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A purification agent for coking wastewater treatment using iron and steel solid wastes

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ABSTRACT

In the present work, a novel iron-carbon micro-electrolysis filler was proposed to address the problems of short service life, blockage of electrolysis device, and clumping of traditional iron-carbon micro-electrolytic fillers. In this study, solid steel wastes were used to prepare a purifying agent to treat coking effluent. By using the solid wastes (steelmaking sludge, blast furnace gas slime, and mill scale) generated in the production process of iron and steel enterprises, with a small amount of anthracite as raw materials, carbon-containing metalized briquettes were prepared after 15 min of reduction under high-temperature conditions in a carbon tube furnace. The briquettes that contained 70%–90% iron, 10%–30% carbon, and had a porosity of 63% could be used as a purifying agent to treat coking wastewater. Under optimal conditions, the chemical oxygen demand of wastewater could be reduced by 40%, and the aerobic biodegradability B/C could be increased by 43%. Thus, adopting the idea of "using waste to treat waste" (coking sewage) is economically and environmentally. Besides, this technology efficiently uses iron and carbon-containing dust and other waste resources from steel plants.

Keywords: Steel solid wastes; Carbon-containing metalized briquettes; Micro-electrolytic fillers; Coking wastewater; Purification agent

1. Introduction

Iron-carbon micro-electrolysis technology, also known as iron-carbon internal electrolysis [1–3], uses iron-carbon and other micro-electrolysis materials to form a closed circuit in wastewater without electricity. It generates a potential difference for treating wastewater by degrading organic pollutants. Presently, due to continuous improvement and development, cost-effectiveness of raw materials, simple operation, relatively short treatment time and less secondary pollution, iron-carbon micro-electrolysis technology has been widely used in the treatment and pretreatment of high-concentration, high-chroma, and refractory industrial wastewater in chemical industries, printing and dyeing, and pharmaceutical industries [4–6]. Studies have shown that the decolorization rate of iron-carbon micro-electrolysis technology for high-color sewage can exceed 90%. However, traditional iron-carbon micro-electrolytic fillers mostly use fine iron and carbon powder as raw materials formed by mechanical-pressing. From the internal structure, iron and carbon only undergo a simple physical combination, resulting in a weak combination. During the micro-electrolysis, problems such as clumping and surface hardening of iron filings and short service life often occur, which severely restricts the wide application of this technology [7,8].

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Hence, herein, the solid wastes of iron and steel enterprises are used to prepare carbon-containing metalized briquettes. The briquettes obtained by reduction are used as the filler of iron-carbon micro electrolysis. Also, the treatment effect is experimentally verified.

2. Materials and methods

2.1. Raw materials and analysis

For this study, the raw materials were all solid wastes generated in the production process of an iron and steel enterprise, such as mill scale, blast furnace gas sludge and steelmaking sludge. Tables 1 and 2 show the composition and particle grading analysis of each raw material. The reducing agent used is anthracite and Table 3 shows its composition.

2.2. Experimental method

2.2.1. Preparation of sewage purification agents

The raw materials were singly ground to 200 meshes, and an appropriate amount of water (2%–5%) was added after mixing in proportion. The sample was pressed into a 15 mm × 20 mm cylindrical specimen using a presser and oven-dried at 110°C for 30 min. Subsequently, the dried specimen was placed in a drying dish (dry storage) for subsequent use.

The specimen was placed in a corundum crucible after drying and then reduced in STGL-2000/9 vacuum carbon tube furnace (Fig. 1) at 1,350°C for 15 min. Afterward, the sample was furnace-cooled to room temperature and then removed. The whole reduction process was supposed to isolate air, preventing the briquettes' oxidation.

2.2.2. Briquettes porosity calculation

Porosity calculations of the final carbon-containing metal briquettes were calculated according to the following equation [9]. The relationship between the porosity (n, %), the packing density (ρ, kg/m^3), and the apparent density (ρ_a, kg/m) of the filler is given as follows:

$$n = 1 - \frac{\rho}{\rho_a} \tag{1}$$

The packing density was determined as follows: the carbon-containing metal masses were dried in a constant temperature drying oven at 105°C until a constant weight was obtained. After natural cooling, the beaker's mass was weighed and denoted as m_1. Next, the beaker was filled with water and weighed as m. Furthermore, the carbon-containing metal masses were added to the beaker to the cup's brim and weighed as m_2. The relationship is given by Eq. (2).

$$\rho = \frac{m_2}{\left(m - m_1\right)} \times \rho_{\mathrm{H20}} \tag{2}$$

Table 3
Anthracite ingredients

Components	C	CaO	SiO_2	Al_2O_3	S	MgO	P
Anthracite	85.13	0.59	5.48	4.28	0.64	0.16	0.02

Fig. 1. STGL-2000/9 vacuum carbon tube furnace.

Table 1
Chemical element analysis of mill scale

Components	Fe_2O_3	SiO_2	Al_2O_3	MgO	CaO	MnO	P_2O_5	SO_3	ZnO
Rolled iron sheet	93.89	1.00	0.53	0.39	0.31	0.20	0.03	0.02	–
Steelmaking sludge	71.02	1.46	0.45	2.58	14.55	0.39	0.14	0.34	4.64
Gas sludge	63.51	8.07	6.02	0.92	3.64	–	0.33	1.05	3.69

Table 2
Analysis of the grain composition of the raw materials

Grain level/mm	+3	–3 + 1	–1 + 0.45	–0.45 + 0.15	–0.15 + 0.074	–0.074 + 0.038	–0.038
Rolled iron sheet	18.85	34.74	20.15	12.82	5.61	7.83	0
Gas sludge	0	0	0	15.32	27.18	30.23	27.27
Steelmaking sludge	0	2.46	5.43	4.84	4.62	17.52	65.13

Apparent density measurement method: The carbon-containing metal briquettes were dried at 105°C until the quality did not change. When they cool down naturally, the mass was weighed as m. Next, the weighed carbon-containing metal lumps were added to a flask filled with half a flask of water. The air bubbles were removed by sufficient vibration. Water was added to the highest scale of the flask, and the mass was weighed as m_1. The volume bottle was then emptied completely and dried. Then, water was added to the highest scale of the bottle, and the mass was weighed as m_2. Eq. (3) is used to calculate ρ_a.

$$\rho_a = \frac{m_2}{m} - m_1 + m_2 \times \rho_{\mathrm{H20}} \tag{3}$$

2.2.3. Experimental methods for coking wastewater treatment

The briquettes (prepared with an optimal C-to-O ratio (C/O) of 1.2, a reduction temperature of 1,330°C, and a reduction time of 15 min) were used as sewage agents to treat coking wastewater using the principle of iron-carbon micro-electrolysis. The coking sewage used here was the wastewater from a coking plant of a steel group, used in an air flotation tank to remove oil and suspended solids completely. Table 4 shows its main components.

The reactor was filled with 2 kg of sewage agent as a micro-electrolysis filler and 2 L of coking sewage with an adjusted pH of 3 [10,11]. After full aeration for 24 h, samples were taken every 4 h for detection and analysis.

3. Experimental results and analysis

The heating process of the clump was observed using a laser scanning confocal microscope (Fig. 2), and the heating curve is shown in Fig. 3. Below and above 800°C, the heating rates were 200 and 60°C/min, respectively. When the temperature exceeded 1,350°C, a 30 min incubation was conducted.

Table 4
Main components of coking wastewater

Composition	COD (mg/L)	BOD_5 (mg/L)	B/C
Content	3,450	850	0.24

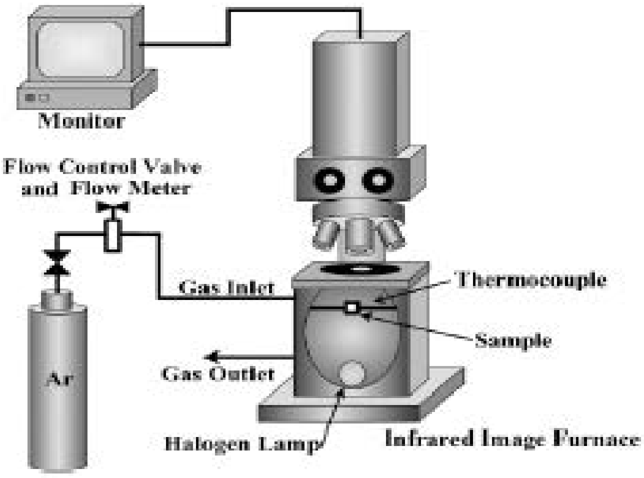

Fig. 2. Laser scanning confocal microscope.

Based on the observation records, the agglomerates began shrinking and deforming at 800°C, and bubbles were generated at 1,020°C. At 1,270°C, the number of bubbles increased, indicating that the reduction reaction was severe and the formation of Ferro beads was observed. At 1,300°C, liquid phases were present in the pellets. After 1,350°C (as shown in Fig. 4), the liquid phases flowed obviously, simultaneously generating more bubbles and Ferro beads. Fig. 4 shows that at 1,350°C, with the increase of reduction temperature, more and more metal Fe is reduced, which looks like small iron beads, and these small iron beads gradually begin to gather and grow up. It can be found that the optimal temperature of the experiment should be 1,350°C.

3.1. Influencing factors of the iron yield in briquettes

3.1.1. Carbon-to-oxygen ratio effect on the iron yield

The yield of Fe under different C/O at 1,300°C, 1,330°C and 1,350°C is shown in Fig. 5. The C/O expresses the carbon-fitting ratio, and C/O = 1 represents the fixed carbon

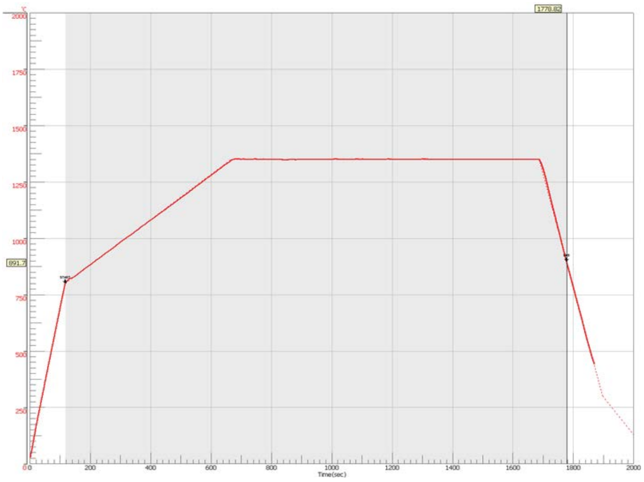

Fig. 3. Heating curve.

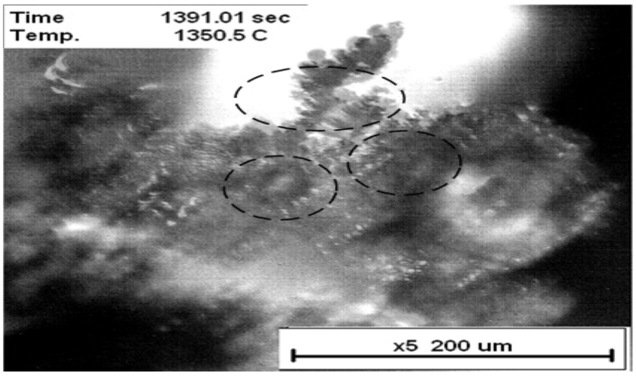

Fig. 4. Recorded images using a laser scanning confocal microscope at 1,350°C.

content consumed when all iron oxides in the agglomerates are directly reduced to iron. As C/O increases from 1.0 to 1.6, the metal yield increases initially and then decreases at the same temperature, because increasing C/O can enhance the reduction rate (Fig. 5). Under the same conditions, the higher the carbon ratio, the higher the volume of C in the agglomeration. Thus, the gasification rate of carbon and iron oxide reduction reaction can be accelerated, improving the metal yield. However, an excessively high C/O reduces the metal yield because unreacted coke powder hinders the aggregation and growth of the metal phase. It can be seen that the maximum Fe metal yield can be obtained at different temperatures with a C/O of 1.2.

3.1.2. Reduction temperature effect on the iron yield

The yield of metallic iron in the temperature range from 1,280°C to 1,380°C with different C/O ratios is shown in Fig. 6. It can be seen that the metal yield increases first and then decreases with the increase of reduction temperature. A high temperature is conducive to the reduction reaction. However, under excessively high temperatures, FeO in the agglomerate reacts with SiO_2, forming a melting-point compound, and a flowing slag phase blocks the voids in the agglomerate and wraps around the particles. Consequently, the environment of the reduction kinetics deteriorates and the metal yield decreases. Hence, we can conclude that the reduction temperature should be appropriate.

3.1.3. Reduction time effect on the iron yield

Under the condition of the ratio scheme of carbon ratio 1.2 and reduction temperature 1,330°C, the reduction was conducted under different reduction time of 5, 10, 15, 20 min. Fig. 7 indicates the results. At the initial stage of the reduction reaction, iron is quickly reduced by C. As the reduction time increases, more iron is reduced. When the reduction time reaches 15 min, the iron yield culminates, and if the reduction time is further prolonged, the metal yield shows little changes.

3.2. Experimental results on coking wastewater treatment

Figs. 8 and 9 show the experimental results on coking wastewater treatment. As the reaction time increases, chemical oxygen demand (COD) gradually decreases, from 3,450 to 2,070 mg/L, with a total decrease of 40%. Five-day biochemical oxygen demand steadily increases, whereas B/C

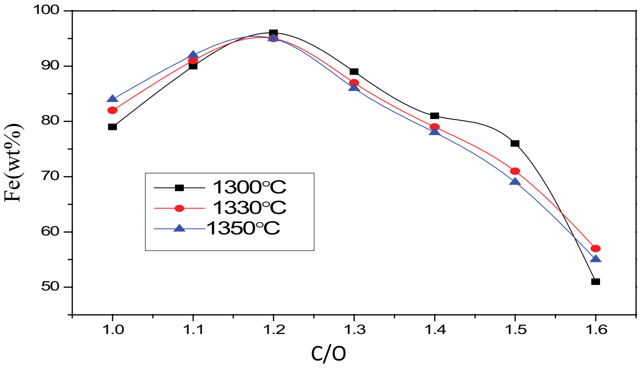

Fig. 5. Effect of C/O on iron yield.

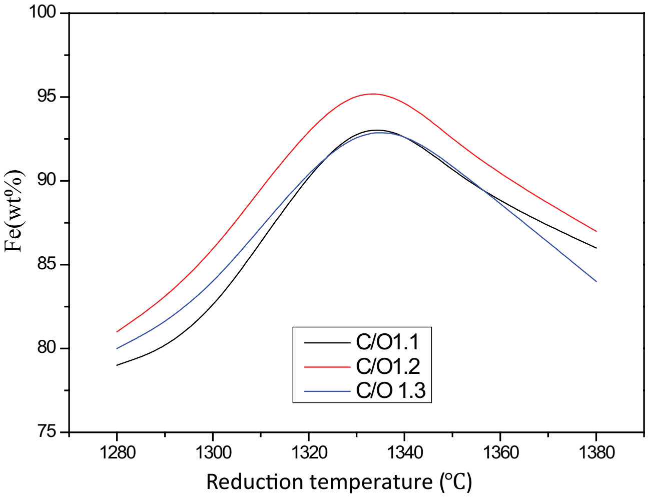

Fig. 6. Effect of the reduction temperature on iron yield.

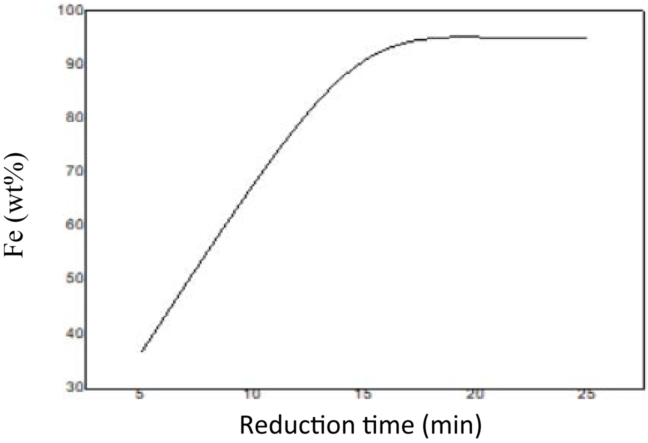

Fig. 7. Effect of reduction time on iron yield.

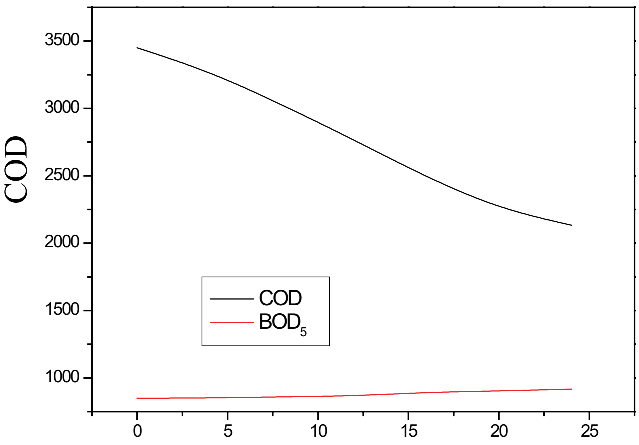

Fig. 8. COD and BOD changes over time.

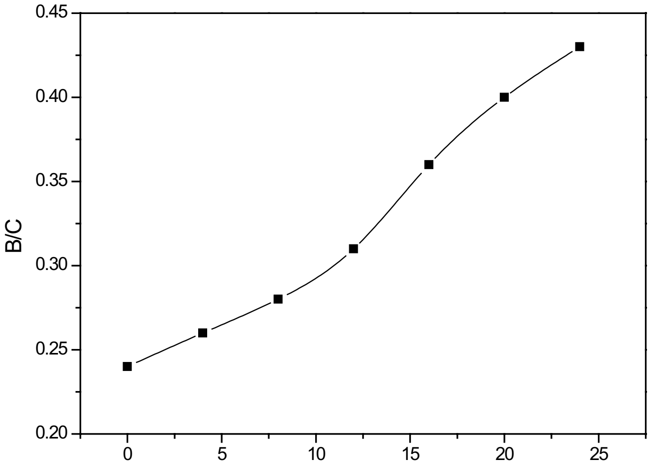

Fig. 9. B/C change over time.

biochemicals increase by 43%. That's because the iron and carbon in the carbon-containing metal blocks were electrolyzed to provide the required electrons for the reduction of oxides in the wastewater and produce a large number of active substances to promote the removal of pollutants in the wastewater. Throughout the micro-electrolysis process, an electric field was formed between the iron and carbon electrodes, making the charged colloidal particles in the coking sewage directional migrate, thus further promoting the enrichment and removal of pollutants [12–14]. $Fe(OH)_2$ and $Fe(OH)_3$ generated in the iron-carbon micro-electrolysis process had strong flocculation-adsorption activity, mightily adsorbing the colloidal particles in the wastewater, and finally coagulating the colloid through the bridge and crosslinking, thus reducing chromaticity and removing the organic matter in the wastewater [15].

3.3. Results and discussion

Solid waste from iron and steel enterprises and a small amount of coke were used as a reducing agent. Carbon-containing metallized briquettes obtained under the conditions of a C/O of 1.2, a reaction temperature of 1,330°C, and reduction time of 15 min could be used as micro-electrolytic fillers for coking wastewater treatment. The experimental results identified the optimal conditions for preparation of carbon-containing metallized briquettes: a carbon ratio C/O at 1.2, a reduction temperature at 1,330°C, and reduction time of 15 min. The recovery rate of iron could reach 95%, and the briquettes contained 70%–90% iron, 10%–30% carbon, and had a porosity of 63%. After treatment, the COD of coking wastewater was reduced by nearly 40%, the B/C increased by 43%, and the biodegradability of wastewater was further improved.

Previous publications [16–19] all mentioned the use of iron-carbon micro-electrolysis technology in coking wastewater treatment. The technology proposed in this study differs from the existing methods mainly in the raw materials for the preparation of iron-carbon fillers. These existing methods all used iron filings and activated carbon, which are quite expensive. While the iron-carbon filler prepared in this experiment has a lower cost than the traditional fillers. The iron and carbon in the filler are evenly dispersed, and the electrolysis effect lasts longer.

4. Conclusion

Carbon-containing metallized briquettes were prepared by sintering secondary iron-containing dust, coke, and a small amount of additives produced in iron and steel enterprises' production process. The briquettes can be used as micro-electrolytic filler for coking wastewater treatment.

Through a large number of experiments, the optimal ratio of the purifying agent and the best experimental temperature were defined. After treatment, the coking wastewater chromaticity was obviously reduced and COD decreased by 40%, and biodegradability increased by 43%. The advantages of the technology are mainly as follows: (1) Most of the coking wastewater treatment methods are biological methods, and chemical methods, while the technology presented here adopts an electrochemical method for treatment. (2) The main raw material used in this technology is the secondary iron-containing dust of iron and steel enterprises, so the cost is lower. (3) Though high- temperature sintering of raw materials, the service life of the purifying agent can be improved.

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Nomenclature

COD: Chemical oxygen demand. The amount of reducing substances that need to be oxidized in water samples was measured by chemical method.

BOD_5: Five-day biochemical oxygen demand. BOD_5 is the amount of free oxygen consumed by aerobic microorganisms to oxidize and decompose organic matter in unit volume of water within five days.

$B/C = BOD_5/COD$: the biodegradability of the wastewater.

References

[1] Z.G. Cui, H. Li, Z.T. Wang, Research progress on the treatment of wastewater by micro-electrolysis, Sd. Chem. Ind., 38 (2009) 21–24.
[2] L.W. Cao, S.J. Zhang, Y.Z. Zhang, X.S. Deng, T.F. Lu, Research progress of micro-electrolytic fillers, Modern Chem. Ind., 35 (2015) 13–17.
[3] Y.-P. Wang, L.-J. Wang, P.-Y. Peng, T.-H. Lu, Treatment of naphthalene derivatives with iron-carbon micro-electrolysis, Trans. Nonferrous Met. Soc. China, 16 (2006) 1442–1447.
[4] Q.W. Zhu, Status and prospects of iron-carbon micro-electrolysis in wastewater pretreatment, Tech. Inf., 2 (2011) 188–120.
[5] Z.J. Zhang, Research and application of microlysis method in wastewater treatment, Ind. Saf. Environ. Prot., 3 (2006) 1442–1447.

[6] P.G. Zhou, D.F. Fu, Research progress on micro-electrolysis process, Environ. Pollut. Contr. Tech. Equip., 2 (2001) 18–24.

[7] Z.Z. Song, J. Li, J. Sun, Research and application of iron-carbon micro-electrolytic filler, Green Tech., 6 (2017) 48–50.

[8] H.X. Yang, J.L. Tian, B. Wang, J. Liu, X.R. Ju, J.J. Ge, L.L. Ren, Q.X. Yu, J.Z. YU, Preparation of high-carbon metallized briquettes and treatment of coking wastewater, Chin. J. Environ. Eng., 12 (2018) 999–1000.

[9] F. Cao, Study on the Preparation and Performance of New Micro-electrolytic Fillers, Jiangsu University, China, 2016.

[10] C.Z. Zhang, H.Y. Sun, Application of Fenton catalytic oxidation process in coking wastewater treatment, Fuel Chem. Ind., 45 (2014) 57–58.

[11] J.L. Tian, J.Z. Liu, X.S. Li, Coking wastewater enhanced pretreatment experiment based on micro-electrolysis technology, 38 (2018) 71–73.

[12] S.H. Choe, S.H. Lee, Y.Y. Chang, K.Y. Hwang J. Khim, Rapid reductive destruction of hazardous organic compounds by nanoscale FeO, Chemosphere, 42 (2001) 367–372.

[13] J.H. Fan, W.Y. Xu, T.Y. Gao, Study on the mechanism of zero-valent iron system for pretreatment of nitrobenzene wastewater, Ind. Water Wastewater, 2 (2001) 18–22.

[14] I.F. Cheng, R. Muftikian, Q. Fernando, N. Korte, Reduction of nitrate to ammonla by zero-valent iron, Chemosphere, 35 (1997) 2689–2695.

[15] L.X. Li, J.D. Chen, M.H. Liao, D.S. Su, J.H. Zhu; X. Li, Application and research of iron-carbon micro-electrolysis technology, Environ. Sci. Manage., 42 (2017) 98–99.

[16] L. Zhang, Y.H. Han, M.L. Liu, Advanced treatment of coking wastewater based on internal cycling micro-electrolysis technology, Chin. J. Environ. Eng., 12(2018) 1462–1470.

[17] F.F. Li, X.M. Li, G.M. Zeng, Research on advanced treatment of coking wastewater by iron-carbon micro-electrolysis, Ind. Water Wastewater, 41 (2010) 46–49.

[18] Y.F. Ming, L.C. Yao, W. Liu, Study on treatment of coking wastewater by Fenton reagent-micro-electrolysis process, Ind. Water Treat., 32 (2012) 78–80.

[19] X.D. Yin, D.H. Li, Y.F. Mao, Pretreatment of high concentration coking wastewater by iron-carbon micro-electrolysis/H_2O_2 coupled Fenton method, Chin. J. Environ. Eng., 10 (2016) 212–216.