

Degradation of H-acid in aqueous solution by microwave assisted wet air oxidation using Ni-loaded GAC as catalyst

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Abstract: A novel process, microwave assisted catalytic wet air oxidation (MW-CWO), was applied for the degradation of H-acid (1-amino-8-naphthol-3, 6-disulfonic acid) in aqueous solution. Ni-loaded granular activated carbon (GAC), prepared by immersion-calcination method, was used as catalyst. The results showed that the MW-CWO process was very effective for the degradation of H-acid in aqueous solution under atmospheric pressure with 87.4% TOC (total organic carbon) reduction in 20 min. Ni on GAC existed in the form of NiO as specified by XRD. Loss of Ni was significant in the initial stage, and then remained almost constant after 20 min reaction. BET surface area results showed that the surface property of GAC after MW-CWO process was superior to that of blank GAC.

Keywords: microwave; degradation; catalysis; nickel; wet air oxidation

Introduction

Wet air oxidation (WAO) is regarded as an effective method for the treatment of wastewater containing high concentrations of organic pollutants, especially for non-biodegradable substances. In WAO process, under typical conditions (180–315 °C, 2–15 MPa) organic pollutants can be oxidized to simple compounds, even to carbon dioxide and water. At the same time the chemical oxygen demand (COD) removal efficiency could reach as high as 90% (Luck, 1996). However, its application is restricted due to its severe operating conditions, requiring high costs for construction and operation. Although catalyst applied in WAO (called CAWO) could moderate operating conditions, it is still necessary to maintain relatively high temperature and pressure (Luck, 1999). It is very significant to innovate upon WAO to treat wastewater under milder conditions even under atmospheric pressure.

Recently, some research progresses in microwave (MW) chemistry have presented the feasibility to apply MW in pollution control. It was found that the reaction time could be shortened and the yields or the purities of the product could increase in some chemical reactions when MW radiated simultaneously to them (Varma, 1999; 2002). It has been reported that MW radiation could alter chemical dynamics and decrease activation energy in some chemical reactions. Some researchers assumed that the acceleration of chemical reactions ascribe to non-thermal MW effect (Pollington, 1991). MW has been used to accelerate chemical reactions, and even to induce refractory reactions (Jin, 1999). MW-assisted process has been used to remedy soils contaminated with persistent organic pollutants (POPs) (Abramovith, 1998), or to regenerate used activated carbon (Liu, 2004). Generally, special materials with excellent capability to absorb MW energy, were recommended to be feed into reaction phase in order to utilize MW energy more effectively (Jin, 1999). Activated carbon or special metal oxides (such as NiO) were the common materials applied for the function (Menendez, 2002). Although MW has been applied in solid treatment under relative dry conditions for pollution control as mentioned above, it has not been reported for the degradation of organic pollutants in aqueous phase using MW related process.

The objective of this work is to investigate the feasibility of MW assisting process in wastewater treatment for the degradation of organic substance in aqueous solution under normal pressure. H-acid (1-amino-8-naphthol-3, 6-disulfonic acid) was selected as model substance. As an initial work, NiO was used as catalyst.

1 Experimental

1.1 Experimental setup

A modified MW furnace (Whirlpool Model T120, China) was used as MW source. A $\phi 50$ mm hole was drilled on its cover, with a copper pipe ($\phi 40$ mm \times 50 mm) inserted to prevent MW emission (Jin, 1999). The quartz column reactor ($\phi 32$ mm \times 350 mm) was installed into MW furnace through the hole of the copper pipe, and the top of the column was connected to a vertical water cooling condenser system. Two bottles, charged with 10 ml distilled water and 10 ml 0.1 mol/L of NaOH solution were used to absorb the gas-off after condensation. Air compressor was used to supply air. All the experiments were performed under the atmospheric pressure. The experimental setup is shown in Fig. 1.

1.2 Materials

Commercial GAC (C. P., Tianjin Chemical Reagent Company, China), with a particle size of 1.0–2.0 mm, was immersed in 10% HCl, washed with distilled water, and dried at 105 °C for 2 h. Afterwards, it was immersed in 15% (wt. %) Ni(NO₃)₂ solution for 4 h. After separation of the GAC from the solution by filtration, it was dried at 105 °C for 2 h, calcined at 300 °C in a muffle furnace for 4 h and stored in a desiccator for use.

H-acid was purchased from Shanghai Chemical Reagent Company, China.

1.3 Characterization and analysis

Powder X-ray diffraction (XRD) pattern of the GAC was recorded with a Shimadzu LabX XRD-6000 X-ray diffractometer using Cu K radiation. The surface morphology of the GAC was determined by scanning electron microscopy (SEM) using Oxford JSM-5600 LV microscope assisted with energy dispersive X-ray (EDX) to analyze atomic composition on the surface examined.

Determination of H-acid concentration in the adsorption solution was performed by a HPLC (Jasco 1575), using a Kromasil ODS (5 μ m, 5 mm \times 150 mm) reverse phase column, with mobile phase of 0.05 mol/L Na₂SO₄:methanol = 98:2 at a flow rate of 1.0 ml/min and UV detector at 234 nm. A total organic carbon analyzer (TOC, Shimadzu TOC-V_{CTH}) was employed to investigate the mineralization levels of the solution treated.

The surface area of GAC samples was determined with BET, and total pore volume was determined with an automated gas sorption system, using N₂ as the adsorbate at 77 K. The samples were heated at 120 °C and degassed under vacuum to around 10⁻⁵ Torr prior to the determination.

Ni amount in GAC and Ni^{2+} concentration in solution were determined with atomic adsorption spectrometer (Perkin-Elmer 5100PC). The pretreatment procedures for determination of Ni in GAC were as follows: approximately 1 g of GAC was heated at 105 °C to constant weight. After cooling to room temperature, 0.500 g of GAC was accurately

weighed. Ni in GAC was extracted by 20 ml mixture of concentrated HCl and HNO_3 solution (2 h of shaking at 250 r/min, followed by 30 min of ultrasonic extraction). The extraction procedure was repeated for 3 times, and the extracts were fully mixed and adjusted pH 3.0 for analysis.

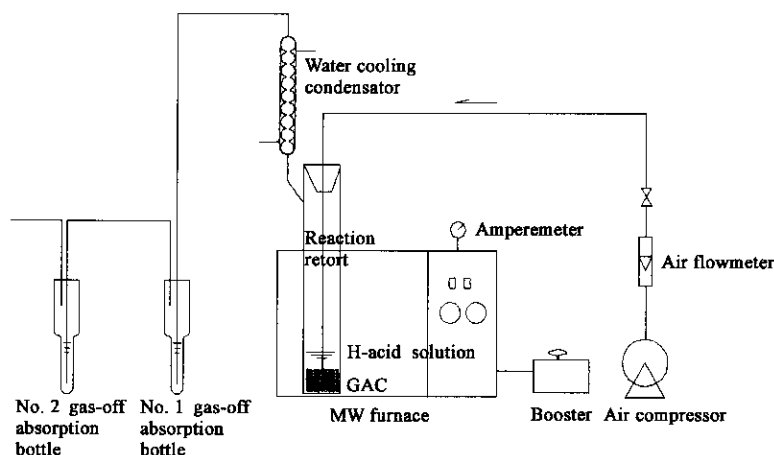


Fig.1 Experimental setup

2 Results and discussion

2.1 Characterization of Ni-loaded GAC

From EDX spectrum (Fig. 2a), there appears no nitrogen peaks, indicating that $\text{Ni}(\text{NO}_3)_2$ had been entirely decomposed. The Ni amount on the GAC was determined to

be 9.31%. Fig.2b shows XRD patterns of Ni-loaded GAC. The sharp intensive peaks at $2\theta = 43.3^\circ$ and $2\theta = 37.3^\circ$, corresponding to NiO crystalline, can be observed, indicating that Ni existed in the form of NiO in the GAC, while there was no evident crystalline structure for blank GAC.

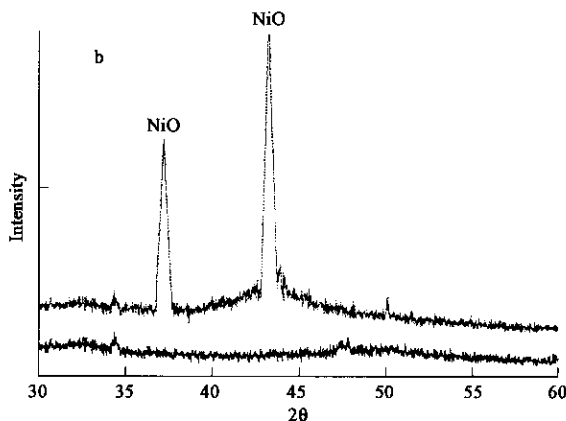
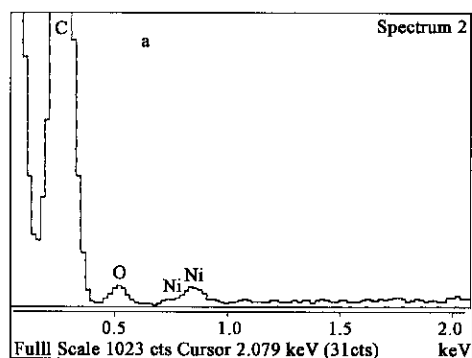


Fig.2 Characterization of GAC

(a) EDX spectrum of Ni-loaded GAC; (b) XRD pattern of Ni-loaded GAC and blank GAC

2.2 Adsorption isotherm of H-acid on blank GAC and Ni-loaded GAC

Before MW degradation experiments, the adsorption equilibrium isotherms of H-acid on blank GAC and Ni-loaded GAC were measured according to the method given by Abdul and Campbell (Abdul, 1996). It is found that adsorption curves obtained well fitted to the Freundlich model: $q = kC^{1/n}$ (Fig.3).

We can also learn from the two regression curves that the equilibrium adsorption amounts of H-acid on blank GAC and Ni-loaded GAC were 96.1 and 63.2 mg/g respectively at the equilibrium concentration of 3000 mg/L. The decrease of adsorption amount on Ni-loaded GAC with comparison to that on blank GAC, was possibly due to the occupation of Ni on partial surface of GAC.

2.3 Effect of Ni on degradation of H-acid

Before MW radiation, both 10 g non-Ni-loaded GAC (for control) and the same amount of Ni-loaded GAC previously adsorbed H-acid through equilibrium of them in 3000 mg/L

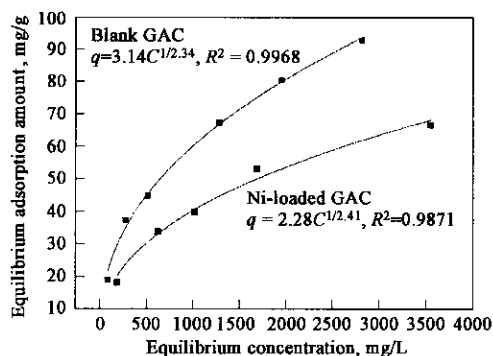


Fig.3 Adsorption isotherms of H-acid on two kinds of GAC at 20 °C

H-acid solution in order to eliminate the decrease of H-acid concentration due to adsorption during MW operation. Then, they and 25 ml fresh H-acid solution (3000 mg/L) were

added into the quartz column reactor. The experiment was carried out under the conditions of 750 MW power and 0.5 L/min airflow rate. It can be seen from Fig. 4 that H-acid was degraded effectively under MW radiation. Ni could accelerate the degradation obviously. The TOC removal reached 87.4% with Ni-loaded GAC in 20 min, whereas it was only 48.8% with non-Ni-loaded GAC in the same time period. The result indicated that GAC alone had also catalytic effect on H-acid degradation, which was similar to the observation by Fortuny *et al.* (Fortuny, 1998) and Aguilar *et al.* (Aguilar, 2003). NiO exhibited the better catalytic effect than GAC alone.

The gas-off produced during MW-CWO process was absorbed using distilled water and NaOH solution in turn for

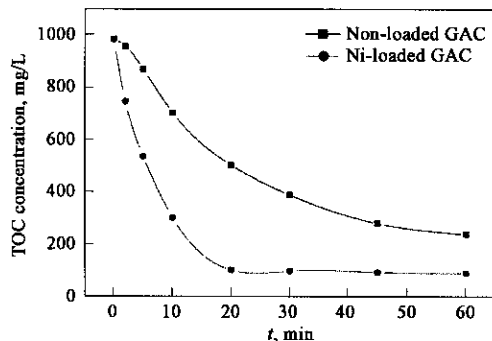


Fig. 4 Effect of Ni on TOC removal in the solution treated

monitoring organic substances. Fig. 5 shows TOC in the distilled water versus reaction time. In the presence of Ni-loaded GAC, more organic substances entered into the gas-off stream and received by the distilled water than under the condition with the presence of non-Ni-loaded GAC. It implied that the reaction was more violent with Ni-loaded GAC than with non-Ni-loaded GAC, and therefore, more organic substances might volatilize. Table 1 presents overall TOC removal and TOC distribution in residues of different phase. The amount of organic substance in gas-off (sum of TOC in the two absorption bottle) was 3.9% under the presence of Ni-loaded GAC and 1.3% under the presence of non-Ni-loaded GAC.

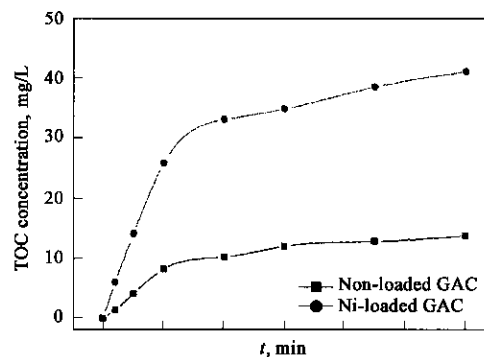


Fig. 5 Influence of Ni on TOC in the No. 1 absorption bottle

Table 1 Comparison of TOC removal in the whole process between Ni-loaded GAC and Non-Ni-loaded GAC after 20 min of MW operation

| | Original TOC, mg | Residual TOC, mg | | | | Removal rate, % |
|-------------------|------------------|------------------|--|--|-------|-----------------|
| | | Aqueous phase | In the No. 1 gas-off absorption bottle | In the No. 2 gas-off absorption bottle | Sum | |
| Ni-loaded GAC | 19.63 | 2.47 | 0.66 | 0.11 | 3.24 | 83.5 |
| Non-Ni-loaded GAC | 19.63 | 10.05 | 0.22 | 0.04 | 10.29 | 47.4 |

2.4 Effect of Ni amount on TOC removal and observation of Ni loss

H-acid removal increased apparently with the increase of Ni loading on GAC. In the range of 0%—5.6% Ni loading, TOC removal increased from 48.8% to 83.1%. However, over 5.6% Ni amount, the acceleration was not significant with the increase of Ni loading (as shown in Fig. 6).

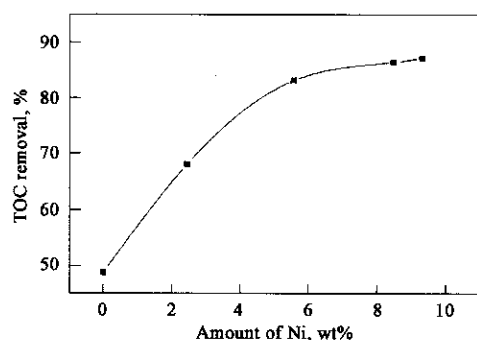


Fig. 6 Effect of Ni amount on TOC removal in 20 min reaction

Similar to conventional CWO, loss of Ni was obvious during the initial stage of reaction. About 30% Ni dissolved and entered into aqueous phase in initial 20 min. After that, the loss rate slowed down, and maintained almost constant, as can be seen in Fig. 7. The reason for the loss was attributed to the decrease of pH in the solution, confirmed by pH determination (decreased from 7.0 to 2.11 in the initial 8 min irradiation), which possibly was the result from the formation of short chain organic acid during the treatment (Zhu, 2002). In CWO process, loss of catalyst is a universal problem, often accompanied with low treatment efficiencies (Chang, 1995). However, due to the batch operation and homogeneous catalysis of Ni^{2+} (Andreev,

1996), it seems to have little influence on TOC removal efficiencies.

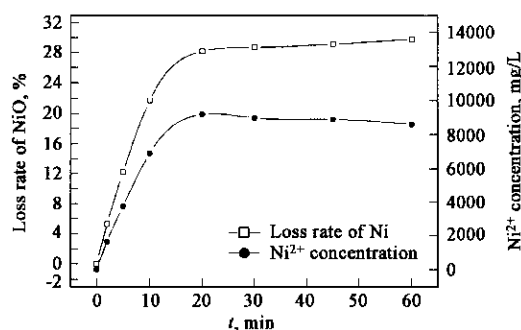


Fig. 7 Loss of Ni in GAC and variation of Ni^{2+} in the solution

2.5 Variation of surface property

Surface morphology of the 4 kinds of GAC, namely, blank GAC, Ni-loaded GAC, non-Ni-loaded GAC by MW process and Ni-loaded GAC by the MW process, were investigated using SEM (Fig. 8) in order to compare the differences between the GAC before and after MW treatment. The surface morphology of the GAC after MW treatment seems a little bit changed. There are many pores with smaller size within the larger and shallow pores, and more changes happened in the surface of Ni-loaded GAC than that of non-Ni-loaded GAC after the MW process.

Their surface properties by BET measure ment are illustrated in Table 2. For non-Ni-loaded GAC or Ni-loaded GAC, their surface area and the total pore volume became increasing slightly after MW treatment, and MW irradiation had more effect on Ni-loaded GAC than on non-Ni-loaded one.

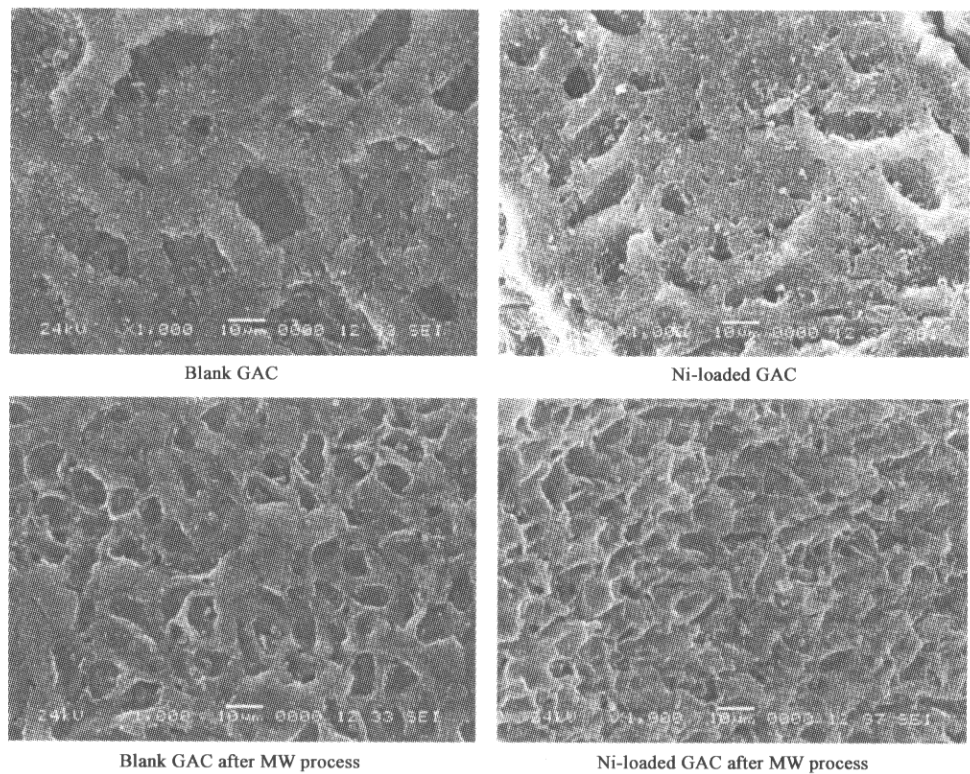


Fig.8 SEM of GAC before and after MW irradiation

Table 2 Surface properties of 4 GAC samples

| Sample | BET surface area, m ² /g | Total pore volume, cm ³ /g |
|------------------------------------|-------------------------------------|---------------------------------------|
| Blank GAC | 871.8 | 0.5290 |
| Ni-loaded GAC | 879.1 | 0.5376 |
| Non-Ni-loaded GAC after MW process | 902.1 | 0.5633 |
| Ni-loaded GAC after MW process | 926.4 | 0.5818 |

3 Conclusions

MW assisting wet process is very effective for degradation of H-acid under normal pressure. Ni-loaded GAC could promote the degradation obviously. There is no doubt that other noble or base metal elements such as Pt, Pd and Cu, utilized in conventional CWO, may also accelerate the H-acid degradation by MW assisting wet process. It is also predicted that the process may have significance in degradation of other refractory organic pollutants in wastewater. Advantage of this novel process is that it may be carried out under lower pressure and temperature than conventional CWO, so that it minimizes the security risk that might be caused by high temperature and pressure.

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