Preparation, Characterization of Coal Ash Adsorbent and Orthogonal Experimental Research on Treating Printing and Dyeing Wastewater

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Abstract. Using high temperature activated sodium flying ash and carboxymethyl chitosan as raw material to prepare carboxymethylchitosan wrapping fly-ash adsorbent (CWF), combined with iron-carbon micro-electrolysis treatment of simulated and actual printing and dyeing wastewater. The conditions for obtaining are from the literature: the best condition for CWF to treat simulated printing and dyeing wastewater pretreated with iron-carbon micro-electrolysis is that the mixing time is 10 min, the resting time is 30 min, pH=6, and the adsorbent dosage is 0.75 g/L. The results showed that COD removal efficiency and decoloration rate were above 97 %, and turbidity removal rate was over 90 %. The optimum dyeing conditions were used to treat the dyeing wastewater. The decolorization rate was 97.30 %, the removal efficiency of COD was 92.44 %, and the turbidity removal rate was 90.37 %.

1. Introduction
In recent years, dye wastewater has a high concentration of organic matter (COD Cr = 1000~100,000 mg/L) and chroma (500~500,000), high content of inorganic salts, complex composition and poor biodegradability and hard decoloration characteristics [1]. such as Yuan et al [2] using chitosan on printing and dyeing wastewater flocculation and removal in color, pH value of 6 and the solution containing 1 % chitosan under the condition of printing and dyeing wastewater decolorization rate can reach 90 %. Yang et al. [3] carboxymethyl chitosan modified, COD removal rate is greater than 95 %, COD removal rate of other dye wastewater is more than 92 % [4]. Alkaline material can destroy the hard outer surface of fly ash particles, thus enhancing the activity. Decolorization of reactive red KD-8B dye wastewater [5], Liu [6] of fly ash was modified after the results show that the best pH value is 12.3, 1 mol/L Ca(OH)2 solution of the modified flying ash was the best, the decolorization rate can reach more than 99.9 %. The weight of the straight. NaOH is used to fly ash pretreatment at a temperature of 500 °C, experiments show that the adsorption material is formed with better performance [7]. Pan et al. [8] used the Iron-carbon Micro-electrolysis method to treat the gold orange G analog printing and dyeing wastewater. The decolorization rate was 89 %, and the removal rate of COD was 41 %.
2. Experimental Part

The fly ash added conical flask with NaOH according to the mass ratio of 2.16:1 and NaOH, together with distilled water at the temperature of 83 °C for 7 h, filtration, washing and drying and cooling. Carboxymethyl chitosan NaOH is stirred into sodium type flying ash by screening after activation of 1 h, fast stirring and then slow stirring, filtration, drying, grinding. According to the study of Pan [9], Liu [10] and He [11-13]. The pretreatment was as follows: preparation of activated purple simulated wastewater, adjusting pH, activated carbon into wastewater, adsorption, adding iron filings, stirring electrolysis.

We conditionally study on the single factor of flocculation effect. There is the treatment effect of changing mixing time. We take the 6200 mL concentration of 0.1 g/L after simulated wastewater pretreatment, regulation of pH was 4.5, the dosage of CWF is 0.15 g, 5 min, 8 min, respectively stirring 10 min, 20 min static 60 min, respectively sampling measured COD, turbidity and absorbance, calculate the removal rate of turbidity, the removal rate of COD and the decolorization rate. Change the incubation time on the treatment effect, which is shows as follows: 6200 mL concentration of 0.1 g/L after simulated wastewater pretreatment, regulation of pH was 4.5, the dosage of CWF was 0.15 g, stirring 10 min, static 10 min, 20 min, respectively 30 min, 60 min, 90 min and 120 min respectively after sampling measured COD, turbidity and calculation of absorbance, the removal rate of turbidity and COD removal rate and decoloration rate.

3. Results and Discussion

Orthogonal experiment is as follows. Conclusions obtained by single factor experiment, pH values, CWF dosages, stirring times and settling times on the treatment results are studied, in order to obtain the experimental data more representative, with pH, CWF dosage and resting time as parameters to the decolorization rates and the removal rates of COD as the study object, the design of three factors four level of orthogonal test, further research on the optimum processing conditions. With pH, CWF dosage and resting time as the parameters, the decolorization rate is the orthogonal Table 1, which as follows:

| Test number | PH | CWF dosage (g) | Resting time (min) | Decolorization rate% | COD removal rate% |
|-------------|----|----------------|--------------------|----------------------|-------------------|
| 1           | 4  | 0.1            | 20                 | 86.92                | 90.18             |
| 2           | 4  | 0.15           | 30                 | 89.99                | 90.43             |
| 3           | 4  | 0.2            | 60                 | 90.72                | 93.54             |
| 4           | 4  | 0.3            | 90                 | 92.53                | 94.94             |
| 5           | 4.5| 0.1            | 30                 | 93.92                | 95.61             |
| 6           | 4.5| 0.15           | 20                 | 98.53                | 97.70             |
| 7           | 4.5| 0.2            | 90                 | 98.62                | 96.90             |
| 8           | 4.5| 0.3            | 60                 | 98.90                | 96.51             |
| 9           | 5  | 0.1            | 60                 | 98.99                | 94.52             |
| 10          | 5  | 0.15           | 90                 | 99.54                | 95.37             |
| 11          | 5  | 0.2            | 20                 | 98.07                | 94.87             |
| 12          | 5  | 0.3            | 30                 | 94.08                | 93.30             |
| 13          | 6  | 0.1            | 90                 | 94.17                | 92.02             |
| 14          | 6  | 0.15           | 60                 | 97.33                | 97.51             |
| 15          | 6  | 0.2            | 30                 | 97.79                | 95.69             |
| 16          | 6  | 0.3            | 20                 | 97.97                | 95.96             |

Decolorization rate:
- k1 360.16 374.00 381.49
- k2 389.97 385.39 374.65
- k3 390.68 385.20 385.94
- k4 387.26 383.48 384.86
- R 30.52 11.39 11.29

COD removal efficiency:
- k1 369.09 373.73 378.71
- k2 386.72 381.01 375.03
- k3 378.06 381.00 383.48
- k4 381.18 380.71 379.23
- R 17.63 8.68 8.45
From the analysis of Table 1 range, CWF in the treatment of simulated wastewater, 3 factors affecting decolorization rates are: pH value, CWF dosage, incubation time, the decoloration rate reached optimum reaction conditions for the highest pH=5, CWF dosage of =0.15 g, holding time =60 min; COD removal the 3 factors are: pH value, CWF dosage, incubation time, COD removal rate can reach the best reaction conditions for the highest pH=4.5, CWF dosage of =0.15 g, holding time =60 min. The pH of the wastewater is the main factor to the removal of COD as the main purpose, and considering the effect of decolorization rate. Selection of optimum conditions for pH=4.5, CWF dosage of =0.15 g, holding time =60 min, the decoloration rate reached more than 98.53 %, COD removal rate reached more than 97.70. Using the best conditions, iron-carbon micro-electrolysis technology was applied to treat actual dyeing wastewater. The absorbance, COD and turbidity of the actual water samples are measured. Take 200mL printing and dyeing wastewater in 500 mL beaker, adding 0.15 g CWF, stirring evenly, and adjusting pH to 4.5 at the same time, stirring 10 min, being static 60 min, testing its absorbance, COD and turbidity. 200 mL printing and dyeing wastewater in 500 mL beaker, measured water sample by pH=11.06, using hydrochloric acid to regulate pH to 2, accurately weighing 4 g activated carbon and putting it in water, stirring, standing 30 min after adding 6 g iron, electrolytic 20 min after filtration. The 0.15 g CWF composite adsorbent was put into the filtrate and stirred evenly. At the same time, the pH was adjusted to 4.5. Then stirred 10 min, and the 60 min was placed at the static position. The absorbance, COD and turbidity were measured and the decoloration rate, COD removal rate and turbidity removal rate were calculated. The processing results are shown in Table 2 and Table 3:

Table 2. Absorbance, COD and Turbidity of Treated Water Sample

| Absorbance (wavelength 540nm) | COD (mg/L) | Turbidity (NTU) |
|-------------------------------|------------|----------------|
| Raw water sample               | 0.243      | 821.0          | 53.7          |
| Water samples pretreated with iron carbon micro electrolysis | 0.062 | 387.5 | _ |
| Water samples treated by iron carbon micro electrolysis combined with CWF adsorbent | 0.006 | 62.1 | 5.17 |
| Water samples were treated only with CWF sorbent | 0.043 | 175.7 | _ |

Table 3. Decolorization rate, COD Removal Rate and Turbidity Removal Rate of Treated Water Samples

| Decolorization % | COD removal efficiency % | Turbidity removal rate % |
|------------------|--------------------------|--------------------------|
| Water samples pretreated with iron carbon micro electrolysis | 74.49 | 52.80 | _ |
| Water samples treated by iron carbon micro electrolysis combined with CWF adsorbent | 97.30 | 92.44 | 90.37 |
| Water samples were treated only with CWF sorbent | 82.30 | 78.60 | _ |

Table 2 shows the use of iron-carbon micro-electrolysis technology combined CWF treatment of actual printing and dyeing wastewater, decolorization rates and COD removal efficiency than using only CWF is increased by 15% and 13.84%, the decolorization rate and COD removal efficiency and turbidity removal rate reached 97.30%, 92.44%, 90.37%. There is electron microscopy characterization
of Carboxymethyl Chitosan Coated flying ash before and after adsorption. CWF respectively before and after the use of SEM characterization, the results are shown in Figure 1, Figure 2.

![Figure 1. SEM Characterization Diagram of Carboxymethyl Chitosan Coated Flying Ash Before Adsorption.](image1)

![Figure 2. SEM Characterization of Carboxymethyl Chitosan Coated Flying Ash Before Adsorption.](image2)

As can be seen from Figure 1, the main structure of CWF is spherical, and its specific surface area is large and has strong adsorption capacity. Figure 1-2 shows that the surface of the sphere is no longer smooth and many fine dye molecules are adsorbed on it to form a dense solid floc. Accordingly, it is indicated that CWF has good adsorption to dye molecules in dyeing wastewater, and is the main mechanism of decoloration.

4. Conclusion
Iron-carbon micro-electrolysis combined with sodium carboxymethyl chitosan modified fly ash composite agent was used to treat simulated printing and dyeing wastewater by orthogonal test, and the optimum experimental conditions were screened. At this time, the mass ratio of fly ash to carboxymethyl chitosan is 6:1. In literature, the adsorbent dosage was 0.75 g/L, and pH was 6, stirring 10 min and resting time 30 min.

(1) Under this condition, the treatment of the actual dyeing wastewater by combined iron-carbon micro-electrolysis process showed that the decolorization rate was 97.30 %, the removal efficiency of COD was 92.44 %, and the turbidity removal rate was 90.37%. The adsorbent dosages and times are effectively saved.

(2) By iron-carbon micro-electrolysis pretreatment wastewater, experimental conditions: iron carbon ratio is 3:2, pH is 2, the activated carbon adsorption time is 30 min, electrolysis time is 20 min, the pretreatment of printing and dyeing wastewater decolorization rate was 74.49 % and the removal rate of COD was 52.80 %. By using this technology and combined with CWF adsorbent, the decolorization rate was increased by 15 % and the removal rate of COD was increased by 13.84 %.

(3) CWF composite adsorbent has excellent adsorption capacity, but it is extremely sensitive to pH. If the pH is in the optimum range, the adsorbent will be added, and the wastewater will be visible at
the same time of mixing. But the best CWF pH in different components of printing and dyeing wastewater are different, this has yet to be explored after day.

Acknowledgments
This work was supported by Water Pollution Control Engineering Technology Research Center of Foshan (2016GA10159), 2016 Foshan Science and Technology Project.

References
[1] Chao Yang. Studying on the treatment of dye wastewater by Chitosan Composite Fly Ash [D]. Nanjing Forestry University, 2009.
[2] Yihua Yuan, Xinghua Lai, Chunxin Chen, et al. There is flocculation and decoloration effect of Chitosan on printing and dyeing wastewater J, Applied Chemistry. 17 (2) (2000)217-218.
[3] Zhikuan Yang, Yang Yuan, Lifen Cao, Studying on decolorization of water soluble dye wastewater by Carboxymethyl Chitosan, J, Environmental Science and Technology. 2 (1999) 8-10.
[4] Pengfei Wang, Research progress of comprehensive utilization of fly ash J, Power Tech and Environmental Protection. 22 (2), (2006) 42-44.
[5] Zhenhua Hao, The application of fly ash in urban road engineering and the exploration of the proportion of two grits and gravel base J, Science and Technology Information. 36 (2007) 171-172.
[6] Hong Liu, Treatment of reactive red KD-8B dye wastewater by fly ash J, Industrial Safety and Environmental Protection. 31 (11) (2005) 13-15.
[7] Shimizu N, Misaka N, Utani K, Selective Formation of Na–X Zeolite from Coal Fly Ash by Fusion with Sodium Hydroxide Prior to Hydrothermal Reaction J, Journal of Materials Science. 28 (17) (1993) 4781-4786.
[8] Quan Pan, Hui Wang, Yujiiao Yang, et al., Study on treatment of printing and dyeing wastewater by iron and carbon micro electrolysis J, Journal of Hubei University (Natural Science Edition). 33 (2) (2011) 165-167.
[9] Lifeng Zhou, Xuefeng Fei, Wanqing Li, et al., Pharmaceutical wastewater by iron carbon micro electrolysis experimental study J, Environmental Science and Management. 35 (5) (2010) 101-102.
[10] Wei Liu. Study on the application of iron carbon micro electrolysis for the treatment of refractory organic wastewater [D]. Central South University, 2011.
[11] 11. He L, Chen Y, Shi L, et al, Application of copper-based heterogeneous catalysts in organic wastewater treatment J, 207(1) (2017) 012088.
[12] Liang Shi, Shichu Chen, Lingfeng He, Yongli Zhang, The composite coagulation of succades wastewater treatment J, Contemporary Chemical Industry. 46 (08) (2017) 1531-1533+1537.
[13] Liang Shi, Shichu Chen, Lingfeng He, Yongli Zhang, Treatment of preserved wastewater on the performance of upflow anaerobic sludge bed reaction J, Contemporary Chemical Industry. 46 (07) (2017) 1303-1306