

Regenerate Cr(VI) Oxidation Bleaching Solution from Wastewater in Process of Oxidation Bleaching of Montan Wax by Indirect Electrochemical Oxidation

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Chromium plays very important role in industry, especially in the process of oxidation bleaching for Montan wax. Chromium(VI) was converted into Cr(III) during this process and it is very difficult to treat the wastewater. In this study, a new indirect electrochemical oxidation method has been used to treat the wastewater from the process of oxidation bleaching of Montan wax to regenerate the oxidation bleaching solution. A series of experiments (5 variation factors at 4 levels) were carried out and an optimized experiment condition was obtained: Current density, 400A/m²; temperature of cell, 55 °C; Cr(III) concentration at anode cell, above 0.5 mol/L; sulfuric acid concentration in cathode cell, 10 % (v/v); and catalyst usage, 10 mL, 1 % (w/w). Under the optimized conditions, high current efficiency and chromium conversion ratio [Cr(III) to Cr(VI)] were obtained, they are higher than reported values. Five cycles of process have been carried out: oxidation bleaching of Montan wax, then treating the wastewater by indirect electrochemical oxidation to regenerate the oxidation bleaching solution. This study provides feasibility for the oxidation bleaching of Montan wax in industry scale at low-cost and industrial wastewater containing chromium would be significantly reduced.

Keywords: Wastewater containing chromium, Indirect electrochemical oxidation, Montan wax.

INTRODUCTION

Over the past few decades, chromium has been widely used in aerospace¹, it also has applications in leather tanning, electroplating, manufacturing of dye, paper printing, glass making and automobile parts manufacturing². Chromium (VI), plays a major role in oxidation bleaching process of Montan wax. Montan wax has considerable applications, it could be used as the replacement for expensive natural botanic wax, such as palm wax. However, a lot of wastewater containing chromium and sulfuric acid is produced in this process.

Chromium(VI) is toxic, carcinogenic, mutagenic and teratogenic³. The direct release of chromium containing wastewater could bring certain catastrophic damages to environment and human health, such as the chromium pollution event in Luliang, Yunnan, China and the toxic capsule event containing chromium. Many projects have been canceled in China because of the chromium contamination. In the manufacture of Montan wax, an environment-friendly method to treat chromium containing wastewater is critical⁴.

Current approaches of removing chromium from the wastewater include chemical precipitation, ion exchange, reverse osmosis, membrane processes, evaporation, solvent extraction

and adsorption⁵. However, these techniques are expensive to use and generate a large amount of secondary chromium containing wastewater⁶. Many of these approaches are inefficient and difficult to be used in developing and developed countries⁷.

Indirect electrochemical oxidation has been used to prevent chromium pollution, it has been applied to the synthesis of 2-methyl-1,4-naphthoquinone⁸ and cyclohexanone⁹, as well as to prepare terephthalic acid¹⁰. If this technique could be applied in the industrial process of oxidation bleaching of Montan wax, chromium can be recovered and re-used. This would have great impact to better environment and achieve greener-industry, also reduce cost.

In this study, a method of regenerate the oxidation bleaching solution by indirect electrochemical oxidation from the wastewater of the oxidation bleaching process of Montan wax was investigated. Five variation factors *i.e.*, Current density, temperature, sulfuric acid concentration, chromium concentration and catalyst usage, were chosen to measure the current efficiency, conversion rate of Cr(VI) and recovery rate of chromium. An optimized experimental condition was selected by orthogonal experiment design and 5 cycles of oxidation bleaching of Montan wax/treating wastewater by the optimized indirect electrochemical oxidation method were carried out.

EXPERIMENTAL

Chromium wastewater was collected from Montan wax bleaching process in the lab. 1 % catalyst, H₂SO₄ and other chemicals were all of analytical grade and purchased from Chengdu Lianhe Huagong Reagent Institute. Deionized water was used throughout the experiment.

Indirect electrochemical oxidation apparatus: The indirect electrochemical oxidation process was carried out in a two-compartment flow cell (150 mm × 100 mm × 200 mm, Hangzhou Saiao chemical-electrical equipment Inc.) as reported earlier¹¹⁻¹³. A Ti/PbO₂ electrode was employed as anode and Nafion 324 membrane was used as separator. The electrolytic mediator was H₂SO₄. A PVC flow distributor was placed on either side of the membrane. PVC nozzles for inlet and outlet ports were fitted through the end plates and the electrodes. The flow of anolyte and catholyte was maintained at desired rate by two circulation magnetic pumps. Chromium oxidation was carried out constantly at 30V/50A by a DC power supply (Dongguan Daxing Company). Anodic cell was in a constant temperature water bath (Jintan Jieruier Electronic device Inc).

Cell design and electrolysis: The scheme of the experimental procedure is shown in Fig. 1. The chromium wastewater produced from Montan wax bleaching process (containing Cr₂(SO₄)₃ and H₂SO₄). It was pumped into the anode cell. Sulfuric acid was added in the cathode cell. Cr³⁺ and H₂O transformed into Cr₂O₇²⁻ and H⁺ through losing electrons in the anode cell. H⁺ in sulfuric acid got electrons and formed hydrogen gas in the cathode cell. Then, the H₂Cr₂O₇ produced in the anode cell, it was pumped into the bleaching reactor and used as oxidant again and the H₂SO₄ were separated by a certain technique and utilized in the bleaching and electrolysis processes. The entire cycle only consumed the electronic energy and no pollutant was discharged.

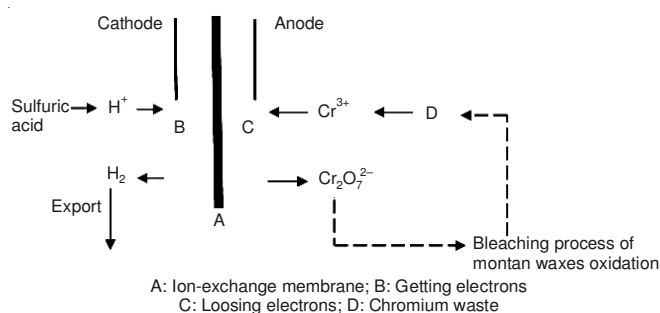
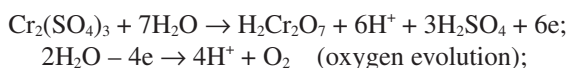
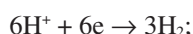


Fig. 1. Cr(III)/Cr(VI) electrochemical oxidation system

The anode reaction is,



Cathode reaction is,



Overall cell reaction is,



Analytical methods: The current efficiency (η) is an important index that reliability and economy. It was calculated using the relation¹⁴.

$$\eta = \text{practical output/theoretical output}$$

where, practical output = $C(\text{Cr}_2\text{O}_7^{2-}) \cdot M(\text{Cr}_2\text{O}_7^{2-}) \cdot V(\text{Cr}_2\text{O}_7^{2-})$
Theoretical output = $1.344 \cdot I \cdot t$.

The chemical oxygen demand at time t (h), I indicates current intensity(A).

Chemical convention ratio as shown in eqn:

$$R = n\text{Cr(VI)}_t/n\text{Cr(III)}_0 = [n\text{Cr(VI)}_t - n\text{Cr(VI)}_0]/n\text{Cr(III)}_0$$

where: $n\text{Cr(VI)}_t$ indicates the quantity of Cr(VI) during the electrolytic process within a duration of t ;

$n\text{Cr(VI)}_t$ indicates the quantity of Cr(VI) after hours;

$n\text{Cr(VI)}_0$ indicates the initial quantity of Cr(VI);

$n\text{Cr(III)}_0$ indicates the initial quantity of Cr(III).

This paper is not only treat chromium waste water, but also achieve environmentally-friendly requirement, there is important indicator that chromium recovery, Y (%) was expressed as a percentage and defined

$$Y(\%) = m_t/m_0 \times 100 \%$$

where m_t is total chromium after time, t (h) of electrolysis time, m_0 is total chromium before.

Orthogonal array experimental set up: Several authors have reported that there is little information available the optimization of indirect Cr(III) electrochemical oxidation. Especially, it is that join in a catalyst in the indirect electrochemical oxidation system¹⁵. However, in these studies, a orthogonal array design involves the selection of some representation combinations of factor and levels for the experiments. This method has proven to be a cost-effective optimization strategy that can obtain the optimal conditions of each parameter in a limited number of experimental trials¹⁶. therefore, this paper discussed five main process conditions in indirect electrochemical oxidation reaction (Table-1). This design obtains 16 electrolytes.

TABLE-1
FIVE FACTOR FOUR LEVELS

| Level | Factors | | | | |
|-------|-------------------------|----------------------|---------------------------------|----------------------------------|------------------|
| | A Current density (j/A) | B temperature (T/°C) | C Cr(III) concentration (mol/L) | D cathode cell (sulfuric acid/%) | E catalyst (/mL) |
| 1 | 8 | 45 | 0.2252 | 5 | 5 |
| 2 | 9 | 50 | 0.5173 | 10 | 10 |
| 3 | 10 | 55 | 0.5658 | 15 | 15 |
| 4 | 11 | 60 | 0.6275 | 20 | 20 |

Determination of current density (factor A): The size of anode plate PbO₂/Ti used in the experiment was 200 mm × 100 mm and the suggested current density for this kind of electrolysis cell is 300-600 A/m². The standard oxidation potential of chromium(III) and that of oxygen evolution are very close (1.33 and 1.229 V, respectively), the oxygen evolution could not be avoid with the presence of sulfuric acid. With the increase of current density, the speed of conversion from Cr(III) to Cr(VI) is much faster than that of oxygen evolution. In the experiments, the oxygen evolution is unfavorable for the electrolysis reaction and increases the energy consumption. Proper current density could inhibit the oxygen evolution. So the current density for the frame electrolysis cell should be around 350-550 A/m².

Determination of temperature (factor B): Chromium(III) oxidation seems to be more affected under certain temperature in the electrolysis cell, if the temperature increase a certain level it can influence the current density and the conversion ratio of Cr(VI). The cell at increasing high temperature only raise the conversion ratio and decrease the cell voltage but increase the diffusion constant of electrolyte material. However, higher temperature causes the growth of cost for the industrial production, which would not benefit the development of the company. Meanwhile, the limit of heat resistance of the material used to build the cell should also be considered. Hence, the temperature for 318-333 K may be used.

Determination of anode concentration (factor C): The influence of the initial concentration of $\text{Cr}_2(\text{SO}_4)_3$ on the indirect electrochemical oxidation process was studied at broad range of $\text{Cr}_2(\text{SO}_4)_3$ concentration (0.2-0.7 mol/L). An increase in the concentration of $\text{Cr}_2(\text{SO}_4)_3$ could benefit the rate of main electrode reaction. In order to raise the current efficiency and reduce the side reaction at the anode cell, the concentration of Cr(III) need modestly higher.

Determination of catholyte concentration (factor D): As the increasing mass fraction of sulfuric acid in cathode cell, the current efficiency was gradually increased. On the contrary, when the cathode concentration reached to a certain level, the current efficiency began to drop. This may be caused by the decrease of conductivity in the cathode, when a high content of sulfuric acid got to a certain value. In order not to corrode the cathode plate and may damage the Nafion membrane, the catholyte concentration must not exceed 30 %. By considering the cell pressure, economy and safety factors, in view of this possibility, the experiment will choose 5-20 % (v/v) H_2SO_4 as the catholyte.

Determination of usage of catalyst (factor E): It is reported that the current efficiency for the oxidation of chromium(III) is dependent on the catalyst. The concentration

of catalyst plays an important role in the indirect electrochemical oxidation process *via* two ways; an increase in the concentration of the supporting electrolyte increases the chromium(III) and the cell conductivity. The former enhances the destruction of organics present in the wastewater and the latter can result in a rise of current density at the same voltage which provides more chance for the production of chromium(VI) in the relatively higher current densities. It is known that the oxygen evolution is inhibited at the anode. For optimum condition, the 1 % (w/w) catalytic of 5-20 mL may be used, which is an expedient temperature for industrial application.

RESULTS AND DISCUSSION

The order and contribution rate of every experiment factor on target index is determined by means of range analysis (Table-2).

Range analysis: The result has been processed by using range analysis method. According to the calculation the optimum process combination of indirect electrochemical oxidation is known as: $A_1B_3C_4D_2E_3$, namely current density, 400A/m^2 ; Temperature of cell, $55\text{ }^\circ\text{C}$; Cr(III) concentration is 0.6275 mol/L at anode cell; sulfuric acid concentration in cathode cell, 10 % (v/v); and catalyst usage, 15 mL, 1 % (w/w). According to range analysis: K and R^{16} , the trivalent chromium concentration had the greatest influence on current efficiency in anode cell. Then according to formula of current efficiency, when the current efficiency would reach about 80 %, initial chromium(III) concentration would be as high as 0.4 mol/L . According to the OA_{16} matrix, 16 experiments has oxidated Montan wax condition, lower chromium(VI) concentration of couldn't deep oxidation Montan wax. A comparison of the K value is shown in Table-2, the numerical difference of K2 and K3 is not big, only 0.054, but considering the high prices of catalysts, we choose the K2, that we used to determine 1 % catalyst 10 mL to add into 1 L chromium(III), the dosage can

TABLE-2
INDEPENDENT VARIABLES AND PREDICTED RESULT FOR INDIRECT ELECTROCHEMICAL OXIDATION

| Trial No. | Factors | | | | | Result | | |
|-----------|---------|-------|-------|-------|-------|------------------------|----------------------------------|-----------------|
| | A | B | C | D | E | Current efficiency (%) | Percent conversion of Cr(VI) (%) | Cr recovery (%) |
| 1 | 1 | 1 | 1 | 1 | 1 | 40.9 | 81.4 | 99.3 |
| 2 | 1 | 2 | 2 | 2 | 2 | 97.5 | 83.7 | 100.9 |
| 3 | 1 | 3 | 3 | 3 | 3 | 99.4 | 78.6 | 100.1 |
| 4 | 1 | 4 | 4 | 4 | 4 | 95.7 | 70.1 | 105.2 |
| 5 | 2 | 1 | 2 | 4 | 3 | 85.8 | 81.7 | 102.3 |
| 6 | 2 | 2 | 1 | 3 | 4 | 45.5 | 95.9 | 98.7 |
| 7 | 2 | 3 | 4 | 2 | 1 | 102.3 | 82.8 | 99.6 |
| 8 | 2 | 4 | 3 | 1 | 2 | 94.8 | 79.8 | 105.8 |
| 9 | 3 | 1 | 3 | 2 | 4 | 82.3 | 78.1 | 104.3 |
| 10 | 3 | 2 | 4 | 1 | 3 | 93.2 | 79.4 | 104.7 |
| 11 | 3 | 3 | 1 | 4 | 2 | 42.7 | 96.7 | 97.6 |
| 12 | 3 | 4 | 2 | 3 | 1 | 87.3 | 90.3 | 104.3 |
| 13 | 4 | 1 | 4 | 3 | 2 | 85.4 | 88.1 | 95.1 |
| 14 | 4 | 2 | 3 | 4 | 1 | 82.2 | 88.2 | 101.1 |
| 15 | 4 | 3 | 2 | 1 | 4 | 82.8 | 95.4 | 103.3 |
| 16 | 4 | 4 | 1 | 2 | 3 | 47.4 | 95.5 | 101.0 |
| K_1 | 3.335 | 2.944 | 1.765 | 3.117 | 3.134 | | | |
| K_2 | 3.291 | 3.184 | 3.534 | 3.302 | 3.204 | | | |
| K_3 | 3.055 | 3.279 | 3.587 | 3.176 | 3.258 | | | |
| K_4 | 2.978 | 3.252 | 3.773 | 3.064 | 3.063 | | | |
| R | 0.357 | 0.335 | 2.008 | 0.238 | 0.195 | | | |

Note: The K values is only corresponding the current efficiency values

not only ensure the cost of the whole craft also keep the maximization of the current efficiency and the conversion rate (Table-3). It is obvious from Table-3 that the electrolyte and chromium wastewater contain a large number of the catalyst. When chromium wastewater rejoin in anode cell, it need not catalyst. Moreover, the effect of catalyst concentration on the current efficiency was also large. The current efficiency increased with increasing catalyst concentration and reached its maximum point ($K_{3E} = 3.258$) at 15 mL 1 wt.%. Beyond the optimal point, the current efficiency decreased dramatically to $K_{4E} = 3.063$. Though temperature is not the biggest influence on current efficiency in the range analysis, when the temperature becomes higher, it improves ion activation energy and its reaction rate.

TABLE-3

QUANTITY OF CATALYST BEFORE AND AFTER (mg/L)

| Step No. | 1 | 2 | 3 | 4 |
|---------------|-------|--------|-------|-------|
| Electrolyte | 75.84 | 103.48 | 48.09 | 66.04 |
| Cr wastewater | 78.60 | 92.94 | 49.41 | 61.92 |
| Acid-washing | 3.82 | 1.27 | 0.61 | 1.12 |
| Water-washing | 2.28 | 0.51 | 1.78 | 0.50 |

The ANOVA results for the current efficiency are shown in Table-4, according to the Wu and Leung¹⁶, the factor effect of catalyst usage is very small and Cr(III) concentration is very big. To increase the reliability of this statistical method (ANOVA), the sum of squared deviation (SS), degree of freedom (df) and the variance for reaction time (V) should be added to the sum of squared deviation (SS), degree of freedom (df) and the variance for the experimental error factors respectively and the factor effect should be regarded as the experimental error¹⁷. As for the inspection level, $\alpha = 0.01$ and 0.05 , the critical value can be found in the distribution table of the F-value: $F_{0.05} = 9.28$, $F_{0.01} = 29.46$. In Table-4, it is clear that $F_A < F_\alpha$, $F_B < F_\alpha$, $F_D < F_\alpha$, $F_C > F_\alpha$. When comparing F_j and F_α , it is clear that the F value obtained in ANOVA was higher than the listed F_α . This shows that the Cr(III) concentration is prominent factor affecting the current efficiency.

TABLE-4

ANALYSIS OF VARIANCE (ANOVA) OF THE CURRENT EFFICIENCY IN THE OA16 MATRIX

| Source | SS | df | V | F | $F_{0.05}$ | $F_{0.01}$ |
|--------|--------|----|----------|----------|------------|------------|
| A | 0.0225 | 3 | 0.007510 | 4.0957 | | |
| B | 0.0171 | 3 | 0.0057 | 3.0999 | | |
| C | 0.6589 | 3 | 0.2196 | 119.7814 | 9.28 | 29.46 |
| D | 0.0074 | 3 | 0.0025 | 1.3412 | | |
| E | 0.0055 | 3 | 0.0018 | | | |

SS: Sum of square deviation; df: The degree of freedom; V: The variance; F: The F ratio

Optimization of the experimental conditions: $A_1B_3C_4D_2E_2$, namely current density 400 A/m², temperature of cell, the initial trivalent chromium concentration (anolyte) is 0.6275 mol/L, the sulfuric acid (catholyte), 10 % (v/v), the dosage of catalyst, 10 mL, 1 % (w/w).

Parallel test

Source of the electrolysis mother liquor: The literatures^{18,19} reported that the mother liquor is almost derived from the

analytical pure in parallel test of the indirect electrochemical oxidation, it can get higher current efficiency and conversion rate, but the prime significance of whole system is at all discarded. This report is based on the investigation and have got the optimum craft combination of indirect electrochemical oxidation technology, the mother liquor is that used is from the oxidation liquid waste of the oxidation Montan wax and circulation utilization by indirect electrochemical oxidation as its core.

Choice of parallel condition: Considering the proceeding of the follow-up work and correspondingly increase the cost of experiment, the rest of the conditions remain the same, except the dosage of the catalyst needs to be changed. Catalyst used as the whole electrolytic system, in the whole process, there is different amount of catalyst in the electrolyte by oxidation of Montan wax. Plenty of catalyst exist in mother liquor. Catalyst need not be added in the electrolytic oxidation, that is to say, the mother liquor which is processed in parallel test can be directly channeled into the anode electrolytic cell. After 5 groups of parallel test, the experimental results also provide the scientific basis for the enlarging experiment and further study on this method (Table-5).

TABLE-5

CONDITIONS OF CYCLE ELECTROLYSIS

| | Current efficiency (%) | Percent conversion of Cr(VI) (%) | Recovery of Cr (%) |
|---|------------------------|----------------------------------|--------------------|
| 1 | 98.6 | 86.1 | 95.3 |
| 2 | 97.1 | 83.4 | 96.8 |
| 3 | 94.1 | 83.8 | 93.4 |
| 4 | 99.3 | 85.4 | 96.8 |
| 5 | 94.6 | 83.7 | 94.0 |

Conclusion

Optimal production condition obtained through the orthogonal experiment and the mother liquor parallel experiment can maximize current efficiency, the mother liquor of parallel experiment is derived from oxidation Montan wax. This can achieve target of the scale-up experiment. The work studied and optimized the indirect electrochemical oxidation technology of wastewater through the orthogonal experiment, an OA₁₆ matrix and parallel experiment. According to the range analysis and ANOVA. Optimization of the experimental conditions is current density 400 A/m², temperature of cell, 55 °C, the initial trivalent chromium concentration (anolyte) is 0.6275 mol/L, the catholyte 10 % (v/v), the dosage of 1 % catalyst, 10 mL.

Optimum indirect electrochemical oxidation technique is verified by parallel experiment, the average current efficiency is 96.74 %, the average conversion rate is 84.48 %, the average recovery rate is 95.26 %. Catalyst has almost no change before and after oxidation in this process.

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