

# Photodegradation of Alachlor Over Fe-TiO<sub>2</sub> on Granular Activated Carbon Support under UV and Visible Light

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**Abstract**—Fe-TiO<sub>2</sub> on granular activated carbon support was synthesized via hydrothermal method without calcination. The crystalline phases were identified using X-ray diffraction whereas the surface morphologies were examined using scanning electron microscopy. Peaks of anatase TiO<sub>2</sub> and graphite were present in the Fe-TiO<sub>2</sub>-GAC sample. Comparisons of the surface features of GAC and Fe-TiO<sub>2</sub>-GAC show that Fe-TiO<sub>2</sub> has been immobilized in the pores and on the outer layer of the GAC. Alachlor photodegradation using Fe-TiO<sub>2</sub>-GAC under UV and visible light were compared to removal by adsorption using GAC only. Both photocatalytic experiments gave higher removal efficiencies than the adsorption process. Photocatalysis under UV and visible light can remove alachlor at the same rate after 30 min of reaction. Complete removal of alachlor was observed from all three experiments after 150 min of reaction. The mechanism of alachlor removal using Fe-TiO<sub>2</sub>-GAC has been a combination of adsorption and photocatalysis.

**Keywords**—Alachlor, Fe-TiO<sub>2</sub>, Granular activated carbon support, Photocatalysis.

## I. INTRODUCTION

TITANIUM dioxide, TiO<sub>2</sub>, has always been one of the primarily used photocatalysts in the removal of organics in wastewater mainly because of its excellent properties including strong oxidizing ability, non-toxicity, and photostability [1]. In spite of these advantages, its photocatalytic activity can be decreased due to the high recombination rate of photo-generated electrons and holes, which facilitate the oxidation of the pollutants in wastewater [2].

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Another limitation to this material is that it can only be used effectively under UV irradiation because its energy bandgap is at 3.2 eV. Doping with metals such as Zn, Ag, Pd, Pt, and Fe has been used to adjust it [3]. Fe<sup>3+</sup> ion has been the most popular choice among others because it shifts the adsorption spectrum of TiO<sub>2</sub> such that it can also be under visible light [4].

Additionally, TiO<sub>2</sub> photocatalysts are hard to use in large-scale operations due to difficulties in its separation from the aqueous solution. The use of a support matrix such as silica, glass, polystyrene spheres, and activated carbon will not only address this problem but also, it will provide a larger surface area for photocatalytic sites [5].

Among the common applications of TiO<sub>2</sub> photocatalysis is the removal of organics, including pesticides in aqueous systems [6]. Alachlor is an herbicide widely used in the world for the control of weed in most agricultural crops [7]. In 1993, the US Food and Drug Administration have listed it as a human carcinogen [8]. Due to its wide usage, it may be very easy for it to contaminate groundwater. The most common methods for alachlor removal include adsorption by activated carbon [9] and photocatalysis with Fe-TiO<sub>2</sub> [10].

The aim of this study is to synthesize Fe-doped TiO<sub>2</sub> immobilized on granular activated carbon (GAC) support via hydrothermal method. The catalyst will be used in the photodegradation of alachlor under UV and visible light.

## II. MATERIALS AND METHODS

### A. Chemicals

Titanium tetrachloride (TiCl<sub>4</sub>, 99%) purchased from Merck Schudardt OHG was used in the synthesis of titanium dioxide. Fe<sup>3+</sup> 1000-ppm standard was the dopant. Granular activated carbon (4-12 mesh) purchased from Sigma-Aldrich was the support matrix for the photocatalysts. Synthetic alachlor, PESTANAL analytical standard, was dissolved in HPLC grade water to prepare a 100-ppm stock solution. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) and ammonia solution (NH<sub>4</sub>OH, 28%) were purchased from Ajax Finechem Pty Ltd and QRëc, respectively. HPLC grade acetonitrile and methanol were purchased from Merck and RCI Labscan Limited, respectively.

### B. Catalyst Synthesis

Fe-TiO<sub>2</sub> catalyst was embedded on granular activated carbon support via hydrothermal synthesis. Amorphous titanium dioxide was mixed with 30% H<sub>2</sub>O<sub>2</sub> in cold conditions until the solution became yellow and transparent. A fixed amount of 0.20 wt % of Fe was added using a 1000-ppm Fe<sup>3+</sup> solution. The required amount of GAC was then added as determined from 20 wt % Fe-TiO<sub>2</sub> on GAC. The mixture was then transferred into a Teflon-lined steel autoclave. The hydrothermal treatment was done for 8h at 150°C. The obtained solids were subjected to the subsequent drying conditions: (i) 2h at 40°C; (ii) 4h at 100°C; and (iii) 4h at 250°C.

### C. Catalyst Characterization

The crystalline phase and crystallinity of Fe-TiO<sub>2</sub>-GAC were determined using an X-ray diffractometer (XRD Model D8 Discover, Bruker AXS). For comparison, XRD analysis was also done on Fe-TiO<sub>2</sub> and GAC samples. The morphological features of the catalysts were investigated under a scanning electron microscope (SEM S-3000N, Hitachi).

### D. Photodegradation of Alachlor

Alachlor removal was done by photocatalysis under UV and visible light and by adsorption only. The reactions were carried out in static reactors, which are 100 mL beakers containing 10 mL alachlor solution with an initial concentration of 50 ppm and initial pH 4. A monolayer was formed at the bottom of each beaker with 1 g of Fe-TiO<sub>2</sub>-GAC and GAC only for the photocatalysis and adsorption experiments, respectively. The photocatalysis experiments were done under three 18-W UVA lamps (Philips) and three 22-W fluorescent lamps (Philips). The reaction times for sampling were 0, 10, 20, 30, 60, 120, 150, and 180 minutes. Samples were collected and filtered using a 0.45 μm nylon filter and were kept in sealed amber bottles. The remaining alachlor concentrations were analyzed using high-pressure liquid chromatography (Waters e2695) at the maximum wavelength of absorption of 197 nm for alachlor.

## III. RESULTS AND DISCUSSION

### A. Characterization

Figure 1 shows the XRD pattern of the Fe-TiO<sub>2</sub>-GAC catalyst as compared to that of Fe-TiO<sub>2</sub> and GAC. The XRD pattern of Fe-TiO<sub>2</sub> shows only anatase peaks whereas that of GAC shows only a graphite peak. Since this method did not involve any calcination steps, a combination of these peaks is present in the XRD pattern of the Fe-TiO<sub>2</sub>-GAC catalyst. This confirms that the Fe-TiO<sub>2</sub> has been successfully immobilized on the GAC support via hydrothermal synthesis.

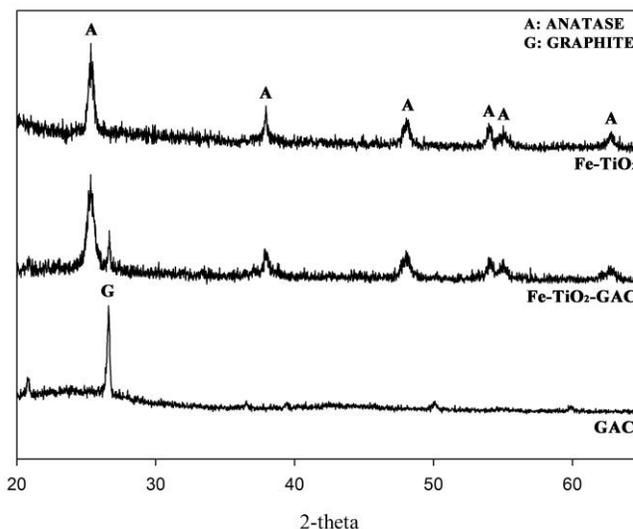


Fig. 1 XRD patterns of Fe-TiO<sub>2</sub>, Fe-TiO<sub>2</sub>-GAC, and GAC

On the other hand, Fig. 2 shows the difference in the surface morphologies of GAC and GAC with Fe-TiO<sub>2</sub>. The surface of GAC is porous and uneven whereas that of Fe-TiO<sub>2</sub>-GAC has a smoother surface. This is a visual confirmation that the Fe-TiO<sub>2</sub> photocatalysts have been embedded on the GAC surface and filled up its pores.

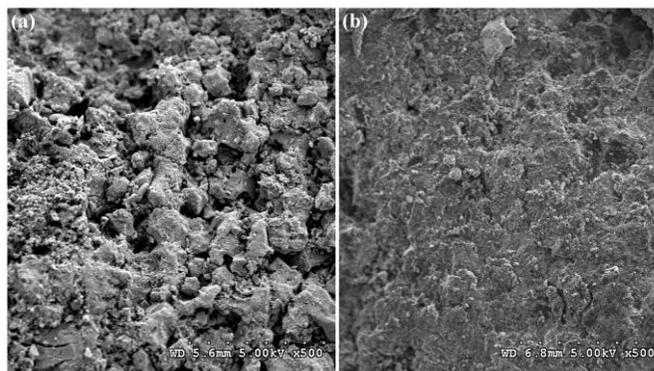


Fig. 2 SEM images of (a) GAC and (b) Fe-TiO<sub>2</sub>-GAC

### B. Alachlor Removal

Fig. 3 shows the different removal efficiencies for alachlor degradation using adsorption and photocatalysis under UV and visible light. It can be observed that all processes have achieved almost 100 % removal after 150 min of reaction. The degradation rates from 120 min to 180 min are almost identical for adsorption and photocatalysis, as the equilibrium point has already been reached. However, the photocatalysis experiments showed higher degradation rates at 30 min to 120 min than adsorption. This confirms that although adsorption still plays a larger role in alachlor removal when Fe-TiO<sub>2</sub>-GAC was used, the photocatalysis was still able to enhance the overall removal efficiency.

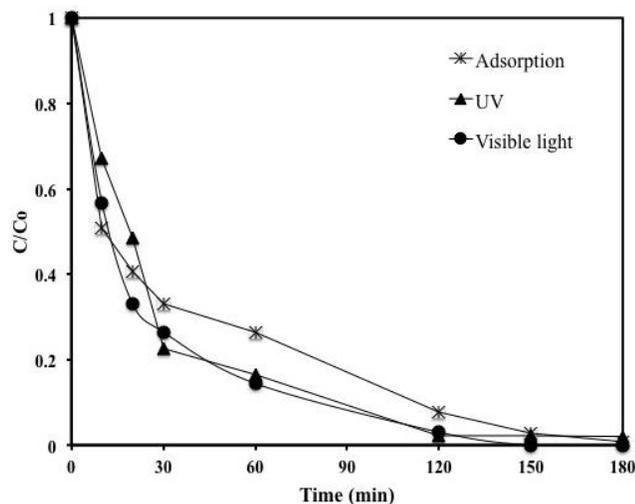


Fig. 3 Alachlor removal by adsorption and photocatalysis under UV and visible light

The degradation rates of the photocatalytic processes under UV and visible light do not differ significantly after 30 min of reaction time. The reactions under visible light at the first 30 min are only slightly faster than those under UV light. Thus, the Fe-TiO<sub>2</sub>-GAC catalysts can be used effectively under both UV and visible light.

#### IV. CONCLUSION

Fe-TiO<sub>2</sub> catalysts were successfully embedded on GAC support directly from the synthesis using hydrothermal method. Photocatalysis under UV and visible light were done using Fe-TiO<sub>2</sub>-GAC whereas adsorption was done using GAC only. Both photocatalytic techniques proved to be more efficient than the adsorption process alone. The performances of the catalyst under UV and visible light are comparable, having been able to remove alachlor to the same extent. This confirmed that the Fe-TiO<sub>2</sub>-GAC catalyst occurred under the synergy of photocatalysis and adsorption processes.

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