

Iron(II)-Impregnated Activated Carbon Composites Applied as Fenton-like Catalysts for Degrading Persistent Organic Compounds

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Abstract. The aim of this work is to investigate the efficiency of a relatively cheap Fenton-like catalyst, Iron-impregnated activated carbon, towards the photo-degradation of organic compounds in aqueous solutions. The catalysts were prepared by wet impregnation method of activated carbons of different textural and chemical properties. Their efficiency as Fenton like catalysts towards Indigo Carmine (IC) degradation in aqueous solution are investigated. UV light irradiation tests are carried out to determine the performance of the prepared Iron-impregnated composite towards the degradation of IC in aqueous solution under different conditions using an UV - Consulting Peschl Laboratory Reactor System. Effects of solution pH and initial concentration of dye onto the process performance are established. Raw and composite materials are characterized by Nitrogen adsorption-desorption isotherms and SEM analysis. The total Iron content of synthesized composites is determined by UV-Vis spectrophotometry using phenantroline. The obtained results emphasize an enhancement of IC degradation in case of the heterogeneous photo-Fenton process conducted with an ozone generating UV lamp.

Keywords: composite, activated carbon, photocatalysis, Fenton, anionic dye.

1. Introduction

The textile industry consumes vast amounts of water in the dyeing and finishing operations, generating significant quantities of wastewaters. Approximately 5 and up to 15% of these wastewaters represent untreated dye that can be released into the environment (Asaithambi *et al.*, 2016; Kumari and Datta, 2016; Vital *et al.*, 2016). In order to obtain an image in absolute terms, it should be recalled that around 100,000 dyes are currently in use by the global textile industry, and 7×10^5 tons of dyestuff is produced annually worldwide (Mohd Adib *et al.*, 2017; Vital *et al.*, 2016). Discharges of untreated dye effluents into the water body produce colored effluents that alterate the cycles of oxygen and nitrogen through photosynthesis (Haham *et al.*, 2015; Mohd Adib *et al.*, 2017). They can also be toxic to aquatic biota (Borhade, 2016; Kumari and Datta, 2016). The wastewater-containing indigo is characterized by a

dark blue color due to cross-conjugated system or H-chromophore, consisting of a single $-C=C-$ double bond substituted by two NH donor groups and two CO acceptor groups (Biasi *et al.*, 2016; Saggiaro *et al.*, 2016).

Conventional physical-chemical methods are known to have several operational problems among which sludge generation, membrane fouling, and phase change of the pollutants are the most often met. To avoid these problems, the use of advanced oxidative processes (AOPs) to degrade the discharged dyes has been proposed (Saggiaro *et al.*, 2016).

Among AOPs, heterogeneous photocatalysis has been very attractive due to it allows energy economy and recovery of the catalyst. The photocatalytic process produces oxidizing species able to promote degradation of organic pollutants through semiconductor as the catalyst (Saggiaro *et al.*, 2014). Photocatalysis is considered a low-cost technique that operates at ambient temperature and pressure and allows the complete mineralization of the target compound (Subramani *et al.*, 2007). Also, the catalysts could be self-regenerated and recycled within the process.

Based on the outstanding adsorption capacity of activated carbon, many studies have focused on the development of novel composites that combine the adsorption capacity of carbon materials with novel properties (Istratie *et al.*, 2016). The aim of this work is to investigate the efficiency of Iron-impregnated activated carbon Fenton like catalyst. Its efficiency as Fenton like catalysts towards Indigo Carmine degradation in aqueous solution is investigated. The adsorption of Indigo Carmine onto activated carbon composites followed by photocatalysis was investigated. The AC was directly contacted with $FeSO_4$ solution using wet impregnation method (Rey *et al.*, 2016). The photolysis was carried out by an UV-V light using an ozone emitting lamp. Effects of solution pH, initial concentration of dye and concentration of H_2O_2 onto the AOP performance are established. Raw and composite materials are characterized by N_2 adsorption-desorption isotherms and thermogravimetric analysis. Total Fe content of synthesized composites is determined by UV-Vis spectrophotometry.

2. Experimental

Activated carbon materials were obtained from PICA-Jacobi (France). Before use, the ACs were washed and dried at 75°C for 24 h. The ferrous sulfate heptahydrate (>99%), and hydrogen peroxide (35 w%) were purchased from Sigma Aldrich. All solutions were prepared using bidistilled water.

Using wet impregnation procedure, 5 g of L27 AC material were contacted with Fe(II) solutions at a theoretical iron content in the resulted composite of 1, 5, 10 and 20 %, respectively. The L27 AC was impregnated for 3h at 45 °C, then filtered, washed several times with water and ethanol and dried at 55 °C for 24 h. The obtained composite is noted further herein as Fe-L27. N₂ adsorption-desorption isotherms (Micromeritics 2020), and scanning electron microscopy (Philips CM20 – 200kV) were used to investigate the structural, textural, and micromorphology of the carbon-based catalyst. Total iron content and iron leakage from catalyst were determined by spectrophotometry using phenantroline.

Photocatalytic tests were performed by means of a lab-scale experimental setup, consisting of a batch reactor equipped with an UV ozone emitting lamp (17 W).

Three types of granular activated carbon matrices were considered in the composite preparation and photocatalytic tests. Having different values of p*H*_{PZC} and different porosity kinds, L27 (acid surface, developed microporous and mesoporous systems), X17 (basic, less developed than L27) and S21 (neutral, only microporous), provided by PICA-Jacobi were tested. Also, several photocatalytic tests were run at different values of IC concentrations (100, 200, 300 and 400 mg/L), solution pH (3, 5, 7 and 10) and H₂O₂ concentration (0.1, 0.25 0.5 and 1 g/L).

In each run, 1 L of 100 mg/L Indigo Carmine solution was placed in a photoreactor (UV - Consulting Peschl Laboratory Reactor System). The mixture was stirred in dark for 24 hours to establish the adsorption-desorption equilibrium between the pollutant model and the catalyst surface. Then UV irradiation was performed for 2h using

an UV ozone emitting lamp (17 W) at room temperature. 0.4 g/L catalyst dose was added to the reactor. H₂O₂ was added in the mixture when UV lamp was turned on. 1 mL of mixture solution was withdrawn at regular time intervals, diluted in distilled water and analyzed by UV-Vis spectrophotometer following the absorbance at 610 nm. After the analysis, the undiluted solution was added back into the photocatalytic reactor to minimize the loss in total volume and maintain the solid/liquid ratio.

3. Results and discussion

3.1. Characterization

Iron-embedded activated carbon composites were prepared by wet impregnation method at several values of iron precursor concentration corresponding to theoretical iron content in composite of 1, 5, 10 and 20%, respectively. By means of the spectrophotometrical method based on phenantroline, the total iron content in composite was determined. The Iron content in the carbon composite increases with the augmentation of the Fe amount contacted with L27 GAC. The highest ratio, about 3% Fe content, is obtained when 1.25 g Fe is contacted with 5 g of L27.

Fig. 1a shows the SEM image obtained for L27 matrix before impregnation. The surface of the prepared Fe-L27 composite is shown in Fig. 1b. The image in Fig. 1b emphasizes the iron oxides aggregates formed on the surface of L27 after the wet impregnation.

Table 1 shows the data of external surface calculated based on the N₂ adsorption-desorption isotherms of L27 AC and thermally treated Fe-L27.

Composite mesoporosity of the impregnated Fe-L27 is slightly higher than that of raw L27. Also, the thermal treatment of iron composite results in a development of mesoporosity and a decrease of the microporosity system which is probably blocked by iron.

In spite of this increase, the total surface of iron composites is slightly lower than that of L27 due to covering of micropores during impregnation.

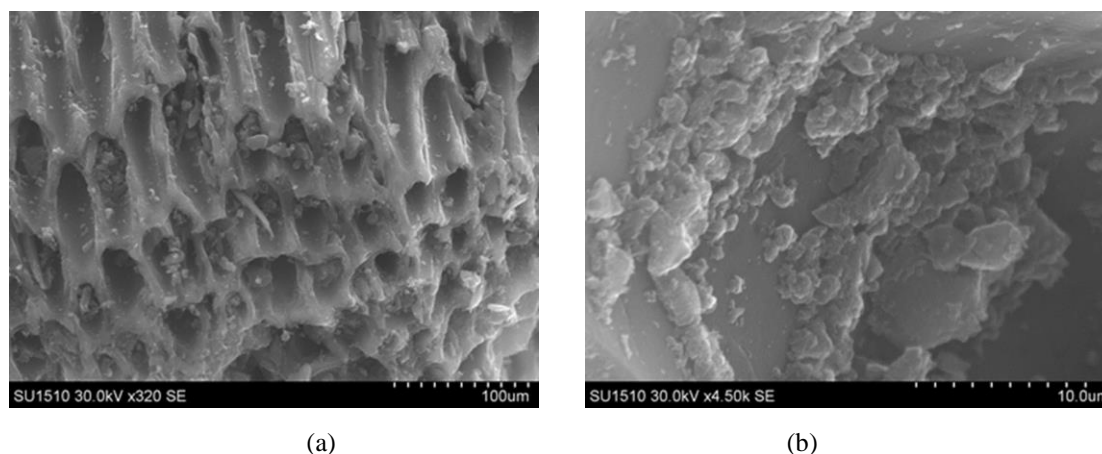


Figure 1. SEM images of L27 (a) and Fe-L27(b)

Table 1. Textural properties of raw and Fe- L27 GAC determined based on N₂ adsorption-desorption isotherms

Material	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	Mean pore size (\AA)	S_{ext} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	S_{total} ($\text{m}^2 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
L27	0.57	18.5	444	616	1060	1575
Fe-L27	0.48	26.8	621	358	979	1380
Fe-L27, T 550°C	0.50	26.4	748	379	1127	1464

3.2. Photocatalytic tests

At first, different Advanced Oxidation Processes (AOPs) were evaluated in order to establish the most performant one towards the degradation of Indigo Carmine (Fig. 2a). In a first test, the simple photolysis was performed to treat a 100 mg/L IC aqueous solution using an UV-C lamp. Then, an Ozone-generator UV-Vacuum lamp was tested as such and by purging air into the photo-reactor with an air pump. Finally, an heterogeneous Fenton process was investigated.

The simple photolysis of an aqueous solutions containing 100 mg/L IC leads to a removal efficiency of about 80% after 5 h of light irradiation using an UV-C lamp. When an UV-Vacuum lamp is used, 99.96% removal efficiency towards Indigo Carmine is reached after only 2 h. If air is purged into the system with an air pump, the Ozone generation by means of the UV-V lamp is enhanced and the complete removal of IC is reached after 40 min.

The Iron(II)-embedded AC composite enhances significantly the degradation process of Indigo Carmine in presence of H_2O_2 . Thus, the complete removal of IC is achieved after only 10 min of light irradiation.

Iron-embedded composites prepared with GAC support of different pH_{PZC} (L27 – acid, X17 – alkaline, S21 – neutral) were investigated in photo-Fenton tests for Indigo Carmine degradation (Fig. 2b).

As can be noted, the catalyst prepared with the neutral-surface support, S21, provided the lowest degradation rate among the three GACs tested. The complete removal efficiency was reached after 30 min of irradiation. The alkaline-surface support, X17, leads to complete degradation of Indigo Carmine after only 25 min whereas the acid-surface support, L27, provides the fastest degradation of Indigo Carmine molecule. In the further investigations only the L27-based composites were considered.

The effect of pH on the performance of the degradation process using Fe-L27 was investigated at four different values of the solution pH (Fig. 3a). In another set of degradation tests, presented in, the effect of initial concentration of Indigo Carmine was established (Fig. 3b). Pseudo-first order kinetics describes well the photo-Fenton degradation process (Fig. 3c).

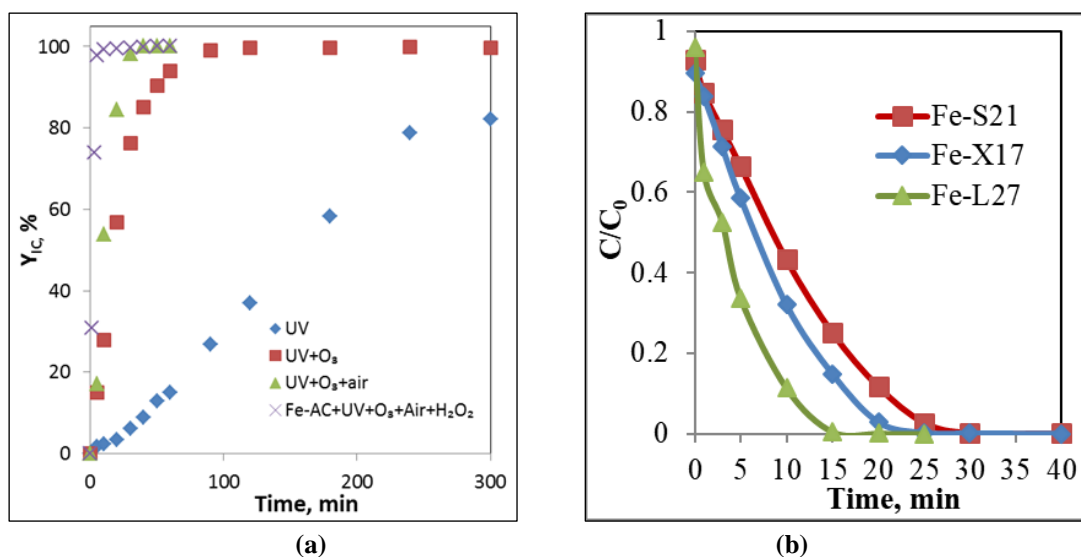


Figure 2. Degradation of Indigo Carmine by different AOPs (a) and in presence of Fenton-like catalysts prepared with GAC support of different pH_{PZC}

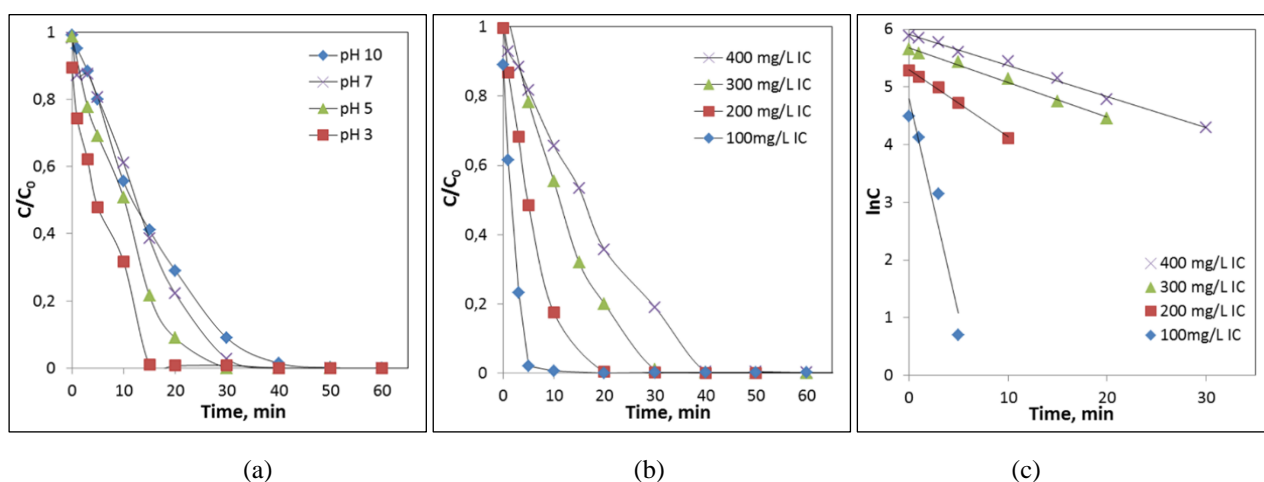


Figure 3. Evolution of IC degradation at (a) different values of pH (100 mg L⁻¹ IC; 0.1 g L⁻¹ Fe-L27; in absence of H₂O₂), (b) initial IC concentration (0.1 g L⁻¹ Fe-L27, 100 mg L⁻¹ H₂O₂, pH = 3), and (c) the process kinetics

Due to the generation of ozone molecules into the bulk solution, the Fenton reaction is developed even without the addition of H₂O₂. As can be noted in Fig. 3a, the more acid the treated solution, the highest degradation rate of Indigo Carmine. At a pH value of 3, the optimum pH condition to degrade Indigo Carmine is met.

Fig. 3b shows that the complete degradation of Indigo Carmine was obtained after 10 min of irradiation of 100 mg/L solution, whereas 40 min of irradiation were necessary to treat a 400 mg/L Indigo Carmine solution. In terms of constant rate, the value decreases from 0.744 min⁻¹ in case of 100 mg/L IC to 0.038 min⁻¹ for a solution of 400 mg/L IC.

Fig. 3c emphasized the enhancement of degradation rate with the lower values of initial IC concentration. Thus, the first order constant rate increases from 0.0738 min⁻¹ in case of 400 mg/L IC up to 0.744 min⁻¹, in case of 100 mg/L IC.

4. Conclusions

Iron(II)-embedded GAC composites were synthesized and used as Fenton-like catalysts for degrading a model pollutant. The textile/food dye Indigo Carmine was considered as model pollutant.

Catalysts containing up to 3 w% of iron were achieved. N₂ adsorption-desorption isotherms show a decrease in total surface after Fe embedment. Photocatalytic degradation tests were conducted under UV light irradiation by using low pressure lamps of 17 W emitting in UV-C and UV-V range respectively.

Fe(II) embedment on L27 having an acid surface provides the possibility to regenerate the AC by photo-Fenton at higher constant rates. It was found that the photo-degradation of Indigo Carmine molecule obeys the pseudo-first order kinetic model. The photo-degradation rate increases at lower values of pH.

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