + \frac{1}{\alpha} \ln \left[\frac{1 - \exp(-\alpha C_{LASO})}{1 - \exp(-\alpha C_{LAS})} \right] = I_0\phi_{LAS}t \quad (6)$$

In the preceding equation, a is a constant with a value of $2.303 L\epsilon_{LAS}$. In accordance with Eq. (6), a plot of the left-hand side vs. time must give a straight line from whose slope ($I_0\phi_{LAS}$) the quantum yield is calculated. Values of ϕ_{LAS} for different initial pH values are calculated, achieving values for the quantum yield at different pH values: 0.548, 1.263, 0.088 and 1.344 mol Einstein⁻¹ for pH=2.2, 3.0, 5.0 and 7.0 respectively. From these results it can be deduced that the pH exerts a great influence on the quantum yield.

The quantum yield can also be calculated by a simplification of Eq. (5). In experiments at high concentrations of LAS, the exponential term becomes negligible (Nicole et al. 1990). Consequently, the rate of disappearance of LAS becomes independent of the concentration. In the experiments carried out in this work the simplification is valid as the range of concentrations used, initial LAS amounts of $2,500 \text{ mg L}^{-1}$ ($7.860 \times 10^{-3} \text{ M}$), are high enough. Thus, the disappearance of LAS is described by a zero-order kinetics, i.e., independent of the LAS concentration. Plotting this zero-order kinetic, values for the quantum yield are obtained, as shown in Fig. 3.

As can be deduced from the results, the simplification derived from using high concentrations of LAS is valid since the values obtained are very similar to those achieved with Eq. (6), achieving values for the quantum yield at different pH values: 0.570, 1.360, 0.088 and 1.344 mol Einstein⁻¹ for pH=2.2, 3.0, 5.0 and 7.0 respectively.

Rate constant calculation

Oxidation with the combination of UV/H₂O₂ is based on the reaction between the hydroxyl radicals and LAS, which leads to an enhancement of the oxidation rates compared to UV radiation alone. At this stage, the kinetic rate constant for the radical attack (Eq. 3) will be determined for different operational conditions to confirm this assertion. In the case of the combination of photolysis and radical oxidation, the mechanism becomes more complex due to the contribution of both degradation pathways. For the radical pathway, a steady state is assumed for hydroxyl radicals for certain conditions where the amount of hydrogen peroxide and consequently of hydroxyl radicals does not vary significantly. Assuming this steady state situation for hydroxyl radicals ($k_R = k_{OH} C_{OH} C_{LAS}$) and the aforementioned simplification of LAS oxidation into a zero-order kinetics, the rate of disappearance of LAS due to both contributions can be described as follows:

$$-\frac{dC_{LAS}}{dt} = I_0 \phi_{LAS} F_{LAS} + k_R C_{LAS} \quad (7)$$

In Eq. (7), F_{LAS} represents the fraction of radiation absorbed by LAS at any time in comparison with the total light absorbed by the compounds in the solution, this absorbed light being the product of the extinction coefficient and the concentration of that compound at a given time. Since it is assumed that the only compounds liable to absorb radiation are the initial LAS and hydrogen peroxide, the value of this parameter varies during the reaction as the concentrations of LAS (C_{LAS}) and peroxide (C_H) decrease over time. However, values for the molar extinction coefficients are assumed to be constant, at 641.5 and 19.6 M⁻¹ cm⁻¹ for LAS and hydrogen peroxide respectively (Baxendale and Wilson 1956).

Analyzing the problem rigorously on the basis of the variation of F_{LAS} , no constant zero-order kinetic for the degradation of LAS by direct photolysis can be expected. However, for ϕ_{LAS} the value obtained in the preceding set of experiments can be assumed. Thus, the term corresponding to the contribution of photolysis can be calculated as far as the photolytic parameters are known. Consequently, by subtracting this term from the overall decomposition in Eq. (7), the rate constant for the radical attack can be calculated by considering a first-order kinetic. Values are presented in Table 1. As can be deduced from the results in the table, the rate constants for the radical mechanism are higher than the ones of the overall reaction, assessing in this way that the radical pathway has the major contribution in the LAS oxidation.

Finally, the contribution of each degradation pathway (radical reaction and photolysis) is quantified by determining the rate constant of the total decomposition. It is assumed that the overall decomposition, i.e. the overall rate of oxidation achieved with the combined H₂O₂/UV system, follows a first-order kinetic (k_T). Consequently, as the rate constant for the radical reaction has already been

Table 1 First-order rate constants ;for the overall reaction (k_T) and for radical reaction (k_R) for different values of molar ratios. Conditions of experiment: pH=3. Rate constants for the radical reaction pathway are very close to the ones of the overall oxidation; consequently, the radical pathway achieves the major contribution in the oxidation of linear alkylbenzene sulfonates

| r_M | k_T (min ⁻¹) | R^2 | k_R (min ⁻¹) | R^2 |
|-------|-------------------------------|-------|-------------------------------|-------|
| 2 | 0.0056 | 0.95 | 0.0033 | 0.836 |
| 3 | 0.0055 | 0.95 | 0.0031 | 0.824 |
| 5 | 0.0084 | 0.95 | 0.0059 | 0.926 |
| 10 | 0.0118 | 0.95 | 0.0099 | 0.983 |
| 20 | 0.0142 | 0.95 | 0.0127 | 0.991 |
| 40 | 0.0140 | 0.95 | 0.0131 | 0.986 |

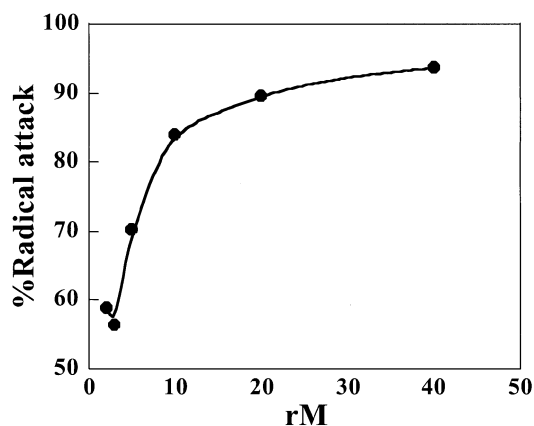


Fig. 4 Contribution of radical reaction to degradation of LAS. Conditions of experiment: pH=3. The contribution of radical attack in the overall oxidation of LAS is always very high compared to the oxidation achieved by photolysis. Even for low molar ratios, contribution of radical reactions is higher than 50% of the total oxidation

determined, the fraction corresponding to this oxidation pathway can be calculated.

The quantification of the contribution of the oxidation due to this oxidation pathway in the overall oxidation of LAS is represented in Fig 4. In this figure we observe that the effect of the radical reaction mechanism is significant in the overall oxidation of LAS. The strong effect of the radical reaction is confirmed, since the contribution to the oxidation of this pathway is higher than that of photolysis, even with low amounts of oxidant. This contribution of the radical reaction increases with an increase in the hydrogen peroxide concentration. This increase in the oxidation due to the radical reaction is limited up to a molar ratio of $r_M=20$, when the radical concentration becomes constant, as at these high amounts of oxidant, the peroxide itself becomes a scavenger of the hydroxyl radicals.

Conclusions

UV combined with hydrogen peroxide is an effective pretreatment for synthetic LAS solutions wastewater containing high LAS concentrations. This assertion is confirmed as the disappearance of 50% of initial LAS is achieved in reaction times of less than 1 h. The degradation of linear alkylbenzene sulfonates (LAS) is favored by the amount of peroxide up to a certain critical value, beyond which no improvement is observed with any further increase in the amount of oxidant. However, pH has no significant effect on oxidation.

The determination of some kinetic parameters such as the quantum yield and the rate constant for the radical reaction for different pH values allows us to model the oxidation system. In addition, the main conclusion obtained from the determination of these two parameters is that oxidation is due mainly to the contribution of hydroxyl radicals generated in the combination UV/H₂O₂, accounting for 60 to 97% of the total removal of LAS.

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