Efficient Removal of Methylene Blue by Fenton-like Reaction using nZVI/GAC Composite as Catalyst

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Abstract—A composite of nano-zerovalent iron (nZVI) supported on granular activated carbon (GAC) was synthesized through adsorption-reduction method, and its performances as catalyst of Fenton-like were investigated to degrade methylene blue (MB) in model wastewater. The results show that homogeneous dispersion of nZVI was greatly improved after supported on GAC. In comparison, the composite (nZVI/GAC) has higher removal efficiency of MB than the same amount of nZVI or GAC. Moreover, the pH values increased and leaching iron was reduced after reaction which were help to further processing with low cost. The use of nZVI/GAC composite provided a selective and viable solution for removing MB from water by Fenton-like reaction.

Keywords—Fenton-like; methylene blue (MB); nZVI/GAC catalyst; removal

I. INTRODUCTION
Organic pollutants have been widely detected in aquatic environment with the increasing of contamination. Fenton and Fenton-like systems either heterogeneous or homogeneous have been extensively studied in view of their high efficiency, simplicity and environmental friendliness [1]. Nano-zero valent iron (nZVI) is currently of an interest catalyst to decompose hydrogen peroxide (H₂O₂) to produce hydroxyl radicals (·OH) owing to its high surface and activity in Fenton-like system. However, nZVI is tend to aggregate because of its small size, which decreases the surface area of nZVI and hinders the regeneration of ferrous ions (Fe²⁺), often resulting in the decrease of catalytic degradation efficiency[2]. Thus, it is necessary to modify the features of nZVI. Granular activated carbon (GAC), as a carrier of commonly used support material, has been proved to be effective for increasing dispersion and impeding aggregation of nZVI [3]. Moreover, recent studies have indicated that iron-carbon microelectrolysis system can be formed between AC and iron spontaneously when iron (anode) and AC (cathode) particles are mixed and contact with each other [4-6]. The X-ray diffraction patterns (XRD) were tested by powder diffractometer (Bruker D8, Germany). Scanning electron microscopy (SEM) (Tescan, VEGA 3 LMH, Czech) was used to view the surface characteristics and morphology of nZVI/GAC composite. MB concentration in aqueous samples was measured by spectrophotometry with wavelength at 665 nm.

Herefore, in the present study, methylene blue (MB) which always causes waste disposal problems in textile industries was selected as the model pollutant. The composite of GAC supported nZVI (nZVI/GAC) synthesized via adsorption-chemical reduction method was used as heterogeneous catalyst in the Fenton-like system. The performances of the catalyst were evaluated aiming to achieve a high efficient catalyst with low environment effect.

II. MATERIALS AND METHODS

The nZVI/GAC composite was prepared by chemical reduction in sodium borohydride solution. First, GAC was adsorption saturated with Fe²⁺ via mixture of FeSO₄·7H₂O and GAC. Then the saturated GAC was separated and reduced using sodium borohydride solution in N₂ atmosphere[8].

The batch experiments were conducted in 250-mL vials placed on a rotary shaker. The temperature and rotate speed were 25°C and 120 rpm, respectively. Each glass was filled with 50mg/L MB solution (200 mL) and a certain amount of H₂O₂. The initial pH value was adjusted by 0.5 M H₂SO₄. At interval time, the supernatant liquid was collected for MB and iron concentration analysis after centrifugation for 10 min at 4500 rpm.

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III. RESULTS AND DISCUSSION

A. Structure of nZVI/GAC Composite

The XRD pattern and SEM images of nZVI in the absence and presence of GAC are presented in Figure I. As shown in the Figure Ia, the representative peak of zero valent (Fe⁰) at 2θ= 45° was observed indicating that the main state of iron was Fe⁰ which was consistent with the results obtained in previous experiment[9]. The peak at 2θ= 25° are typically peak of C 002 which confirmed the presence of GAC in the composite. From Figure Ib and c, it is obvious that the bare nZVI was liable to be agglomeration due to the high active surface of nanoparticles (Figure Ib). However, as comparison nZVI particles well dispersed on GAC carrier (Figure Ic), illuminating the homogeneous dispersion of nZVI was greatly improved after supported on GAC. This might be a big potential to enhance Fenton-like catalytic efficiency in real application.

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B. MB Removal by nZVI/GAC Fenton-like

The removal efficiency in the presence of nZVI, GAC, and nZVI/GAC composite was investigated with 50 mg/L MB, 5 mmol/L H$_2$O$_2$, 0.015 g/L nZVI, 0.5 g/L GAC, 0.5 g/L nZVI/GAC, and initial pH of 4.02. As shown in Figure II, the removal ratio of MB for nZVI, GAC, and nZVI/GAC was 27.1, 41.4, and 84.6% respectively. It is clear that the higher removal was achieved with nZVI/GAC composite as Fenton-like catalyst. Moreover, the removal ratio for the composite was higher the sum of nZVI and GAC, implying that synergistic effect was existence when association nZVI with GAC in virtue of internal iron-carbon microelectrolysis formed spontaneously in such a composite.

![Figure I](image1.png)

**FIGURE I.** XRD PATTERN AND SEM IMAGES of nZVI and nZVI/GAC composite

![Figure II](image2.png)

**FIGURE II.** Changes of Removal ratio to MB

C. Environmental Effects after Reaction

Previous studies show that the efficiency of Fenton reaction is very dependent on pH values, and an optimum working pH range is 2.8 ~ 3.2 for classical Fenton reaction[10]. Nevertheless, such a low pH is not desired for the effluent of Fenton reaction because of the costs of acidification during subsequent processing and neutralization after treatment. In addition, iron leaching is also a problem that must be considered for Fenton reaction. Thus, environmental effects including pH and dissolved iron was detected in the process of reaction with 50mg/L MB, 0.5 g/L nZVI/GAC, 0.015 g/L nZVI, 5 mmol/L H$_2$O$_2$, and 4.02 of pH, and the results are shown in Figure III. From Figure IIIa, the pH values slightly increased from 4.02 to 4.12 for nZVI, but for nZVI/GAC the pH values dramatically increased from 4.02 to 5.13. Similarly, the leaching of iron was significantly reduced compared to nZVI individually (Figure III b). Hence, the increase of pH and decrease in leaching iron are great of advantages for Fenton-like process as cost saving in the water subsequent processing.

![Figure III](image3.png)

**FIGURE III.** pH values and dissolved iron concentration changes in Fenton-like reaction
IV. CONCLUSIONS

This study revealed the potential of nZVI/GAC composite for the removal of MB from aquatic environment. The catalytic effect of Fenton-like was significantly improved as nZVI supported on GAC carrier owing to the internal iron-carbon microelectrolysis. Furthermore, pH values increase and leaching iron decrease after reaction are more desirable trends for polluted water treatment by Fenton method.

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