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Study on Preparation of Coke-making Wastewater Purifying Agent Based on Iron-carbon Micro-Electrolysis Principle

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Abstract: In light of Chinese goal to achieve carbon neutrality by 2035 and carbon peak by 2060, this study utilizes solid wastes from iron and steel production processes, such as OG sludge, coal ash, and iron oxide scale. These materials are processed in a high-temperature carbon tube furnace with anthracite as a reducing agent and a small amount of binder after compression molding. Reduction at 1350°C and subsequent cooling yields carbon-containing metal pellets with iron content ranging from 70% to 90%, carbon content from 10% to 30%, and porosity at 53.8%. Furthermore, the use of coking wastewater with metal aggregates reduces COD by 40% and increases B/C by 45%. Additionally, this process effectively utilizes iron and carbon-containing dust and other waste resources from steel-making plants during coking wastewater treatment.

Keywords: Double Carbon; Coking Wastewater; Purifying Agent; Iron-carbon Micro-electrolysis; Iron and Steel Production Wastes

1. Introduction

Iron-carbon microelectrolysis technology utilizes closed-circuit formation in wastewater, generating potential differences to treat and degrade organic pollutants without electricity [1-6]. Widely applied in chemical, printing, dyeing, and pharmaceutical industries, it effectively treats high-concentration, high-chromaticity industrial wastewater. Advantages include low raw material costs, simple operation, short treatment times, and minimal secondary pollution [7-10]. Studies show iron-carbon microelectrolysis achieves over 90% decolorization rates in high-color wastewater.

Traditional iron-carbon microelectrolysis fillers typically use iron concentrate and carbon powder, mechanically pressed into shapes. However, the physical combination of iron and carbon lacks durability, leading to issues such as iron filings caking and short service life during operation, limiting widespread adoption.

This paper aims to address these issues by utilizing solid waste from iron and steel enterprises to prepare carbon-containing metal agglomerates, and to obtain carbon-containing metal agglomerates from iron-containing waste through reduction as a new type of iron-carbon micro electrolytic filler for the treatment of coking effluent. The efficacy of this new filler will be experimentally verified.

2. Materials and Methods

2.1 Raw Materials and Analysis

The experimental raw materials consist of solid wastes generated during steel production, including rolling iron, blast furnace gas sludge, and steelmaking sludge. Tables 1 and 2 present the composition and particle size analysis of each raw material. Anthracite coal is employed as the reducing agent, and its composition is detailed in Table 3.

Table 1. Raw Material Chemical Element Analysis

Composition	Fe_2O_3	SiO_2	Al_2O_3	MgO	CaO	MnO	P_2O_5	SO_3	ZnO
Rolled steel skin	92.98	1.05	0.56	0.49	0.37	0.21	0.02	0.03	-
Steelmaking sludge	70.52	1.76	0.41	3.58	13.57	0.28	0.17	0.45	3.98
Blast furnace gas sludge	62.41	9.07	5.02	0.86	3.57	-	0.31	1.07	3.54

Table 2. Analysis of Particle Size Composition of Raw Materials

Particle size/mm	+3	-3+1	-1+0.45	-0.45+0.15	-0.15+0.074	-0.074+0.038	-0.038
Rolled Steel skin	17.75	35.72	19.15	13.82	5.51	6.83	0
Blast furnace gas sludge	0	0	0	14.42	28.28	29.23	28.27
Steelmaking sludge	0	2.56	5.33	4.74	4.72	16.52	66.13

Table 3. Anthracite Composition

Composition	C	CaO	SiO_2	Al_2O_3	S	MgO	P
Anthracite	86.13	0.49	4.38	4.38	0.54	0.14	0.04

2.2 Experimental Method

2.2.1 Sample preparation

To prepare the carbon-containing metal agglomerates, the various raw materials are first ground to 200 mesh one by one, and mixed according to the ratio (Fe/C=3:1) and then add the appropriate amount of binder (2%-5%), pressed into 15 mm×20 mm cylindrical specimens with the sample press (Figure 1). The specimens are then dried at 110℃ for 30 minutes in an oven before being stored in a drying dish.

To obtain the carbon-containing metal agglomerates, an appropriate amount of dried sample and place it in a corundum crucible. The crucible is heated rapidly to 1350℃ in an STGL-2000/9 vacuum carbon tube furnace (Figure 2) for reduction. After 15 minutes of reduction, cool it down to room temperature in the furnace and remove it. The entire reduction process requires isolation of air to avoid oxidation of the agglomerates.

Figure 1. Compacted Cylindrical Pellets

Figure 2. Vacuum Carbon Tube Furnace

2.2.2 Calculation of porosity of agglomerates

The boiling method was used to determine the porosity of iron-carbon microelectrolytic pellets in the experiments. The sample was first dried to evaporate the water present in the sample and the dry weight of the specimen was weighed on a precision balance scale and recorded as M1 (Figure 3). The specimens were placed in a dry beaker and deionized water was injected into the beaker until the specimens were completely submerged. The beaker is then heated and boiled on an electric stove for two hours to allow the deionized water to thoroughly penetrate into the empty space of the iron-carbon microelectrolytic pellets, then the heating is stopped and the specimen is returned to room temperature. The water on the surface of the specimen was wiped off, and the mass of the iron-carbon microelectrolytic pellet specimen was quickly weighed and recorded as M3 (Figure 4), and the porosity of the iron-carbon microelectrolytic pellet was calculated by the formula K [11-15].

$$K = (M_3 - M_1)/(M_3 - M_2) \quad (1)$$

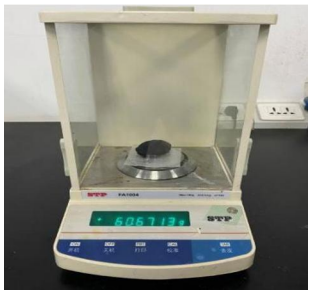


Figure 3. The Dry Weight of the Sample

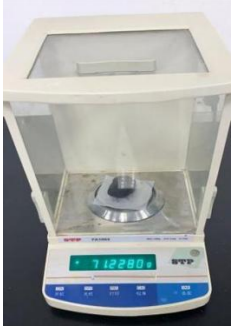


Figure 4. Mass of Iron-carbon Micro-electrolysis Pellets

Test results: M3=71.2280g; M2=51.116g; M1=60.6713g; K=53.8%

Compared with the porosity of traditional iron-carbon packing, the porosity of iron-carbon microelectrolytic pellets in this project is 3-5% higher than the porosity of traditional iron-carbon packing. After testing, the wastewater treatment agent prepared using the optimized process is found to be superior to products produced by comparison companies. The deactivation of the treatment agent and the pore clogging problem can be effectively controlled.

2.2.3 Experiment on coking wastewater treatment

The optimal agglomerates, prepared with a Fe/C ratio of 3:1, C/O ratio of 1.2, reduction temperature of 1330°C, and reduction time of 15 minutes, were chosen as the treatment agent for coking wastewater using iron-carbon microelectrolysis principles. The coking wastewater utilized in this experiment originates from a coking plant within an iron and steel group, having undergone complete removal of oil and suspended solids through air flotation tank sedimentation. Table 4 lists the main components of the wastewater.

Table 4. Nature of Raw Water

pH	COD(mg/L)	NH_3-N (mg/L)	BOD_5(mg/L)	Chromaticity (times)
≤hr	1000-3600	≤000	≤000-	300-500

In the reactor, 2kg of the effluent agent was introduced as microelectrolysis filler along with 2L of coking effluent adjusted to a pH of 3. After thorough aeration over 24 hours, samples were collected every 4 hours for subsequent testing and analysis.

Figure 5. Iron-carbon Micro-electrolysis Treatment Device

The treatment capacity of the iron carbon microelectrolysis treatment unit is at 25L/h, which meets the required experimental content of the experiment.

Iron carbon micro-electrolysis pellets which weigh 5 Kg were put into the iron carbon micro-electrolysis experimental device, and 15 L of coking wastewater was added, the amount of coking wastewater added must cover the iron carbon micro-electrolysis pellets. Turn on the power of the experimental device and adjust the aeration volume of the experimental device to 0.4 m^3/h. Measure the indexes of the untreated coking wastewater before the experiment starts, and design seven groups of experimental aeration time such as 2, 4. 6, 12, 24, 48, 72, etc. At each designated time interval, collect experimental water samples and measure the COD and ammonia nitrogen content values. Calculate the corresponding removal rates of the treatment's COD and other key performance indicators. These performance indicators will facilitate the assessment of the final treatment efficacy of iron-carbon microelectrolysis pellets. (As shown in figure 5)

3. Results and Discussion

The heating process of the agglomerates was observed by laser confocal microscopy (Figure 6), and the heating curve is shown in Figure 7. below 800℃, the heating rate was 200℃/min; above 800℃, the heating rate was 60℃/min. when reaching 1350℃, the temperature was held for 15min.

Based on the observation records, we can conclude that at a temperature of 800℃, the pellet began to shrink and deform. At 1020℃, bubbles began to form, indicating that the reduction reaction intensified. At 1270℃, a significant increase in the number of bubbles was observed, indicating that iron beads were being generated. At 1300°C, the liquid phase was generated in the pellet, and after 1330°C, the liquid phase flow in the pellet was obvious, and bubbles were generated at the same time, and more iron beads were produced. At 1350℃, using laser confocal microscopy to observe the new filler, it can be found that the reduced iron gathers together to form iron beads (Figure 8). Figure 8 shows a new type of iron carbon filler prepared using a carbon tube furnace. Figure 9 shows the SEM and EBSD diagrams of the new iron carbon filler.

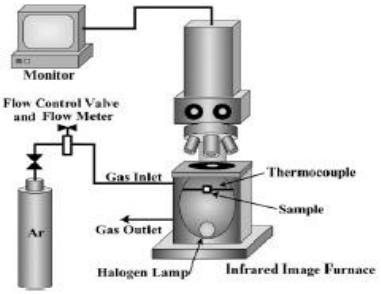


Figure 6. Laser Confocal Microscopy

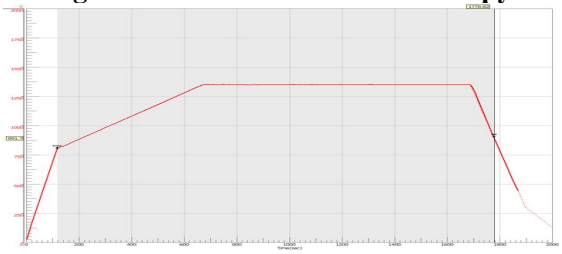


Figure 7. Temperature Rise Curve

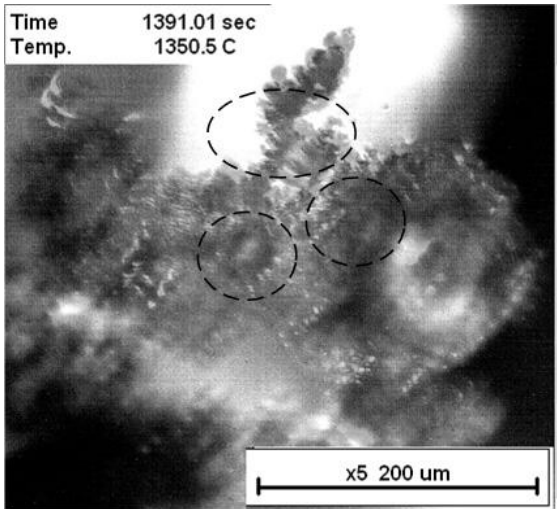
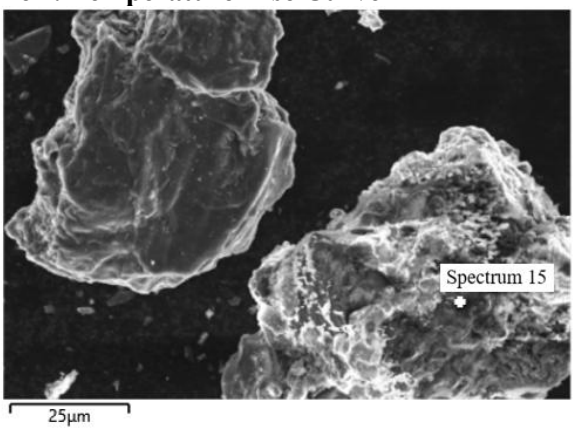


Figure 8. Recorded Images Using a Laser Scanning Confocal Microscope at 1350℃



Element	Wt%	Wt% sigma
C	13.08	0.31
O	28.68	0.39
Na	1.89	0.09
Si	5.24	0.12
Ca	0.84	0.11
Fe	50.26	0.61
Total	100.00	

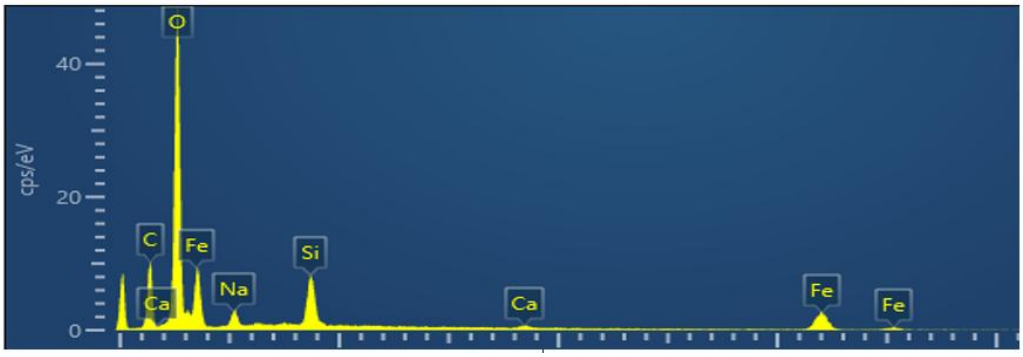


Figure 9. The SEM and EBSD Diagrams of the New Iron Carbon Filler

3.1 Factors Influencing the Fe Yield in Agglomerates

3.1.1 Effect of carbon ratio C/O on Fe yield

The carbon allocation ratio, expressed as C/O where C/O = 1 indicates the amount of fixed carbon required for complete reduction of all iron-containing oxides to metallic iron. As depicted in Figure 10, at the same temperature, the metal yield initially rises and then declines with increasing C/O ratio from 1.0 to 1.6. This trend occurs because a higher C/O ratio accelerates the reduction rate. Increasing the carbon ratio within the same conditions enlarges the carbon volume within the agglomerate, thereby enhancing the carbon gasification rate. This acceleration promotes the oxidation-reduction reaction of iron, thereby increasing the metal yield. However, we also observed that an excessively high C/O ratio can leave unreacted coke powder that impedes the aggregation and growth of metal phases, leading to a decrease in metal yield.

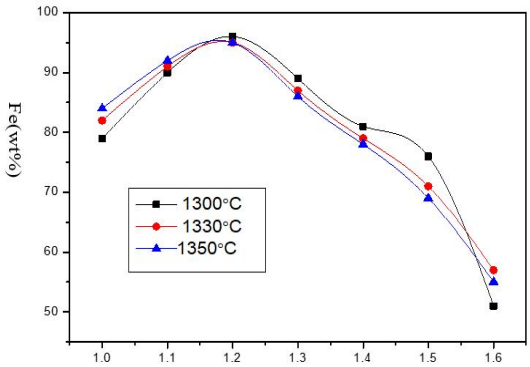


Figure 10. Effect of C/O Ratio on Iron Yield

3.1.2 Effect of reduction temperature on the yield of Fe

Based on Figure 11, the metal yield initially increases and then decreases as the reduction temperature rises. Higher temperatures generally promote the reduction reaction; however, excessive temperatures can lead to FeO in the agglomerate reacting with SiO_2, forming low-melting-point compounds. This results in a mobile slag phase that obstructs the voids among the agglomerate, tightly enveloping particles and impeding the desired reduction reaction. Consequently, the reduction kinetics deteriorate and the metal yield decreases. Therefore, it is evident that while higher reduction temperatures initially benefit the process, there is an optimal range beyond which the yield diminishes.

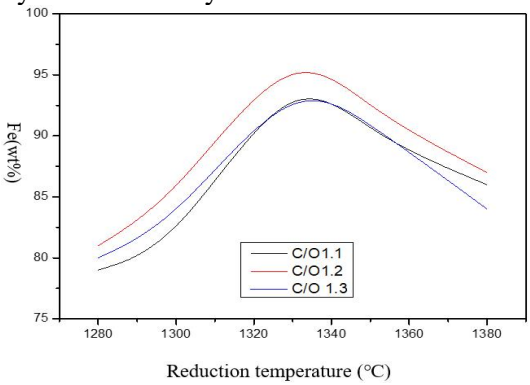


Figure 11. Effect of Reduction Temperature on Iron Yield

3.1.3 Effect of reduction time on Fe yield

Figure 12 illustrates the results for reduction times of 5, 10, 15, and 20 minutes at a carbon ratio of 1.2 and a reduction temperature of 1330°C. Initially, rapid reduction of the metal by carbon is observed upon commencement of reduction. With increasing reduction time, a greater amount of metal is reduced. At 15 minutes of reduction time, the metal yield reaches its peak; further extension of time shows minimal change in metal yield.

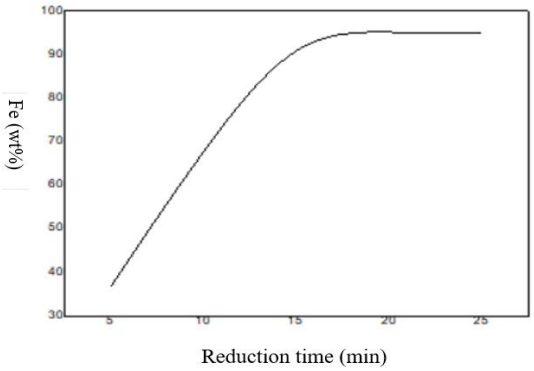


Figure 12. Effect of Reduction Time on Metal Yield

3.2 Experimental Results of Coking Effluent Treatment

The experimental findings, depicted in Figures 13 and 14, illustrate significant changes over the reaction time. Initially, the Chemical Oxygen Demand (COD) decreases gradually from 3450 mg/L to 2070 mg/L, marking a 40% reduction. Concurrently, Biochemical Oxygen Demand (BOD_5) shows steady improvement, while Biochemical Oxygen Demand to Chemical Oxygen Demand ratio (B/C) increases by 45%. The newly synthesized iron-carbon filler initiates an electrolytic reaction involving iron and carbon, releasing electrons that induce reduction reactions on oxide pollutants in wastewater, generating active compounds. This facilitates effective pollutant removal. Throughout the micro-electrolysis process, an electric field forms between the iron and carbon electrodes, causing charged colloidal particles in coking wastewater to migrate directionally, enhancing pollutant enrichment and removal.

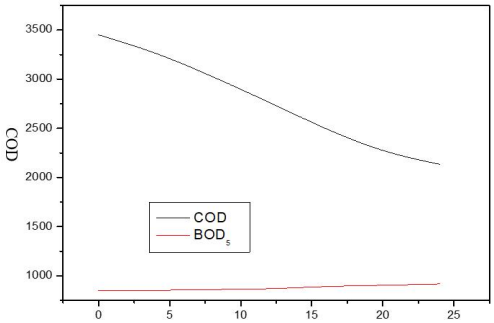


Figure 13. Cod and Bod5 Vary With Time

During iron-carbon micro-electrolysis, the production of $Fe(OH)_2$ and $Fe(OH)_3$ contributes to strong flocculation-adsorption properties. These compounds efficiently adsorb colloidal particles in wastewater, promoting their coalescence through bridging

and cross-linking mechanisms. Consequently, this process reduces wastewater coloration and eliminates organic matter presence.

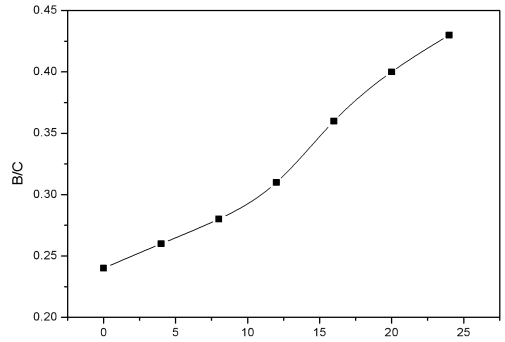


Figure 14. B/C Changes with Time

4. Conclusion

In conclusion, by utilizing solid waste from the iron and steel industry, a small amount of coke as a reducing agent, and maintaining a carbon ratio of 1.2, along with a reaction temperature of 1330°C and a reduction time of 15 minutes, we can produce carbon metal agglomerates suitable as new fillers for iron-carbon microelectrolysis in treating coking wastewater. Optimal conditions yield agglomerates with a porosity of 53.8%, iron recovery rates reaching up to 95%, and carbon content ranging from 70% to 90%.

The treated coking effluent shows a significant reduction in COD by approximately 41% and an increase in the B/C ratio by 45%, thus markedly improving the effluent's biochemical properties.

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