



The study of the effect of different variable on H_2O_2 /UV decolorization of three azo dyes in the continuous circulation photoreactor

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Abstract

Wastewater from textile processing plant can be highly colored and difficult to decolorize. Combined UV and hydrogen peroxide oxidation has been applied successfully to the treatment of various water pollutants. In the present study, advanced oxidation treatment, UV/ H_2O_2 was applied to decolorization of three azo dyes, Acid Orange 7, Acid Orange 8 and Methyl Orange. The study described herein is an investigation of treatability of these dyes in the continuous circulation photoreactor. The UV radiation was carried out with a 15 W low-pressure mercury lamp. Rate of color removal have been studied by measure of the absorbency at characteristic wavelength. We have observed that the decolorization reaction is pseudo-first order with respect to the dye concentration. The effect of H_2O_2 dosage, dye initial concentration and pH on decolorization kinetic in the continuous circulation photoreactor was investigated.

Introduction

Effluents streams from dyestuff manufacturing and textile dyeing processes can be highly colored and difficult to decolorize. This is an environmental problem for the dyestuff manufacturing and textile industries. Due to the large degree of aromatics present in these molecules and the stability of dyes, most conventional treatment methods are ineffective for decolorization and degradation. Combined UV and hydrogen peroxide oxidation, is one of the Advanced Oxidation Processes (AOPs) which has been successfully applied to the treatment of

various water pollutants[1-4]. These processes imply such simple reactions as UV photolysis of H_2O_2 . It is characterized by the generation of a very powerful oxidizing species, well known as hydroxyl radicals in relative high steady-state concentrations. These reactive radicals can decompose and even mineralize the organic contaminates with high efficiency. The main advantages of this process are that no additional disposal problems are generated after the completion of the above treatment and they are non-selective to a very broad range of chemicals.

Galindo[5] have demonstrated that the UV/ H_2O_2 process is able to totally destroy the chromophore structure of azo dyes and that the reaction rate of azo dyes depends on the basic structure of the molecule and on the nature of auxiliary groups attached to the aromatic nuclei of dyes. Colonna[6] reported that UV irradiation in the presence of H_2O_2 leads to their complete decolorization and mineralization of sulphonated azo and anthraquinone dyes.

The purpose of this study is to conduct experimental investigation of the decolorization of three azo dyes in water in a continuous circulation photochemical reactor. The effects of the key operating variables such as hydrogen peroxide dosage, pH and dye concentration on the decolorization kinetics were studied for each molecule. The experiment was conducted by changing one variable at a time while keeping other parameters constant.

Materials and experimental methods

Acid Orange 7 (AO7) 90% and Acid Orange 8 (AO8) 65% were obtained from Aldrich Chemical, methyl orange (MO) 95% is obtained from Merck, and used without further purification. The characteristics of these dyes are given in the Table1.

Table 1: Characteristics of the three commercial dyes

Dye	M_w (g.mol ⁻¹)	λ_{max} (nm)	$\epsilon.10^3$ (l.mol ⁻¹ .cm ⁻¹)	Structure
AO7	350	483	19,43	
AO8	364	488	28,12	
MO	327	463	26,05	

Hydrogen peroxide (30% w/w) was obtained from Prolabo. The optical absorption spectra of each dye were determined by a V-530 UV/VIS spectrophotometer. The reactor used in this study is a continuous column circulation photoreactor fitted with a 15 Watt electric power, low-pressure mercury lamp (Philips emission at 253.7 nm) as shown in Figure1. The radiant flux of this lamp was determined by means of the chemical actinometer hydrogen peroxide[7]. The incident photon flux was 6.1×10^{-6} Einstein s⁻¹. This irradiation frequency was selected because a number of papers have reported the

efficient degradation of chemicals in water using the same emission (253.7 nm) produced by mercury[8-9].

We determined the following maximum absorption wavelengths (λ_{\max}): 483 nm for AO7, 488 nm for AO8 and 463 nm for MO. Absorption spectra of the dye solutions irradiated by UV light were recorded. It was found that the position of the maximum absorption wavelengths varied, depending on the solution concentration. In addition, no new absorption peaks occurred near the original maximum. As a result, we can conclude that the absorption bands are not disturbed by intermediate oxidation products. Furthermore, the molar extinction (ϵ) of H_2O_2 varies between 15– 25 ($\text{mol.l}^{-1}.\text{cm}^{-1}$) for the wavelength (λ) between 450– 650 nm. As a result, the measurement error that might be caused by H_2O_2 in the mixture is low. The photolysis of blank samples containing the same dose of H_2O_2 without dye was carried out, so that the interference due to H_2O_2 could be eliminated. The concentrations of dye solutions irradiated by UV could also be determined by spectrophotometry.

The unit for continuous circulation reactor used in the experiments consisted of a 4.25 cm inner radius glass column with a 3.25 cm outer radius quartz tube. The UV lamp was fitted inside the central column.

A total of 2500 ml of dye solution in the reservoir was used for the treatment while the liquid level in the radiation column was kept constant at 1600 ml. The liquid inside the column was exposed to a 15 watt UV lamp. The treated wastewater was returned to the reservoir and then left to circulate back to the reactor column at a constant flow rate of 3.5 l.min^{-1} .

In our study dye concentrations were set at values, in most cases $5 \times 10^{-5} \text{ mol.l}^{-1}$, which were within the range of typical concentration in textile wastewater. Each selected dye was dissolved in deionized water prior to use. A large excess of hydrogen peroxide in comparison to the dye was added to this solution ($4.89 \cdot 10^{-2} \text{ mol.l}^{-1}$), so that $[\text{H}_2\text{O}_2]$ could be considered as constant during the whole experiment. The pH was adjusted to the desired value by addition of sodium hydroxide or by hydrochloric acid and then it was measured by a Swott Gerate pH meter CG817T in the solution.

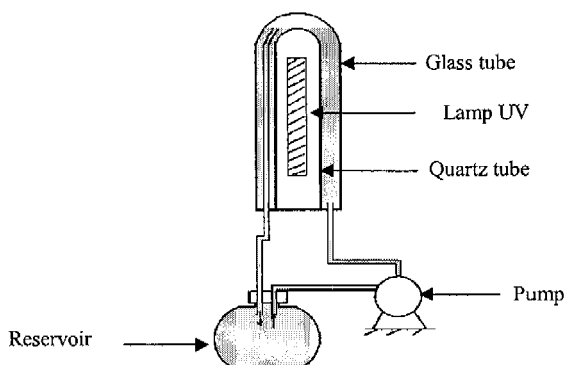


Figure 1: Continuous circulation photochemical reactor

Results and discussion

In Figure2 the results of decolorization of AO7, AO8 and MO by using UV/H₂O₂ are presented. Dye decolorization was investigated by using the above reactor. At regular time intervals samples were collected and analyzed by UV/VIS spectrophotometer to determine the decolorization rate. Repeated operations were performed to examine the reproductivity of the results. For the three dyes studied in this work the action of UV alone or H₂O₂ in the absence of UV irradiation was negligible after three days of treatment. Galindo[10] reported that the photooxidation reactions are indeed not sensitive to small temperature changes in the range 22-45° C.

Color degradation is due to action of the hydroxyl radicals generated upon photolysis of hydrogen peroxide[3, 11] according to the following reaction:



This radical is a very powerful oxidizer with an oxidation potential of 2.8 V and can react with dye molecules resulting in the destruction of color.

When the kinetics of the photocatalytic decolorization reactions were studied, it was found that the correlation between $\ln C/C_0$ and the irradiation time was linear as shown in Figure3. This is a typical first order reaction plot. The kinetic expression can be presented as follow:

$$\ln \frac{C}{C_0} = -kt \quad t_{1/2} = \frac{\ln 2}{k} \quad (2, 3)$$

C : dye concentration at instant t (mol.l⁻¹); C_0 : dye concentration at $t = 0$ (mol.l⁻¹)
 k : pseudo-first order rate constant (min⁻¹); t : time of reaction in minute.
 $t_{1/2}$: half-life period.

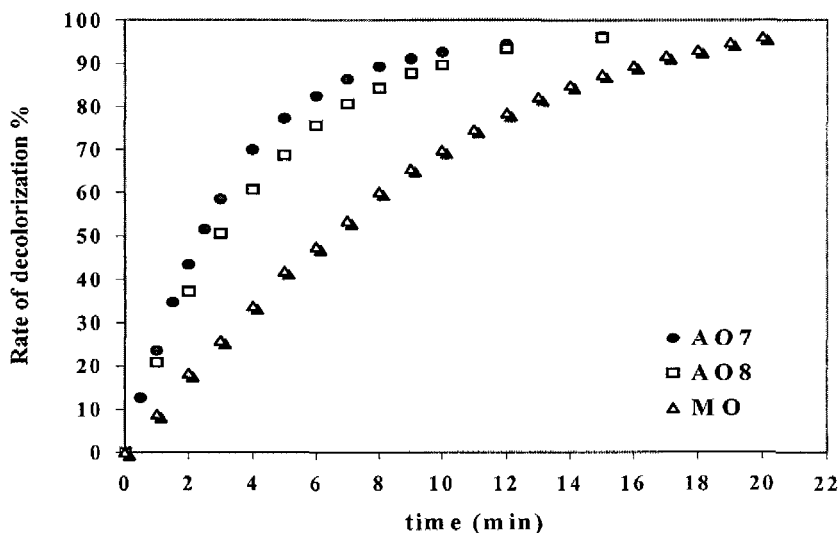


Figure 2: Decolorization of three dyes by UV/H₂O₂

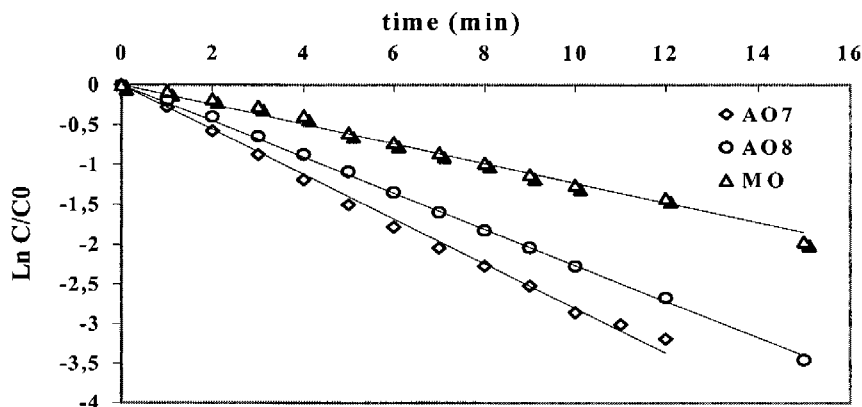


Figure 3: Plot of $\text{Ln } C/C_0$ versus irradiation time of three dyes.

The correlation coefficient that can explain the fitting extent of the function equation and the experimental data is presented by R^2 . The values of these correlation coefficients confirm the goodness of the assumed kinetics for the $\text{UV}/\text{H}_2\text{O}_2$ photocatalytic decolorization reactions of these dyes. The slopes of the lines give the apparent rate constant (k). For the three dyes, the values of R^2 , k and $t_{1/2}$ are given in Table2

The difference between the decolorization rate constant for these dyes can be explained by their different molecular structure. AO7 and AO8 have nearly the same structure, the presence of the CH_3 group in the AO8 molecular structure can decrease slightly the reactivity of this dye. The reactivity of the dye can be increased by the presence of the labile hydrogen. In the natural or basic milieu, MO has not labile hydrogen in his molecule; therefore it is less reactive than AO7 and AO8.

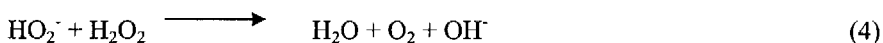
Table 2: Correlation coefficient, half-life period and kinetic constants of three dyes under the following experimental conditions: $\text{pH}=6.0$, $[\text{dye}]_0=5.10^{-5} \text{ mol.l}^{-1}$, $[\text{H}_2\text{O}_2]=0.02 \text{ mol.l}^{-1}$.

dye	Correlation coefficient (R^2)	$k \text{ (min}^{-1}\text{)}$	$t_{1/2} \text{ (min)}$
AO7	0.994	0.2804	2.472
AO8	0.999	0.2298	3.016
MO	0.991	0.1236	5.608

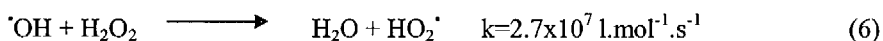
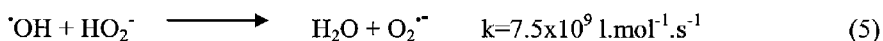
The effect of pH

Since dyes to be removed can be at different pH's in colored effluents, we have studied the effect of pH on the rate of decolorization reaction. Comparative irradiation experiments were performed following the evolution of the absorbency with time. The solutions of the dyes were adjusted to the pH between 2 up to 11 by addition of the HCl or NaOH. In the case of the AO7 and AO8, the decolorization rate constants present a few lower value at pH=2.5 and similar values at pH between 2.5 and 9.5 Figure4. It indicates non influence of this operating variable on the decolorization rate of these dyes in this interval. For pH greater than 9.5 the decolorization rate constants decrease sharply. It can be explained by taking into account the following two parameters:

1). In alkaline medium hydrogen peroxide undergoes decomposition leading to dioxygen and water, rather than producing hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration in $\cdot\text{OH}$ is lower than expected. The base catalyzed decomposition involves the HO_2^- anion: the conjugated base of H_2O_2 react with a non-dissociated molecule of H_2O_2 according to Eqn(4)



Furthermore, the deactivation of $\cdot\text{OH}$ is greater when the pH of the solution is high, the reaction of $\cdot\text{OH}$ with HO_2^- being approximately 100 times faster than its reaction with H_2O_2 .



The reactivity of HO_2^{\cdot} and $\text{O}_2^{\cdot-}$ with organic pollutants is very low[10].

2). The decolorization kinetic notably depends upon the basic molecular structure of the dyes. In the solution, AO7 and AO8 exist as an azo-hydrazone mixture Eqn(7).

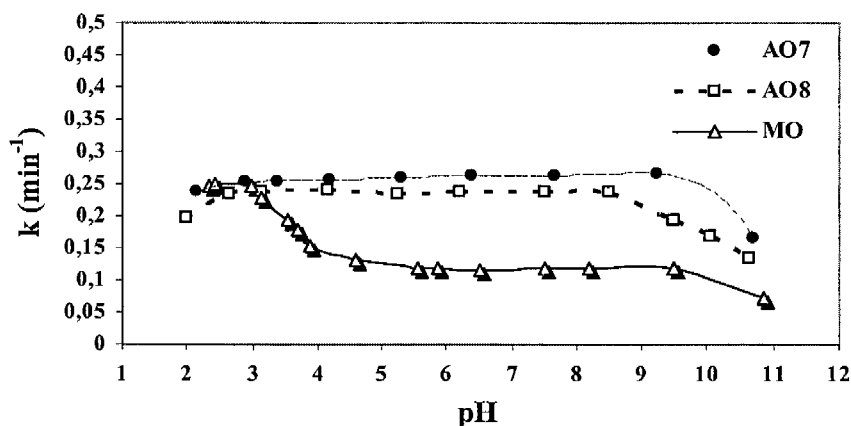
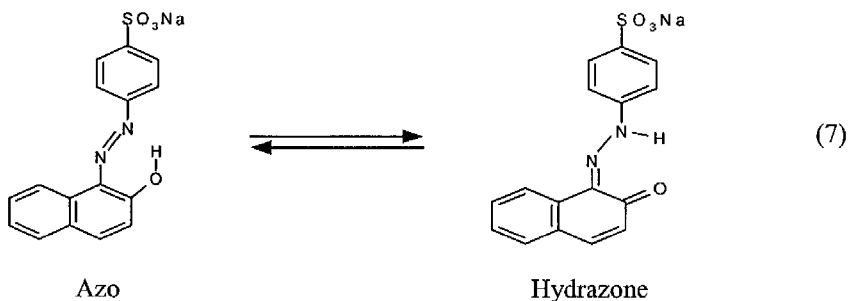


Figure 4: Effect of pH on the rate of decolorization of the dye solutions. $[\text{H}_2\text{O}_2]_0 = 4.98 \cdot 10^{-2} \text{ mol.l}^{-1}$, $[\text{dye}]_0 = 5 \cdot 10^{-5} \text{ mol.l}^{-1}$.



Factors such as the solvent, plays a significant part in determining the tautomeric equilibrium. We have studied the evolution of the intensity of the maximum absorption band of three dyes at characteristic wavelength as a function of the pH. From Figure5 we can observe that in the high basic solution the intensity of the band at maximum absorption wavelength decreases. It can be explained by the presence of the azo form and O-H band dissociation and loss of the conjugation.

The behavior of MO is very particular; from the Figure4 we can see that in the neutral or alkaline solution, the reactivity of MO is significantly less than AO7 and AO8 solutions. But at lower pH values, its decolorization rate constant rises sharply. This can be explained by a change in the molecular structure Eqn(8). Indeed, when the pH of the solution is lower than the pK_a of dye ($pK_a = 3.4$), MO is protonated.

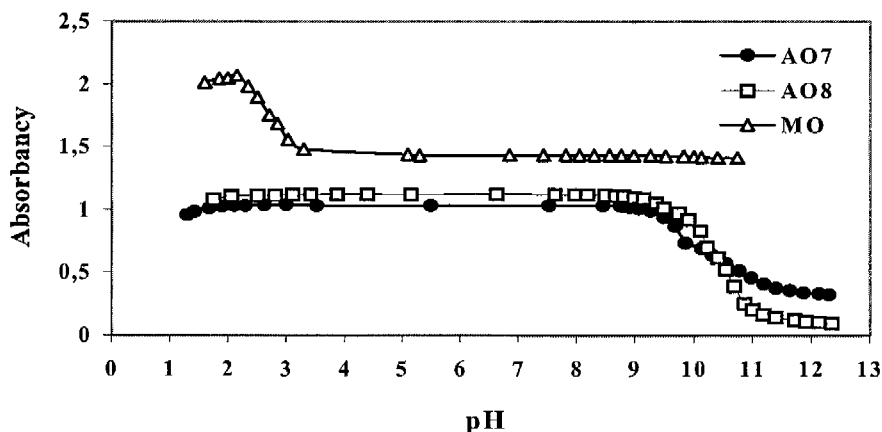
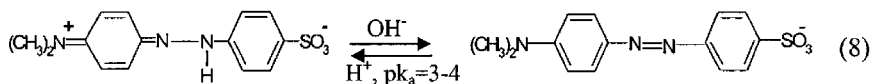


Figure 5: Evolution of the intensity of the maximum absorption band of the three dyes as function of pH.

The protonated molecule is subject to ammonium- azonium tautomerism and the latter form is stabilized by resonance[12]. The azonium configuration presents a similarity to the hydrazone form of MO. In both cases, the β nitrogen atom of the azo band carries an H atom and the labile H atom make the molecule of MO especially vulnerable toward attack of OH radicals [10].

The decrease of the color removal rate at high basic solution (pH higher than 10.5), is not due to dye, but to the oxidation species that we have already mentioned in the above paragraph.

The effect of initial hydrogen peroxide

Hydrogen peroxide concentration is an important parameter for the degradation of the dyes in the UV/H₂O₂ photo reactor. Theoretically, the more the initial hydrogen peroxide added, the faster is the dye removal rate. However, the \cdot OH free radicals will eventually reach equilibrium with hydrogen peroxide. At this point even an increase in the hydrogen peroxide concentration cannot increase the free radical concentration. The results for three dyes in Figure6 show that increasing H₂O₂ concentration from zero to 0.02 mol.l⁻¹ leads to an important rise of the rate constant. A further increase in the H₂O₂ concentration provides an inhabitation of the degradation rate. This study concludes that increasing the [H₂O₂] can increase the decolorization rate of these dyes, but there is an optimal hydrogen peroxide dosage at which the rate of the reaction is maximum. Indeed, the \cdot OH free radicals produced upon photolysis of H₂O₂ can react with dye molecules eqn(9) but also with an excess of H₂O₂ eqn(6).

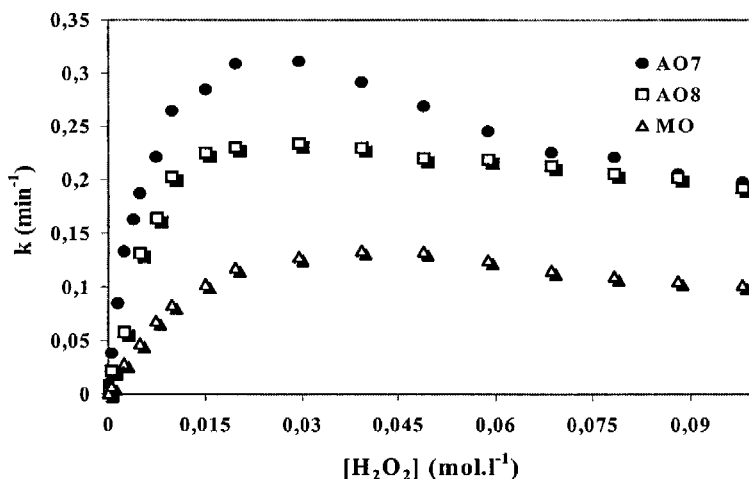
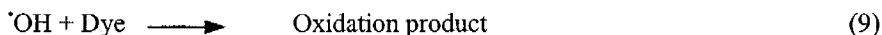


Figure 6: Effect of the initial hydrogen peroxide concentration on the rate of decolorization, [dye]₀ = 5.10⁻⁵ mol.l⁻¹, pH= 6.0.

At low H_2O_2 concentration, formation of $\cdot\text{OH}$ is the kinetic determining step. H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. Further, most of free radicals are directly consumed by the dye. In the presence of high concentration of H_2O_2 , we could expect that more $\cdot\text{OH}$ radicals would be produced. However these radicals preferentially react with the excess of H_2O_2 . This undesirable reaction competes with the degradation of the color. We have defined H as the best molar fraction resulting from the optimal concentration of hydrogen peroxide and the concentration of the dyes. $H \approx 400$ for the three dyes.

The effect of initial dyes concentration

The effect of initial dye concentration can be expressed in Figure 7. The decrease in decolorization rate with increasing initial dye concentration has been observed. The reason for this is that the higher the azo dye concentration, the more the absorption of UV light. Indeed, the extinction coefficients (ϵ) of the three dyes at 253.7 nm are high, so that an increase in the dye concentration induces a rise of the internal optical density. The solution becomes more and more impermeable to UV radiation. Hydrogen peroxide can then only be irradiated by a smaller portion of UV light to form lower free radicals and the color degradation rate decrease.

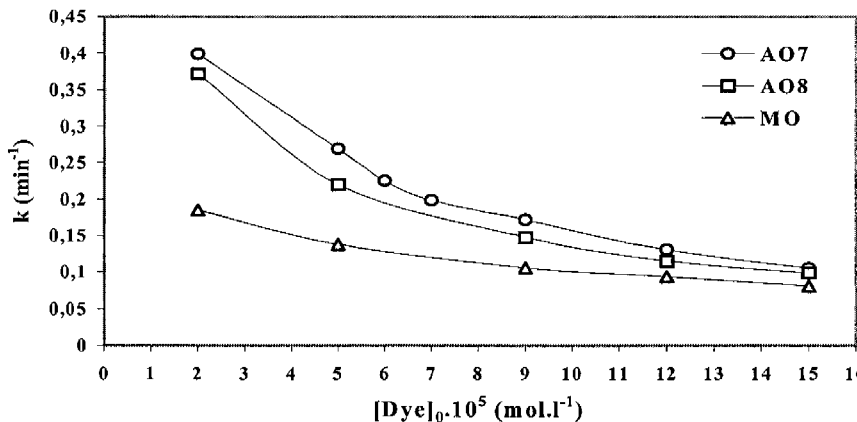


Figure 7: Effect of initial concentration of dyes on the kinetics of decolorization, $[\text{H}_2\text{O}_2]_0 = 4.98 \cdot 10^{-2} \text{ mol.l}^{-1}$, $\text{pH} = 6.0$.

Conclusion

It can be concluded that the $\text{UV}/\text{H}_2\text{O}_2$ process using continuous circulation reactor provides good performance in the decolorization treatment of the AO7, AO8 and MO in water. It is important to set a suitable pH in order to optimize

the operating conditions. In the neutral or acidic solution the rate of decolorization is improved. The impact of H_2O_2 in color removal was investigated. It was found that the rate of decolorization increases with increasing the initial concentration of H_2O_2 up to 0.02 mol.l^{-1} at which it reaches a maximum and beyond which it is inhibited. Increasing the initial concentration of dye is in fact, like a filter absorbing more and more UV and decreasing the kinetic of removal.

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