Application of Fe/SiO_2 prepared from rice husk pyrolytic residue to treat banknote printing wastewater

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Abstract: Iron-incorporated mesoporous silica (Fe/SiO_2) with different Fe/Si molar ratio was successfully prepared from rice husk pyrolytic residues (RHR). The obtained materials were characterized by XRD, BET, FT-IR, UV-vis spectroscopy, ICP-AES, XPS and TG-MS. The characterization results indicated that the materials were mesoporous structure with highly dispersed iron species. The materials, not only as flocculant but also as catalyst, were applied to treat banknote printing wastewater. Under the optimal conditions of 100mL diluted wastewater, 0.1 g $8Fe/SiO_2$(5.03wt.%), 5 mL H_2O_2, 30 ℃ and pH at 3.0, 90% removal rate of chroma and turbidity, 86% TOC reduction and 79% COD reduction were obtained.
Keywords: Fe/SiO_2, catalyst, flocculant.

1. Introduction

Banknote printing wastewater is one of the industrial effluents with high organic content, high viscosity, deep color and strong alkalinity. Thus, reduction of chroma and turbidity, and degradation of organics are the main purposes in the treatment of this kind of water. Various methods were applied to solve the problem, for example, neutralization, ultra-filtration, flocculation, sedimentation and advanced oxidation processes (AOPs). [1, 2]

In recent years, researchers have paid attention to convert rice husk into bio-oil through pyrolysis methods [3], leaving large amount of residues, named rice husk pyrolytic residues (RHR). Making full use of RHR is of great significance and modifying RHR to prepare useful materials or catalysts is a promising task, for its sustainable character. The combination of flocculation and AOPs in the treatment of banknote printing wastewater with a material prepared from RHR might be a prospective work.

2. Experimental

Fe/SiO_2 with Fe/Si molar ratio over the range of 0.00 - 0.15 ($0Fe/SiO_2$, $2Fe/SiO_2$, $5Fe/SiO_2$, $8Fe/SiO_2$, $10Fe/SiO_2$, $15Fe/SiO_2$) were prepared by co-precipitation method. The RHR with a particle size of 40–80 mesh was washed by distilled water and then dried. The treatment of RHR by alkali, co-precipitation, and calcination obtained Fe/SiO_2. The obtained materials were characterized by XRD, BET, FT-IR, UV-vis spectroscopy, ICP-AES, XPS and TG-MS. The typical conditions of the wastewater treatment were as follows: 100 mL diluted wastewater, 5 mL H_2O_2, 0.1 g Fe/SiO_2, and temperature at 30 ℃. Before the process, the wastewater was diluted 50 times and its pH was adjusted to desired values by diluted H_2SO_4. The chroma and turbidity was detected by UV-vis absorption, and organic content was detected by TOC and COD methods, respectively.

3. Results and discussion

The XRD results showed all calcined Fe/SiO_2 were mesoporous structure and $0Fe/SiO_2$ possessed a classic hexagonal lattice characteristic of MCM-41[4]. ICP-AES, FT-IR, UV-vis and XPS results proved iron was successfully incorporated into the silica skeleton or highly dispersed on its surface. The BET results shown in Figure 1 revealed the samples were mesoporous(3-8 nm) with a large specific surface area. TG-MS analysis (shown in Figure 2) of the newly calcined $8Fe/SiO_2$ and recycled $8Fe/SiO_2$ certified the function (flocculation and catalysis) of Fe/SiO_2 in different treatment conditions, where 0, 1, 2 represented the newly calcined $8Fe/SiO_2$, $8Fe/SiO_2$ recycled from system 1(water treatment with $8Fe/SiO_2$ alone) and system 2(water treatment with both $8Fe/SiO_2$ and H_2O_2), respectively.

Under the optimal conditions: 100mL diluted wastewater, 0.1 g 8Fe/SiO_2(5.03wt.%), 5 mL H_2O_2, 30 ℃, pH at 3.0, the removal rate of chroma and turbidity was 90% in 90min.(shown in Figure 3). It revealed that Fe/SiO_2 and H_2O_2 exerted influence on wastewater. Moreover, it could be supposed that Fenton-like system [5] might form to exert chemical degradation (AOPs) when Fe/SiO_2, H_2O_2 and H^+ existed together, where Fe/SiO_2 play a role of catalyst. The TOC and COD results shown in Table 1 also indicated the efficient removal of organics, where the reduction rate of TOC and COD reached 86% and 79%, respectively.

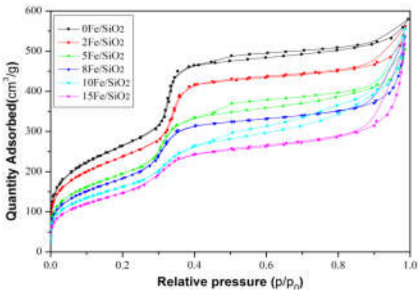

Figure 1. N_2 adsorption-desorption isotherms

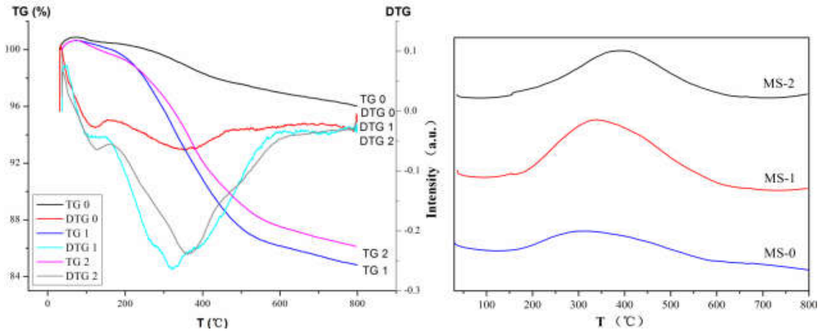

Figure 2. TG curves and MS results of CO_2

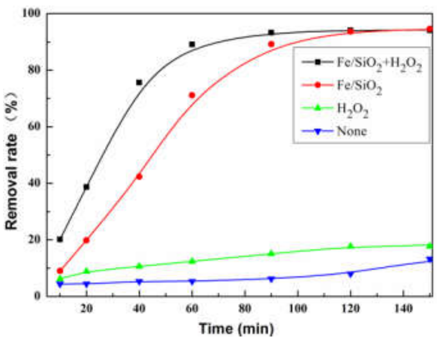

Figure 3. Removal rates under different conditions

Table 1. TOC results of different water samples

Value(ppm) / Samples	TIC	TC	TOC	TOC_0	COD
H_2O	3.4	3.4	0	--	0
ww [a] -50	85.1	223.3	138.2	6910	71
ww-50-pH=3 [b]	3.4	66.4	63.0	--	--
H_2O_2	3.3	76.1	72.8	--	1126
Fe/SiO_2	3.3	42.7	39.4	--	13
Fe/SiO_2+H_2O_2	3.5	22.5	19.0	--	15

[a]-ww-wastewater-diluted 50 times
[b]-diluted 50 times and adjusted to pH=3

4. Conclusions

Mesoporous Fe/SiO_2 was successfully prepared from RHR by co-precipitation methods and it was applied to the treatment of banknote printing wastewater with 90% removal rate of chroma and turbidity in 90 min, 86% TOC reduction and 79% COD reduction. That is to say, Fe/SiO_2 was not only a flocculant but also a catalyst in the treatment process. The whole program achieved the purpose of treating one kind of waste by using another, which adhered to the concept of sustainable development.

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