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## DEGRADATION OF ORANGE II BY HETEROGENEOUS PHOTOCATALYTIC REACTION USING MONTMORILLONITE KSF

Jing Li <sup>a</sup>, Feng Wu <sup>a\*</sup>, Nansheng Deng <sup>a</sup>, Evgeni M. Glebov <sup>b\*</sup>  
and Nikolai M. Bazhin <sup>b</sup>

<sup>a</sup>Department of Environmental Science, Wuhan University, Wuhan, 430079, P.R. China

<sup>b</sup>Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia

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### Abstract

Degradation of Orange II in montmorillonite KSF (KSF) suspensions under irradiation by a 250 W metal halide lamp ( $\lambda \geq 365$  nm) was investigated. The degradation kinetics of Orange II in KSF suspensions followed the Langmuir-Hinshelwood model. The effects of KSF concentration, solution pH, initial Orange II concentration, carboxylic salts were studied.

*Keywords:* Montmorillonite KSF, Orange II, heterogeneous photocatalysis

## INTRODUCTION

Azo dyes constitute a significant portion of dyestuffs, and the untreated disposal of water containing azo dyes may exhibit toxic effects toward microorganisms and human beings [1]. As for the degradation of azo dyes, heterogeneous photocatalysis is a promising and effective process.

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\* Corresponding authors. E-mail addresses: fengwu@whu.edu.cn; glebov@ns.kinetics.nsc.ru

Recently, clay minerals have been developed as heterogeneous catalysts for the remediation of dye wastewater by photocatalysis and photo-Fenton reaction. Feng *et al.* reported heterogeneous catalysts containing Fe, a bentonite-clay-based Fe nanocomposite (Fe-B) which was employed for the photo-Fenton discoloration and mineralization of Orange II [2]. They found that, at an initial pH of 3.0 and 6.6, the photocatalytic activity of Fe-B was higher than that of FeOOH and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Alex Chi-Kin Yip *et al.* found that the photodegradation of Acid Black 1 by bimetallic Cu/Fe was effective and the catalytic performance of bimetallic Cu/Fe was much less pH sensitive [3]. However, most of the researches focussed on clay-photo-Fenton reaction and the modified clay photocatalysis due to their high photocatalytic activity as well as their prospective application [4, 5]. To the best of our knowledge, there are rare studies reported about the raw clay, or simply treated clay as a heterogeneous photocatalyst applied to the degradation of dye-containing wastewater.

KSF has been used as a catalyst for numbers of organic synthesis reactions, an absorbent and an ion-exchange material in the removal of heavy metals from solutions [6, 7]. In this paper, KSF was used as a photocatalyst for the degradation of an azo dye Orange II. Orange II is non-biodegradable, and is used extensively in textile industry. The aim of the study was to investigate the photocatalytic ability of KSF for the degradation of Orange II in aqueous solutions. The main influencing factors, such as the pH of the suspension, the concentrations of KSF and Orange II, carboxylic salts (oxalate, citrate and pyruvate) were investigated.

## EXPERIMENTAL

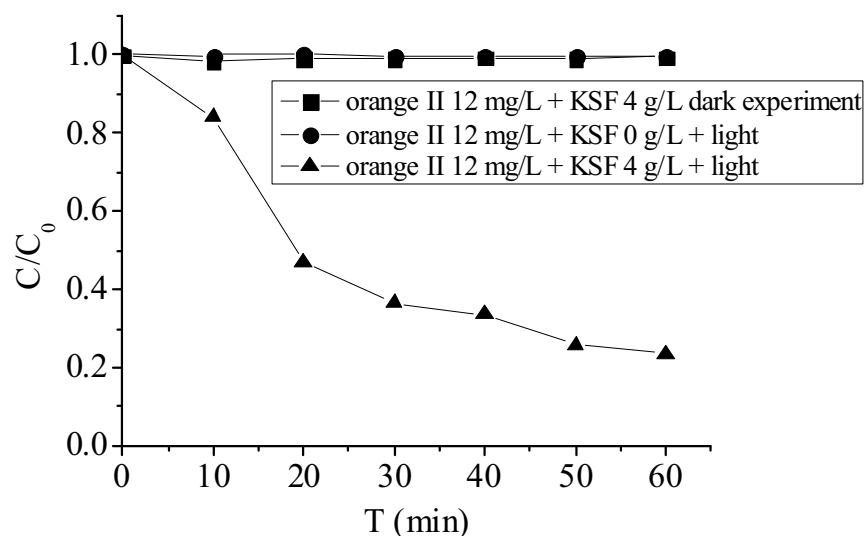
### Material and chemicals

KSF was purchased from Alfa Aesar (A Johnson Matthey Company, Ward Hill, MA, USA). The size of the particles was 20 - 25  $\mu$ m. The surface area of KSF was 20 - 40 m<sup>2</sup>/g (data are provided by the supplier). The chemical composition of KSF determined by XRF is as follows: Na<sub>2</sub>O, 0.0573; MgO, 4.31; Al<sub>2</sub>O<sub>3</sub>, 16.3; SiO<sub>2</sub>, 49.1; P<sub>2</sub>O<sub>5</sub>, 0.0547; SO<sub>3</sub>, 22.3; K<sub>2</sub>O, 0.495; CaO, 2.30; TiO<sub>2</sub>, 0.210; MnO, 0.0191; Fe<sub>2</sub>O<sub>3</sub>, 4.76; Ignition loss, 2.68. Orange II was purchased from Shanghai SSS Reagent Co. Ltd. Sodium oxalate, sodium citrate and sodium pyruvate were used as carboxylic salts. All the other reagents were of analytical grade. Water was treated with an ultrapure water system (Liyuan Electric Instrument Co., Beijing, PRC) and purified water with 18 M $\Omega$  cm resistivity was used throughout this work.

### Photochemical Experiment and Analysis

The photoreactor was designed with a cylindrical cell (25.5 cm length, 9.5 cm diameter, 4 mm wall thickness), and the lamp with a glass-jacket was fixed through the central axes of the cell. The light source was a 250 W Metal Halide Lamp (MHL,  $\lambda \geq 365$  nm, 250 W, Wuhan Yaming lamp Co. Ltd., China). A total volume of 500 mL of the suspension containing the desired amount of montmorillonite KSF and Orange II were prepared. The pH of the suspension was adjusted by using dilute HCl or NaOH. Before reaction, the suspension containing KSF and Orange II solution was stirred in dark for 30 min to achieve adsorption equilibrium. The temperature of the irradiated solution was maintained at  $25 \pm 1^\circ\text{C}$  by circulating water. To suspend the clay effectively in the reactor, compressed air was bubbled from the bottom to the top of the reactor at a flow rate of about 1000 mL/min, and a magnetic stirrer was used during irradiation. Samples were collected at different times and centrifuged at 10000 rpm for 30 min. Control experiments were carried out under identical conditions, but in the dark. Determination of the blank was also carried out in a similar manner without clay.

The concentration of Orange II in water was determined by the absorption intensity at 484 nm using an UV-vis spectrometer (Shimadzu UV 1600).

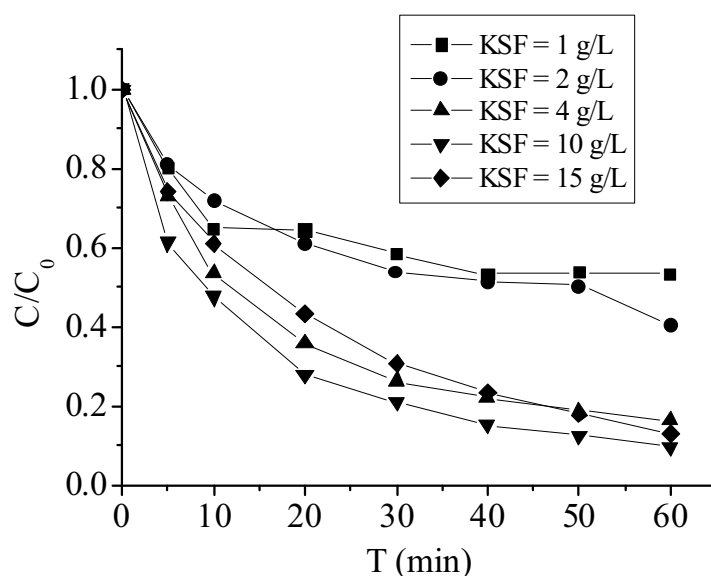


**Fig. 1.** Degradation of Orange II under different conditions (KSF 4 g/L, Orange II 12 mg/L, pH=3.2)

## RESULTS AND DISCUSSION

### Degradation of Orange II using KSF as a catalyst

As shown in Fig. 1, degradation of Orange II was not observed even in 60 min in the absence of KSF under visible light irradiation, or in the presence of KSF in the dark. The results suggested that the direct photolysis of Orange II can be ignored, and KSF shows no catalytic activity for degradation of Orange II in the dark. However, a degradation efficiency of Orange II of 76.4% was achieved after 60 min irradiation in KSF suspension. Thus, KSF shows high photocatalytic activity for Orange II degradation.

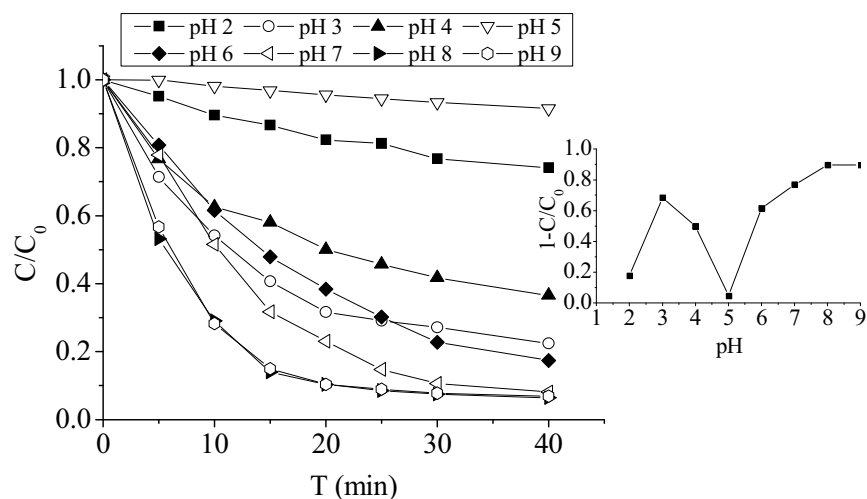


**Fig. 2.** Influence of clay concentration on the degradation of Orange II in aqueous solutions containing KSF (Orange II 12 mg/L, pH=3.2)

### Effect of clay concentration

As shown in Fig. 2, the degradation of Orange II increased with increasing concentration of KSF in aqueous solutions in the range of 1 - 4.0 g/L. This is due to the increase in the amount of KSF particles, which increases the quantity of photoreactive species in clays and the dye molecules adsorbed. However, at an increase of the KSF concentration from 4 to 15 g/L, the degradation of Orange II was inhibited. Increasing the KSF concentration beyond 4 g/L may

cause light scattering and screening effects, which reduces the photocatalytic activity of the catalyst [9]. In this work, the optimal concentration of KSF was 4 g/L.

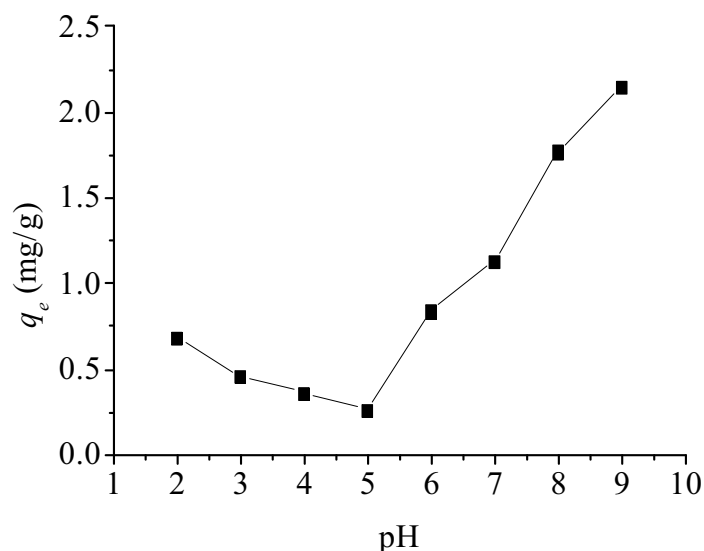


**Fig. 3.** Influence of pH on the degradation of Orange II in aqueous solutions containing KSF (KSF 4.0 g/L, Orange II 12 mg/L). The inset shows the degradation efficiency of Orange II ( $1 - C/C_0$ ) after 20 min irradiation as a function of pH

### Effect of initial pH

Figure 3 shows Orange II (12 mg/L) degradation at various pH values in irradiated suspensions containing 4.0 g/L KSF. In the pH range of 2 - 5, the degradation rate of Orange II was maximal at pH=3 and decreased strongly above and below this pH. At pH 5, the degradation rate dropped to its lowest value. However, the degradation rate of Orange II increased significantly with increasing the pH of the KSF suspensions from pH 5 to 9. At pH=9, 93.1% degradation was achieved in 40 min. This demonstrates that KSF could exhibit a good photocatalytic activity also at a high pH value. Two possible mechanisms for this observation may be considered: the pH dependence of Orange II adsorption on KSF and the photoactivity of the iron species in the solution. Figure 4 shows the effect of pH on the amount of Orange II adsorbed at equilibrium. The minimum adsorption capacity of Orange II from aqueous solution takes place at pH=5, and the adsorption capacity of Orange II increased sharply with increasing the pH of the KSF suspensions from pH 5 to 9, which has the same trend as the pH effect on Orange II degradation (the inset in Fig. 3). From these data it can be concluded that the pH dependence of

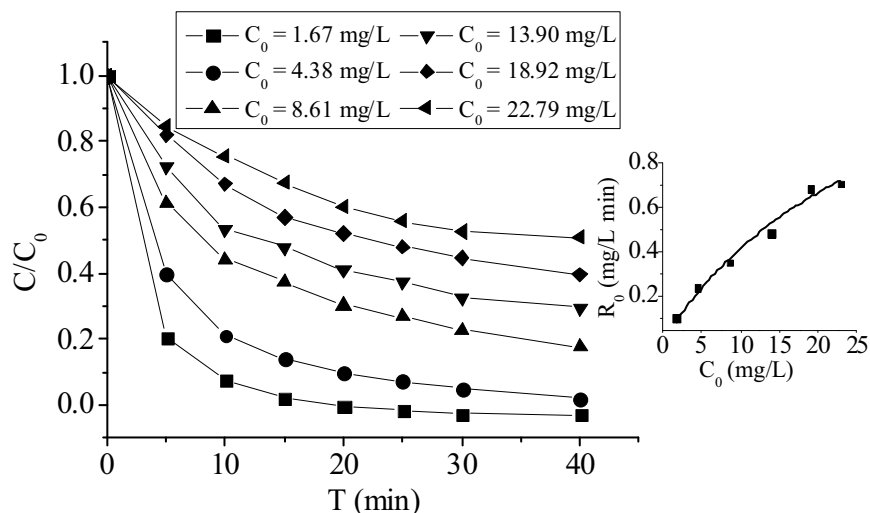
Orange II adsorption on KSF determines to a large extent the pH dependence of Orange II degradation. However, in the acidic pH, the adsorption capacity of Orange II was maximum at pH=2 that is not the same pH value at which the maximum degradation rate of Orange II was achieved KSF contains 4.76% of the iron component that is composed of free iron oxides that distribute randomly on the clay surface, and of structural iron in the octahedral lattice [10]. Under acidic pH, the photoactive iron species can dissolve from the clay into the suspended solutions. The ferric ion species, especially  $\text{Fe}(\text{OH})^{2+}$ , are important sources of hydroxyl radicals which can oxidize most of the organic compounds, and they have higher photoactivity at acidic pH values, near to 3 [11]. The degradation efficiency of Orange II was higher at pH=3 than that at pH=2, reflecting the pH dependence of the photoactivity of iron species in the solution.



**Fig. 4.** pH dependency of the adsorption capacity of Orange II on KSF (KSF 4.0 g/L, Orange II 12 mg/L,  $q_e$  is the amount of Orange II adsorbed on the KSF (mg/g) at equilibrium)

### Effect of initial Orange II concentration

As shown in Fig. 5, the lower the initial Orange II concentration, the higher the degradation efficiency in the same reaction time. The increase in the concentration of dye from 1.67 to 22.79 mg/L decreased the degradation from 100 to 40.9 % in 20 min.



**Fig. 5.** Influence of the initial concentration on the degradation of Orange II in aqueous solutions containing KSF (KSF 4.0 g/L, pH 3.2). The inset shows the initial rate of Orange II degradation as a function of the initial concentration

It is well known that the heterogeneous photocatalytic degradation of organic pollutants follows the Langmuir-Hinshelwood (L-H) kinetics [12].

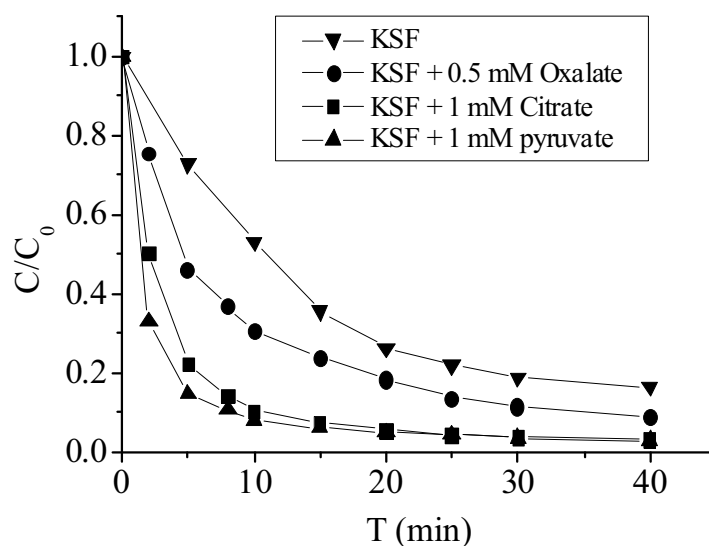
$$R = -\frac{dC}{dt} = \frac{kKC}{1+KC} \quad (1)$$

where  $C$  is the concentration of the dye at time ' $t$ ', and  $k$ ,  $K$  are the rate constant and the adsorption coefficient, respectively. As shown in the inset of Fig. 5, the initial rates of Orange II degradation increased with increasing the initial concentration of Orange II, and the initial reaction rate and initial concentration fitted well into the L-H equation.  $k$  and  $K$  are calculated to be 1.32 mg/L min and 0.050 l/mg, respectively.

### Effect of carboxylic salts

As shown in Fig. 6, the degradation efficiency of Orange II increased by adding 1 M citrate, 0.5 mM oxalate and 1 M pyruvate, respectively, into the KSF suspensions. KSF contained a high content of iron (4.76%). It is well

known that carboxylic salts such as citrate, oxalate and pyruvate could form complexes with iron as Fe (III)-carboxylic salts complex which has higher photoreactivity to produce hydroxyl radicals under visible light irradiation [13]. Also, it was reported that iron oxide in clay minerals could dissolve in suspensions in the presence of carboxylates under irradiation [14]. Thus, the degradation of Orange II was enhanced with more photoactive iron ions in the KSF suspensions.



**Fig. 6.** Influence of carboxylic salts on the degradation of Orange II in aqueous solutions containing KSF. (KSF 4.0 g/L, Orange II 12 mg/L, pH=3.2)

## CONCLUSIONS

The heterogeneous photocatalytic reaction using KSF as a photocatalyst can remove the color of Orange II effectively. The optimum concentration of KSF was 4 g/L. The degradation rate of Orange II catalyzed by KSF was strongly pH-dependent. The degradation efficiency of Orange II increased as the initial Orange II concentration decreased and the degradation kinetics of Orange II followed the L-H rate law. Furthermore, the addition of carboxylic salts to the KSF suspensions can enhance the degradation of Orange II. Thus, KSF as a new photocatalyst, could be considered as a promising alternative to color wastewater purification.



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