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Removal of methyl orange wastewater by heterogeneous Fenton-like reaction over activated carbon pre-treated by nitric acid

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ABSTRACT

Activated carbons from coconut shells were treated with different concentration of nitric acid and used as carriers. Fe catalysts supported on treated and untreated activated carbons were prepared by the equivalent-volume impregnation method to remove methyl orange by Heterogeneous Fenton process. The catalysts were characterized by using Brunauer–Emmett–Teller (BET) surface area characterization, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The results are as follows: The order of the activity of adsorption reaction is AC-67%<Fe/AC<AC<Fe/AC-20% < Fe/AC-40% < Fe/AC-67%; The order of the activity of catalytic reaction is AC-67%<Fe/AC-40%<Fe/AC-67% <Fe/AC-20% < Fe/AC< AC; The specific area of Fe/AC-67% is less than that of the activated carbon only infiltrated with $FeSO_4{\cdot}7H_2O$ solution as well as the original activated carbon; Nitric acid treated can increase the surface functional groups of activated carbon, especially increasing –C=O– and –COOH functional groups, which is also not good in the Heterogeneous Fenton process.

Keywords: Heterogeneous Fenton-like reaction; Nitric acid; Methyl orange (MO); Activated carbon (AC); Surface functional groups

1. Introduction

Fenton oxidation [1] is one of the most promising advanced oxidation processes (AOPs) in the treatment of wastewater. Rivas et al. [2] treated p-hydroxybenzoic acid by Fenton's reagent, and assumed a mechanism of reactions based on the classical Fenton's chemistry; they computed concentration profiles of the parent compound, ferrous ion and dihydroxybenzene and compared to experimental results. Kusic et al. [3] compared the efficiency of Fenton and UV-Fenton for treating dye wastewater, and found that UV-Fenton had a better TOC removal. However, some problems still exist in homogeneous Fenton processes, such as the difficulty in separation of the reactant and reaction products in homogeneous reaction and in recycling the catalyst. Thus, it is imperative to study the heterogeneous catalyst. The preparation and optimization of catalysts is one of the most important problems in the heterogeneous Fenton system.

A large number of studies have shown that acid-treated catalyst will lead to different activities. Guo et al. [4] used acids to treat Ni-imbedded coal-based activated carbon (AC) for desulfurization, and discovered that the acid can remove some inorganic contaminants in AC, thus increasing the surface area and the associated reaction activities of the Ni-imbedded AC. Luo et al. [5] modified AC by heating it in an inert atmosphere and then impregnating it with benzoic acid solution to remove gaseous mercury chloride; they found that acid-tread AC could increase the amount of C=O and C-O- oxygen. It is also found that the sorbents will have different surface areas and total (often smaller) pore volume after modified by different acid [6]. However, the relationship between the AC structure after acid-treated and activity of catalysts in the heterogeneous Fenton process for treatment of textile wastewater has not been studied.

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To fill this knowledge gap, HNO_3-treated Fe-imbedded AC (Fe/AC) was prepared in this study by using the dip-molding method [7], and then used as a platform to evaluate the influence of the acid-treated Fe/AC structure on remove methyl orange (MO) in synthetic textile wastewater. The effect of catalyst preparation and the relationship between the structure and activity of the catalysts were evaluated via different tests and data interpretations. The activity of the catalysts was evaluated through the structure analysis of the catalysts via Brunauer-Emmett-Teller (BET) tests, Fourier Transform Infrared (FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Experiment

2.1. Materials and reagents

The original coconut shell activated carbon (AC) was provided by the National Engineering Research Center for Flue Gas Desulfurization (Chengdu, China). 30% H_2O_2 solution, 67% HNO_3 solution (density = 1.4 g/cm^3), $FeSO_4·7H_2O$ (used as the iron precursor of the catalyst), and other reagents were provided from Chengdu Kelong Chemical Reagent Company (Chengdu, China). All chemicals mentioned in this work were of analytical grade. Deionized (DI) water was made with a water purifier (Ulupure UPT-II-10T, Chengdu Ultrapure Technology Co., Ltd, Chengdu, China) with a resistivity of 18.25 MΩ-cm. MO solution was prepared as synthetic textile wastewater (30 mg/L). The selection of MO as a model dye compound in this study is because it is commonly or widely used in many industries nowadays and typically considered as non-biodegradable.

2.2. Preparation of acid-treated carbon catalyst

Activated carbon was washed with DI water three times in order to remove the soluble material on the surface of the activated carbon, and then dried out. To each 250 mL beaker, 10 g original washed activated carbon and 100 mL HNO_3 solution of a mass fraction of 0, 20%, 40% and 67% were mixed, respectively in a thermostatic oscillator (SHA-2(A), Baita Xinbao Instrument Factory, Changzhou, Jiangsu, China) at 50°C and 200 rev/min (rpm) for 3 h. Then wash the solids with DI water until the pH of the effluent is neutral and dry out in the Electric Oven Blast (DHG-9030A, Shanghai Hongdu Electronic Technology Company, Shanghai, China) at 100°C for 24 h. 0.7446 g $FeSO_4·7H_2O$, 18 mL DI water and 5 g four kinds of acid-treated activated carbon were mixed in each baker respectively in a water bath at 30°C for 24 h. All catalysts were dried at 100°C overnight and calcined at 500°C for one hour under a nitrogen atmosphere (the heating rate is 10°C/min, heating from indoor temperature to 380°C and keep 380°C for 1 h). The iron loading on the activated carbon is 3% theoretically by weight. All chemicals mentioned in this work are of analytical grade. The original activated carbon, denoted as AC; the activated carbon treated with 67% HNO_3 without infiltrated with $FeSO_4·7H_2O$ solution, denoted as AC-67%; the activated carbon infiltrated with $FeSO_4·7H_2O$ solution without treated by 67%HNO_3 denoted as Fe/AC; the activated carbon treated with different concentration of HNO_3 and $FeSO_4·7H_2O$ solution, denoted as Fe/AC-20%, Fe/AC-40% and Fe/AC-67%.

2.3. Activity evaluation

All the experiments were carried out in glass baker (total volume is 1 L), which were shaken (in a Thermostatic Oscillator) and water-bathed (30°C). Add 1 L synthetic wastewater in the glass flask. The pH is adjusted to 3 by 1 mol/L sulfuric acid and 0.1 mol/L sodium hydroxide. 0.1 g catalyst was added in the glass flask at setting time 0 min and 0.6 mL 30% H_2O_2 was added at setting time 30 min. Collect samples at setting time of 0, 10, 20, 30 (before adding H_2O_2 solution), 40, 60, 80, 100, 120, 140 and 160 min the liquid phase was separated by a glass syringe with a 0.45 μm filter membrane and the solute concentration determined at the characteristic absorbances of 464 nm (all samples) using a UV/vis spectrophotometer (UV-1100/UV-1200/V-1200, Mapada, Shanghai, China) equipped with a quartz cell of 1.0 cm path length. Calculate the decoloration rate of MO solution. The TOC of the samples at setting time 0, 30, 40, 80, 120 and 160 min were detected by a TOC analyzer (Liqui TOC II, elementar, Germany) to calculate the mineralization rate of MO solution [8].

The MO removal (%) is calculated by following formula:

$$\text{MO removal}(\%) = \frac{X_0 - X_t}{X_0} \times 100\% \tag{1}$$

X_0 - the original concentration of MO, mg/L; X_t - the concentration of MO at t time, mg/L

The TOC removal (%) is calculated by following formula:

$$\text{MO removal}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100\% \tag{2}$$

TOC_0 - the TOC of original MO, mg/L; TOC_t - the TOC of MO at t time, mg/L.

2.4. Analytical methods and characterization of catalyst

A Micromeritics ASAPM2020 apparatus was used to determine the specific surface area and pore size of activated carbon before and after modification.

X-ray photoelectron spectroscopy (XPS) were carried out on a spectrometer (XSAM-800, KRATOS Co.) to get the possible functional groups of catalyst. The elements C, O was detected.

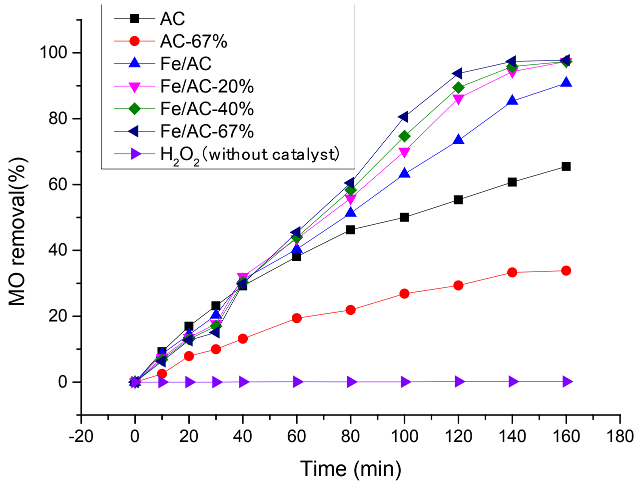
Fourier transform infrared spectroscopy (FTIR) was applied with a FTIR-650 Fourier Transform Infrared Spectrometer (Gangdong company, Tianjin, China). Its resolution factor was 2 cm^{-1} from 400 to 4000 cm^{-1}.

The absorbance at 464 nm was related to the color of MO in the solution and was used to calculate the decolorization rate of MO from aqueous solution [8].

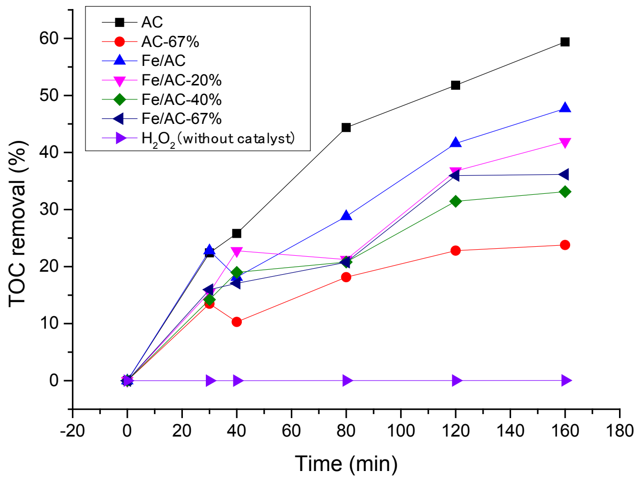
3. Results and discussion

3.1. Adsorption and catalytic performance of catalysts

The adsorption and catalytic performance of catalysts are presented in Fig. 1. Catalytic reaction began after adding H_2O_2 at setting time 30 min. As shown in Fig. 1a,



(a) Decolorization rate of the reaction



(b) Mineralization rate of the reaction

Fig. 1. Performance of catalysts in the reaction.

the decolorization efficiencies of catalysts loaded with Fe treated by NA (i.e., Fe/AC-20%, -40% and -67%) or not treated by NA (i.e., Fe/AC) were above 90% after 160 min. However, the decolorization efficiency was low for AC (<65% at 160 h) and AC-67% (AC treated by 67% NA) (< 35% at 160 h). Therefore, the heterogeneous Fenton system (i.e., Fe/AC + H_2O_2) is very effective to remove MO from wastewater. In this study, filtrate TOC was measured for samples collected at different times. Thus, the removal of TOC indicates the sorption of MO onto the catalysts and/or transformation of MO to CO_2 and H_2O. As shown in Fig. 1, after 30 min adsorption, the decolorization efficiency of the MO is 23.19%, 17.7%, 17% and 15.1% for Fe/AC, Fe/AC-20%, Fe/AC-40% and Fe/AC-67% respectively while the TOC removal rate efficiency is 22.4%, 15.46%, 14.2% and 15.96% respectively. These results indicate that without Fenton reaction, the TOC removal rate of MO by AC or Fe/AC with or without NA treatment would be very limited, and thus, the associated decolorization of MO during the 30-min reaction period is mainly due to the sorption of MO onto the catalysts. After catalytic reaction at setting time 160 min, the TOC removal efficiency is 59.38%, 41.9%, 33.12% and 36.15% for Fe/AC, Fe/AC-20%, Fe/AC-40% and Fe/AC-67%, respectively. Comparing Fig. 1a and 1b, it can be concluded that the Fe/AC can sorb > 90% MO and transfer about 60% of the MO in the wastewater into CO_2 and H_2O, while Fe/AC treated with 20%, 40% and 67% NA can sorb > 90% MO but mineralize about 42%, 33% and 36% of MO in the wastewater.

Table 1
The specific surface areas of samples

Samples	S_{BET} (m^2/g)	Average pore size(nm)
AC	1027	2.1
Fe/AC	985	2.22
AC-67%	293	2.5
Fe/AC-67%	683	2.34

According to the results, the order of adsorption activity and catalytic performance of catalysts from poor to good is as follows: Fe/AC-67% ≈ Fe/AC-40% < Fe/AC-20% < Fe/AC. As for original AC, the TOC removal efficiency was almost the same as the decolorization efficiency of MO, which means that only the adsorption process (and thus, no catalytic reaction of MO) was involved in the AC system because there was no Fe loaded on the surface of AC.

The TOC removal efficiency was generally lower than the decolorization efficiency of MO except AC. The difference between decolorization rate and TOC removal rate suggests that some of the MO is transformed to intermediate compounds rather than CO_2 and H_2O. Liou and Chen [9] and Quintanilla et al. [10] obtained the similar results for catalytic wet peroxide oxidation using Cu/AC and Fe/AC. Fig. 1 shows that after treated with NA and $FeSO_4\cdot7H_2O$, AC has poor adsorption performance as well as better catalytic performance, but the catalytic reaction is not complete.

3.2. Surface area of samples

The specific surface areas of the untreated and treated activated carbon are listed in Table 1.

The results showed that the BET surface of samples followed a descending order: AC>Fe/AC >Fe/AC-67%>AC-67%. Meanwhile, the average pore size of the samples showed the opposite tendency to the order of BET surface area staying close to micro pore range (2 nm). AC has a high surface area (1027 m^2/g), whereas that of Fe/AC decreases to 985 m^2/g. It is possibly because that the loading of Fe species on AC blocked some microporous on the surface [11]. After HNO_3 treated, the BET surface of AC-67% decreased to 293 m^2/g. That may because some of the thin pore walls on AC are destroyed by strong oxidation of HNO_3 [6] as well as the formation of new functional groups through oxidation reactions. Combining the two roles, the BET surface of Fe/AC-67% is reach to 683 m^2/g. In Fig. 1, it is also confirmed that the acid-treated catalysts have lower adsorption performance compared with Fe/AC because of the decrease of BET surface areas [12].

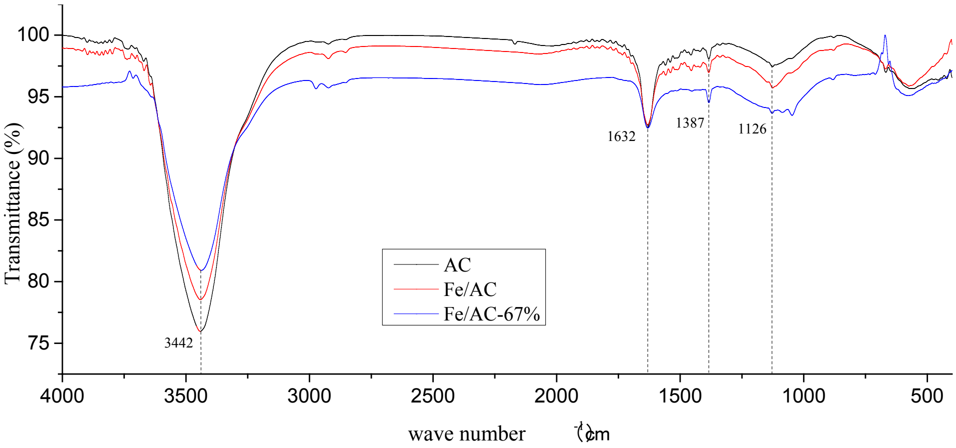


Fig. 2. FT-IR spectra of AC, Fe/AC, Fe/AC-67%.

3.3. FT-IR study

In order to investigate the changes in the surface groups, FT-IR chatacterization was carried out on AC, Fe/AC, Fe/AC-67% samples. The FT-IR spectra were recorded between 400 cm^{-1} and 4000 cm^{-1}. The results are shown in Fig. 2.

The mutual peaks at the bond of 3442 cm^{-1} were corresponded to –OH stretching vibration originating from H_2O molecular [13,14]. The peak of Fe/AC-67% at the bonds of 1632 cm^{-1} was corresponded to Stretch of C=O in carboxylic groups or Carbonyl groups [13], which is relatively stronger than those peaks of the Fe/AC. It means that the surface chemical properties of AC samples changed in the process of modification by acids. The absorption band at 1126 cm^{-1} was attributed to the vibration of C-O bond. What's more, the adsorption band at 1387 cm^{-1}, assigned to the COO$^-$ symmetric vibration, also showed a higher shape in the spectra of Fe/AC-67% rather than Fe/AC. The activity of catalysts decreased with the increase of –C=O–, –C–O– and –COOH.

3.4. XPS study

XPS analysis was performed to investigate the surface functional groups of the AC, Fe/AC and Fe/AC-67% catalysts. The results of C 1s spectra of AC, Fe/AC, Fe/AC-67% are shown in Table 2. The XPS pattern of the C 1s region is shown in Fig. 3.

The samples contain several carbon mixtures. Fe/AC has one major peak at 284.58eV, with three shoulders at 285.64eV, 287.19eV and 289.09eV. The peak near 284.58eV corresponds to graphitic carbon; the peak around 285.64eV refers to carbon atoms in phenol, alcohol or ether groups; the peak closed to 287.19eV corresponds to carbon atoms in carbonyl or quinine groups; and the peak at 289.09eV relates to carbon atoms in carboxylic, lactone or ester groups [15,16]. The C 1s BE values of Ni/AC-HNO_3 and Ni/AC-H_2SO_4 are close to the C 1s BE values of Ni/AC, indicating that the carbon properties of the original activated carbons do not change after acid treatment, except for the presence of oxygen groups on the surface. Although the relative intensity of –COOH of Fe/AC-67% is less than that of Fe/AC, the peak area of –COOH of Fe/AC-67% is actually more than that of Fe/AC. It illustrates that –C=O– and –COOH functional groups of catalyst increases after the activated carbon is treated by nitric acid, which has the same results with FT-IR study. With the change of the functional groups amount, the catalysts got different catalytic performance. We believed that –C=O= and –COOH of catalyst has no good in the Heterogeneous Fenton process. That may because the increase of –C=O– and –COOH decomposed more H_2O_2 into O_2 and H_2O rather than Hydroxyl radicals, which cannot contribute to MO removal. The H_2O_2 decomposition on carbon surfaces into H_2O and O_2 involves two steps. First, the exchange of a surface hydroxyl group with H_2O_2 anions, and second, the surface peroxide that is formed decomposes another H_2O_2 molecule with the release of O_2 and H_2O [17].

Table 2
Relative contents of functional groups in C 1s from XPS spectra

Samples	Element concentration (wt%)		Functional quality score(wt%)			
	C	O	–C=C–	–C–O–	–C=O–	–COOH
AC	80.82	16.79	65.6	21.3	6.6	6.3
Fe/AC	79.82	18.42	65	21.3	5.9	7.7
Fe/AC-67%	79.51	18.74	65	20	8.4	6.8

3.5. Iron leaching of samples

In terms of stability, the Fe/AC-67% catalyst presented the higher levels than Fe/AC. The iron leaching of the samples after reaction (160 min) are shown in Table 3. The iron leaching is related with the nature of the iron species and their location on the AC carrier [18]. The difference of iron leaching between Fe/AC and Fe/AC-67% may be caused by the differences of natural AC and AC-67% for changing the iron species and iron location. The best catalytic performance, together with a lower iron leaching, makes Fe/AC a better catalyst in heterogeneous Fenton-like reaction compared with Fe/AC-67%. What's more, the lower iron leaching is important for reutilization of the catalyst.

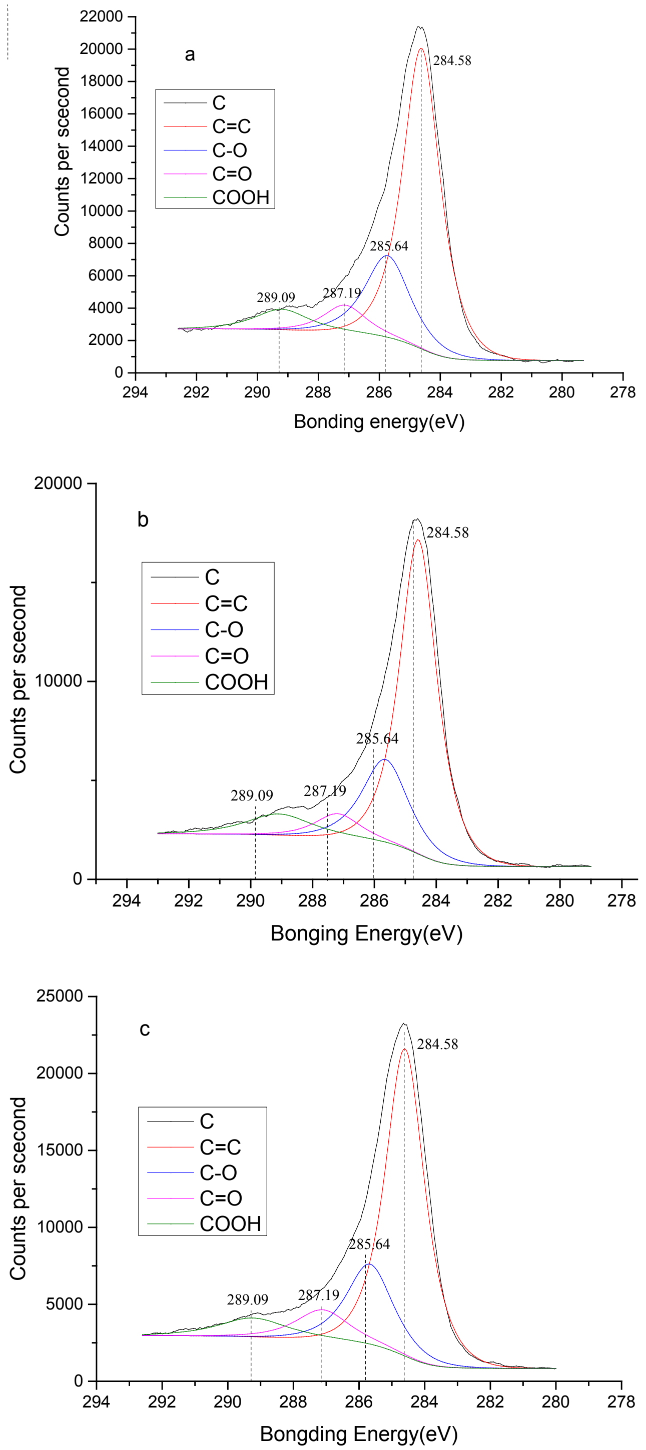


Fig. 3. The binding energy patterns of C 1s for AC (a), Fe/AC (b) and Fe/AC-67% (c).

Table 3
The iron leaching of the samples

Samples	Fe/AC	Fe/AC-67%
Leaching (mg/L)	1.17571	1.814036

4. Conclusions

HNO_3-treated original activated carbons will slightly decrease the performance of catalysts in the Heterogeneous Fenton process to remove methyl orange. It can decrease the BET surface of AC, which leading to the less adsorption of MO. Meanwhile, HNO_3-treated original activated carbons can increase the –C=O– and –COOH functional groups, which may also bad for the catalytic reaction in the Heterogeneous Fenton process.

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