Photocatalytic Degradation of the Herbicide "Paraquat"

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Introduction

Paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) is the active component of several commercial herbicides which are used to destroy any type of weeds by inhibition of the photosynthesis process [1]. Residual paraquat from low concentration water solutions can be adsorbed on any type of soil particles where it can be degraded by microbiological and photochemical processes [2]. However, it is well know that any pesticide solution may contaminate the environment. Therefore, all the pesticide rinsate solutions must be degraded before disposal. It has been demonstrated [3] that low concentration aqueous solutions of paraquat can be completely oxidized by photocatalysis using TiO_2 illuminated with UV light. That study did not provide information about the reaction pathway nor the kinetic behavior of the degradation process. In this research project, We have studied the effect of several reaction parameters on the reaction rate of the photocatalytic degradation of paraquat solutions.

Experimental

Photocatalytic degradation experiments of Paraquat (99.8 %, Aldrich) solutions were carried in a homemade reactor system [2]. It has a Pyrex glass tube reactor that can be irradiated with four UV light lamps (λmax =365 nm, 15 Watts). We carried out two sets of experiments. In the first set, We placed 200 cc of paraquat solution with a concentration of 100ppm in a quartz reactor and bubbled 100 cc/min. of helium, air or oxygen through the system without any catalyst. The reactor was illuminated with the four UV lamps. Samples for analysis were taken at different times to monitor the reaction by HPLC and TOC analysis. Then, We repeated the experiments using 0.2 grams of TiO_2 (Degussa P-25) as catalyst and bubbling 100 cc/min of helium, air or oxygen. On the second set of experiments, We studied the effect of initial paraquat concentration on the reaction rate using 0.2 grams of catalyst and bubbling saturated oxygen through the system. Samples of the reaction mixture were analyzed by TOC and HPLC analysis

Results and Discussion

The experimental results of the first set of experiments clearly indicated that paraquat solutions are not degraded by UV light in the absence of oxygen. It also confirmed that paraquat can be slowly degraded by direct photolysis in the presence of dissolved oxygen and that the presence of TiO_2 increases the rate of reaction and the overall conversion. The results of the second set of experiments

showed that the concentration profiles can be correlated by a pseudo-first order reaction rate equation (Figure 1). The rate constant change from 0.0714 min^{-1} for an initial concentration (Co) of 20 ppm to 0.00189 min^{-1} for a Co of 400 ppm. It is know that photocatalytic degradation reactions follow a LH-HW rate expression [4]

$$-r_a = \frac{k_1 C}{1 + K_2 C + \sum K_i C_i}$$

where K2C represents the adsorption of paraquat and Σ KiC represent the adsorption of all the intermediate products. If the experimental results are analyzed at time = 0 and C=Co, the term for the adsorption of the intermediate products can be neglected and the LH-HW model can be linearized to obtain the reaction rate constant (k1=0.0921 min^{-1}) and the adsorption constant for paraquat (K2=0.0452 ppm^{-1})

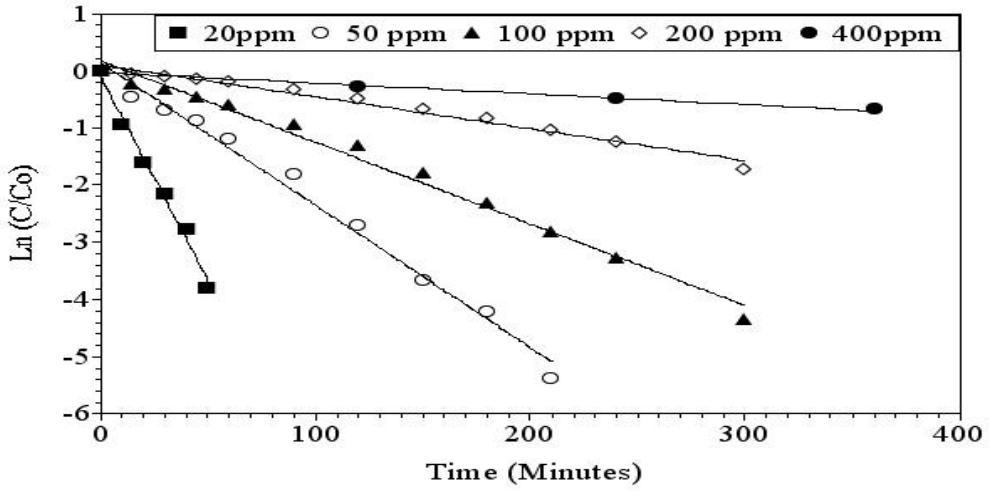

Fig. 1 Effect of initial concentration on the photocatalytic degradation of paraquat (catalyst 0.2 gr. of TiO2/liter, λmax=365 nm, 100 cc/min of oxygen)

References

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