Internal Micro-electrolysis Using Fe/C Material for Pre-Treatment of Concentrated Coking Wastewater

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Untreated coking effluent presents a great challenge for sustainable development of the steel industry and environment preservation. In this study, an internal micro-electrolysis method using Fe/C materials was employed for pretreatment of real coking wastewater with high mass concentration. The Fe/C materials were prepared by Fe powder and graphite powder; and the characteristics of surface morphology, structure, composition of the synthesized materials were examined by Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDS). The effects of factors namely dosage of Fe/C material, treatment time, initial pH and temperature were investigated via chemical oxygen demand (COD) and phenol removal efficiencies. Optimal treatment efficiency was attained at pH of 4, Fe/C dosage of 40 g/L, treatment time of 360 minutes and temperature of 25°C. After the internal electrolysis process, the values of COD, BOD₅, and phenol of the wastewater were 6500, 4850 and 0.1 mg/L, respectively.

Keywords: internal micro-electrolysis; Fe/C material; wastewater treatment; coking wastewater.

INTRODUCTION

The efficient and effective treatment of coal gasification wastewater (CGW) plays a crucial role in developing the coal industry. Coking wastewater is one of the most difficult wastes to treat due to its complexity and widely variable composition, which contains a large amount of organic, aromatic and cyanide contents¹⁻⁵. As such, combinations of physical, chemical and biological processes are usually employed to resolve the issue⁶⁻⁷. In physical methods, activated carbon, in the form of powder or granular, is often used to remove toxic substances such as aromatic compounds or cyanide from coking wastewater with high efficiencies⁸⁻¹⁰. Meanwhile, chemical processes commonly adopt extraction, flocculation, Fenton or oxidation by O₃ to treat the wastewater¹¹⁻¹⁴. However, the two processes share a common shortcoming of having expensive operational costs and causing secondary pollution. Moreover, chemical processes also present difficulties in the treatment of highly concentrated wastewater and require complex instruments that are difficult for upscaling.

Internal electrolysis has been an emerging technique suitable for the pre-treatment of wastewater containing pollutants with low biodegradability and at high concentrations. The technology applies to various industries such as textile, pharmaceuticals, paper, fertilizer and or pesticide^{9, 11, 14}.

Internal electrolysis allows the following reactions to occur [7, 8, 13, 15]:

(1) The effect of electric fields: Micro-batteries in wastewater will generate electric fields and have the effect of causing charged pollutants to move to opposite electrodes. Then at the surface of the electrodes, there will be a redox reaction against charged pollutants. As a result, the chemical structure of the pollutants would be transformed or degraded.

(2) The reducing effect of hydrogen: Iron is a metal with strong reducing properties, in an acid environment, the following reaction:

The reaction takes place at the electrodes and will produce hydrogen atoms [H], which have strong reducing activity. Then in solution, they will reduce pollutants. For example, NO₂⁻ grouped pollutants will be reduced and converted to amino group compounds.

(3) The effect of metallic iron: The metals behind iron in the action series can exchange electrons on the metallic iron surface. Then metal ions with strong toxicity or organic substances will be reduced by iron to metal ions in a less toxic state. For example, Cr (VI) with E⁰ (Cr₂O₇²⁻/Cr³⁺) = 1.36V has strong oxidizing properties, in an acidic environment, metal iron will react:

Then Cr⁶⁺ with strong oxidizing properties will be converted to Cr³⁺ with weak reducing properties.

Or in acidic conditions, iron will reduce organic substances containing NO₂⁻ group to NH₂ group:

Or in acidic conditions, iron will reduce ion metal substances to metal:

(4) The reducing effect of Fe²⁺ ions: Iron is oxidized to iron Fe²⁺, Fe²⁺ has high reducing properties. For Cr (VI), the reduction reaction occurs as follows:

For pollutants such as azo dyes, the dye-generating radicals of the dye will be reduced by Fe²⁺ and converted to amine compounds, at which point the color of the wastewater will be reduced. The reaction goes as follows: 4Fe²⁺ + R-N = N-R' + 4H₂O → RNH₂ + R'NH₂ + 4Fe³⁺ + 4OH⁻.

(5) The flocculation effect of iron ions. In the condition of acidic wastewater, metallic iron will corrode and produce more Fe^{2+} and Fe^{3+} ions. In the presence of O_2 , reactions will occur in alkaline environments:

The newly born $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ have a high ability to adsorb organic substances. Through the internal electrolysis reaction, the pollutants are chemically changed and the newly formed substances will be flocculated by $\text{Fe}(\text{OH})_3$.

(6) The effect of chemical precipitation:

Fe^{2+} and Fe^{3+} ions in water when meeting with inorganic elements will precipitate into compounds such as FeS , $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ and $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. This compound will quickly settle down and be easily removed.

After pre-treatment of coke wastewater with Fe/C materials, the content of COD, BOD_5 , and phenolic compounds, cyanide will be reduced, efficiency for biological treatment.

The reaction efficiency of the zero-valence iron (Fe^0) could be further improved by employing an internal electrolysis reaction combining iron with carbon element, which has more high voltage values^{16–19}.

In this study, we aim to improve the treatment efficiency of coking wastewater by investigating several experimental conditions of the internal hydrolysis process. Considered parameters included pH, temperature, treatment time, dosage of Fe/C materials and their impacts were monitored to the removal of coking waste in real wastewater of a steel plant. The results are expected to aid in the justification of internal electrolysis using Fe/C material into real applications and contribute to mechanism elaboration of the internal electrolysis reaction.

MATERIALS AND METHODS

Fabrication of Fe/C material

Chemicals including Fe powders with a particle size of less than $50\ \mu\text{m}$ and 99.9% purity were obtained from Meiqi Industry and Trade Co.Ltd (Xihe Village, Beishankou Town, Gongyi, Henan, China), natural graphite

powder with the particle size of smaller than $50\ \mu\text{m}$ and 99.9% purity was obtained from Dingyida international trade (Dalian) Co., Ltd; and $(\text{NH}_4)_2\text{CO}_3$ 99.9% purity was purchased from Sigma Adrich.

Fe/C materials were prepared as follows. The first following ingredients were mixed at a defined weight ratio: 95% Fe, 3% graphite and 1.5% bentonite binder and 0.5% $(\text{NH}_4)_2\text{CO}_3$ 99.9%. The mixture was pressed into blocks, at the pressure of $5\ \text{ton}/\text{cm}^2$ and dried at $80\text{--}105^\circ\text{C}$ for 2 hours. Dried blocks were then sintered at $500\text{--}600^\circ\text{C}$, for 4 hours and subsequently stored in a desiccator for use in subsequent studies.

Collection of coking wastewater

Real coking wastewater was collected from a steel factory located in Thai Nguyen Province, Vietnam (Luu Xa Steel Co. Ltd). Some indicators of the wastewater sample were given as in Table 1.

Method and instruments

As-synthesized Fe/C sample material was characterized using several techniques and instruments including scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) methods (SEM-EDS, S4800, Hitachi) and XRD (Siemens/Bruker, D5000).

Values of COD, BOD_5 , phenol, cyanide, and NH_4^+ are determined according to standards SMEWW 5220D:2012: 2008, ISO 5815-2 : 2003; SMEWW 5530C:2012, SMEWW-4500CN⁻. C&E:2012, ISO 14911 : 1998 respectively (at VILAS 424, VIMCERTS 054, Environmental Analysis, Hydraulic Monitoring Center)²⁰.

RESULTS

Material characterization

SEM-EDS analysis of Fe/C

SEM-EDS image analysis results are shown in Figures 1, 2 and Table 2. Visually, Fe and C powder particles were distributed relatively evenly on the material surface with the size of smaller than $50\ \mu\text{m}$. EDS analysis results

Table 1. The characteristics of coking wastewater

Samples			No	N1	N2
No	Parameter	Unit			
1	pH	—	8.2	8.0	7.8
2	COD	mg (O_2)/L	8785	8800	8835
3	BOD_5	mg (O_2)/L	5490	5500	5530
4	Total P	mg/L	4.5	3.7	3.5
5	Total N	mg/L	265	255	270
6	NH_4^+	mg/L	185	175	190
7	SO_4^{2-}	mg/L	7.5	8.0	8.5
8	Cl^-	mg/L	14	15	13
9	S^{2-}	mg/L	0.3	0.3	0.4
10	CN^-	mg/L	0.1	0.2	0.3
11	Phenol	mg/L	110.3	110.8	111.3
12	Ca^{2+}	mg/L	10	8	7
13	Mg^{2+}	mg/L	23	20	15
14	Pb^{2+}	mg/L	0.2	0.1	0.1
15	Cd^{2+}	mg/L	0.02	0.02	0.03
16	Zn^{2+}	mg/L	0.5	0.6	0.3
17	Al^{3+}	mg/L	0.05	0.06	0.05
18	Mn^{2+}	mg/L	0.2	0.2	0.3
19	Ni^{2+}	mg/L	0.2	0.1	0.1
20	Total Cr^{6+}	mg/L	0.01	0.01	0.02
21	Cu^{2+}	mg/L	0.4	0.1	0.1
22	Fe^{3+}	mg/L	0.3	0.4	0.3

(Table 2) showed that the main elements of materials were Fe, C, O. There was the presence of impurity elements such as Si, Al, Ca. The occurrence of O in the analytical results indicates the occurrence of sample oxidation on the surface. Other impurity elements (Si, Al, Ca) appear due to the bentonite binder.

Figure 1. SEM image of Fe/C material

Figure 2. EDS pattern of Fe/C material

Table 2. Elemental analysis of Fe/C material

Element	Weigh (%)	Atomics (%)
C K	14.59	23.57
O K	50.16	60.86
Al K	1.89	1.36
Si K	5.47	3.78
Ca K	5.40	2.61
Fe K	22.48	7.81
Totals	100.00	100.00

XRD analysis of Fe/C

The results of XRD analysis (Fig. 3) showed that Fe in the Fe/C sample was oxidized, as indicated by structures of Fe_3O_4 and Fe_2O_3 on the surface of the material. The peaks of Fe_3O_4 and Fe_2O_3 and Fe were observed at 45.5° ; 63° , at 36° and 34.5° respectively.

Impact of experimental parameters on treatment efficiency of coking wastewater.

Influence of pH

pH value is an important parameter that may affect the reaction efficiency. In this investigation, the pH was

Figure 3. XRD pattern of Fe/C material

allowed to vary from 3 to 7. Other parameters included 4.0 g of Fe/C material for 100 ml coking wastewater (the sample N1), the temperature of 25°C and shaking speed of 160 rpm, processing treatment time of 6 hours. Figure 4 illustrates phenol and COD variations to different pH values. From the pH range from 3 to 5, no clear changes in removal of COD and phenol were observed and the treatment efficiency was about 24.5%, corresponding to the COD and phenol content of around 6500 and 0.3 mg/L respectively. Although higher pH could facilitate the subsequent biological treatment, current results support low pH for optimal COD and phenol removal. Because very low pH may raise the cost for pH adjustment, we selected a pH value of 4 for the next study.

Figure 4. (a) Effect of removal COD by Fe/C at different pH; (b) Effect of removal phenol by Fe/C at different pH, processing treatment time of 6 hours

Influence of temperature

In this investigation, 4.0 g of Fe/C material was used, and 100 mL of wastewater was added into 250 mL flasks under shaking (160 rpm). The reaction was performed under the temperature from 25 to 40°C. The results are shown in Figure 5. COD and phenol content in wastewater seemed to deplete more quickly under the temperature of 40°C than under 25°C. However, after 6 hours, the attained processing efficiencies from the two examined temperatures were almost identical, reaching the COD of around 6500–6550 mg/L and phenol of around 0.1–0.3 mg/L.

Figure 5. The influence of temperature on the efficiency of coking wastewater treatment

Temperature plays a crucial role in practical wastewater treatment since temperature influences both treatment efficiency and the economic aspects of the process. As a result, technological processes are often designed to refrain from veering the process temperature from natural conditions. The reaction rate is proportional to temperature, but the change is small. Given that the final treatment indicators achieved after 6 hours were indistinguishable between 25 and 30°C, a temperature of 25°C was selected as the condition for subsequent studies. This temperature is also consistent with that of ponds and streams in Vietnam.

Influence of Fe/C dosage

In this investigation different dosages including 0.5, 1.0, 3.0, 4.0, 5.0, 7.5 and 10 g were selected. The experiment commenced by adding 100 mL of wastewater into 250 mL flasks, followed by pH adjustment to 4. The reaction time was 6 hours, the agitation speed was 160 rpm and the temperature was set to 25°C. Experiment results are presented in Figure 6.

Figure 6. Effect of dosage of Fe/C material on efficiency of coking wastewater treatment

As the dosage increased from 30 to 100 g per 1 liter of wastewater, removed COD removed in coking wastewater increased from 1350 mg/L to 2250 mg/L and phenol removal efficiency was also improved from 25 to 99.95%.

Identification of a suitable material dosage carries important implications for optimization of treatment efficiency and process scalability. An increased amount of used internal electrolysis materials might result in a larger surface area of the reaction electrode and necessitate a larger volume for wastewater storage. On the other hand, stronger electrochemical oxidation may produce excessive $[\text{OH}^*]$ and $[\text{OH}^-]$, Fe^{2+} . For optimal processing efficiency, 40 g of Fe/C materials per 1 liter of wastewater was selected as the appropriate dosage for the next study.

Influence of time

The influence of time on treatment efficiency was investigated in the reaction time ranging from 1 to 8 hours. Other conditions included dosage of 4.0 g of Fe/C material, pH value of 4, reaction temperature of 25°C and shaking speed of 160 rpm. The results are shown in Figure 7.

Within the first hour, a decline in COD and phenol was moderate but then accelerated as the reaction time elapsed past 1 hour. After 2 hours value of COD dropped from 8500 mg/L to about 6800 mg/L and phenol content dropped from 75 mg/L to about 18 mg/L. In the period from 2 to 4 hours, COD and phenol decomposition performance was stagnant and eventually reached the

Figure 7. Influence of time on the efficiency of coking wastewater treatment

minimum after 6 hours, at which point phenol was no longer detected and COD was approximately 6500 mg/L.

Table 3 summarizes the main indicators of the wastewater treated with Fe/C electrolytic material. Overall, COD treatment efficiency was approximately 24.5%. However, NH_4^+ treatment efficiency was still modest. This highlights the importance of pretreatment processes

Table 3. The characteristics of coking wastewater after pretreatment by the Fe/C material, pH 4, 40 g/L Fe/C, 100 mg/L of PAM (Polyacrylamide, Xunyu Group Co., Limited, China) flocculant, 6 hours treatment

Samples			N1
No	Parameter	Unit	
1	pH	–	7.5
2	COD	mg (O_2)/L	6500
3	BOD ₅	mg (O_2)/L	4850
4	Total P	mg/L	1.5
5	Total N	mg/L	245
6	NH_4^+	mg/L	165
7	SO_4^{2-}	mg/L	6.0
8	Cl^-	mg/L	10
9	S^{2-}	mg/L	0.1
10	CN^-	mg/L	0.0
11	Phenol	mg/L	0.1
12	Ca^{2+}	mg/L	5
13	Mg^{2+}	mg/L	3
14	Pb^{2+}	mg/L	0.05
15	Cd^{2+}	mg/L	0.01
16	Zn	mg/L	0.3
17	Al	mg/L	0.03
18	Mn	mg/L	0.1
19	Ni	mg/L	0.05
20	Total Cr^{6+}	mg/L	0.0
21	Cu	mg/L	0.05
22	Fe	mg/L	0.3

using internal electrolysis for enhancing biological degradability of coking wastewater^{17, 18}.

CONCLUSIONS

The Fe/C material was successfully prepared from Fe powder and graphite powder. The samples were characterized for surface characteristics, structure and composition by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS), respectively. The synthesized material was applied for the treatment of real coking wastewater and the process was optimized by varying several factors including pH, time, temperature and dosage of Fe/C. Optimal efficiency was achieved after 6 hours of treatment, at pH 4.0, with the dosage of 40 g Fe/C material per 1 liter of wastewater and at the temperature of 25°C. COD and phenol were reduced from 8800 mg/L to 6500 mg/L and from 110 mg/L to 0.1 mg/L, respectively. Interestingly, the treatment efficiency of toxic ingredients such as phenol, cyanide is very effective at 99.95%, after 6 hours of treatment. The initial concentration of phenol is 110 mg/L high, and then 0.1 mg/L after the internal electric treatment, which is favorable for the biological process of further treatment. This is the preeminence of the internal electrolysis process to treat coke wastewater. Current results implied the stability of the internal electrolysis in the treatment of coking wastewater and demonstrated that the process can be used to improve the biodegradability of coking wastewater.

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