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Research Article

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Environment friendly bleaching methods of montan wax

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ABSTRACT

Montan wax of removed resin of E'shan from Yunnan province as the investigation object, L value of the chroma as the main investigation index, environment friendly bleaching techniques of montan wax of removed resin were explored. The bleaching effect of three kinds of oxidation systems, i.e., Peroxide (P), Peracetic acid (Pa) and P & Pa was explored, which showed that P & Pa combined system was better than the single systems of P and Pa. The optimization of main process parameters of P & Pa combined system by using the response surface method drew to the optimal conditions: the material ratio of Pa bleaching stage in the combination-20:1, the material ratio of P bleaching stage in the combination-36.7:1, time(t)-80min, temperature(T)-118.5 ℃. And under this condition, the L value of the product was 62.02, which was almost consistent with the model prediction.

Key words: montan wax of removed resin; environment friendly; oxidation bleaching

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INTRODUCTION

Montan wax is a natural product that is obtained from the young lignite by using the selective extraction of the organic solvent, which includes two main parts as montan wax of removed resin (RRMW) and montan wax resin[1]. RRMW oxidation bleaching made of light colored wax, is the fundamental way to expand its scope of application, enhance product value, and then expand the economic benefits[2]. Currently a more mature approach is Cr^{6+} oxidation method[3], but the heavy metal chromium is not environmentally friendly, and the requirement of the recycling equipment is higher[4]. Therefore, seeking lower-cost environmentally friendly oxidant has been a hot topic in this field. Peroxide (P) and Peracetic acid (Pa) as two excellent environmental oxidizing agents, have been widely used in bleaching of pulp and fabric [5-9]. This article will use the P and Pa relevant tests for montan wax and provide certain theoretical basis for the new environment friendly oxidation bleaching techniques of RRMW.

EXPERIMENTAL SECTION

The method of oxidation bleaching under the P system.

(1) Each component was weighed and then fully blended to get oxide additive of P according to the ratio of quality ($MgSO_4$:$NaSiO_4$:TAED=1:1:1). (2) According to a percentage representing the quality by P, the oxide additive of P was added to a certain quality score of P solution after being fully mixed, and later the P oxidation liquid was obtained after adjusting the pH. (3) 100g RRMW was weighed into 1000ml three-necked flask and was heated to a molten state. Then it was stirred continuously at a certain temperature and the rate of 150r/min, and the P oxidation liquid was slowly dropped into the three-necked flask according to a certain mass ratio. Waste liquid was discharged after a certain reaction time, then the deionized water was sequentially added and the wax was washed at 100℃.

After the washed fluid was discharged , the product was dried at 70℃. And then it was cooled and can be obtained after being hot melted at 105℃.

The method of oxidation bleaching under the Pa system.

(1) Each component was weighed and then fully blended to get oxide additive of Pa according to the ratio of quality ($Na_4P_2O_7$:EDTA=1:1). (2) According to a percentage representing the quality by Pa, the oxide additive of Pa was added to a certain quality score of Pa solution with fully mixed, and later the Pa oxidation liquid was obtained after adjusting the pH. (3) 100g RRMW was weighed into 1000ml three-necked flask and was heated to a molten state. Then was stirred continuously at a certain temperature and the rate of 150r/min, and the Pa oxidation liquid was slowly dropped into the three-necked flask according to a certain mass ratio. Waste liquid was discharged after a certain reaction time, then the deionized water was sequentially added and the wax was washed at 100℃. After the washed fluid was discharged , the product was dried at 50℃. And then it was cooled can be obtained after at 105℃ hot melted.

Combination selection experiments of P and Pa combined system.

(1) Method A: With Pa for the initial bleaching, P was used to rebleach after the waste liquid had been discharged. (2) Method B: With P for the initial bleaching, Pa was used to rebleach after the waste liquid had been discharged. (3) Method C: With Pa for the initial bleaching, oxidation system of P was directly used to rebleach without the discharging of waste liquid. (4) Method D: Pa and P were directly used to bleach after being mixed according to a certain mass ratio.

Optimization tests of the best combination of P and Pa combined system.

By choosing the best selection of P and Pa combined system, single factor test on the four factors was carried out, i.e. Pa:RRMW, P:RRMW, t and T. And then optimization test was done by the response surface method according to the results of the single factor experiment.

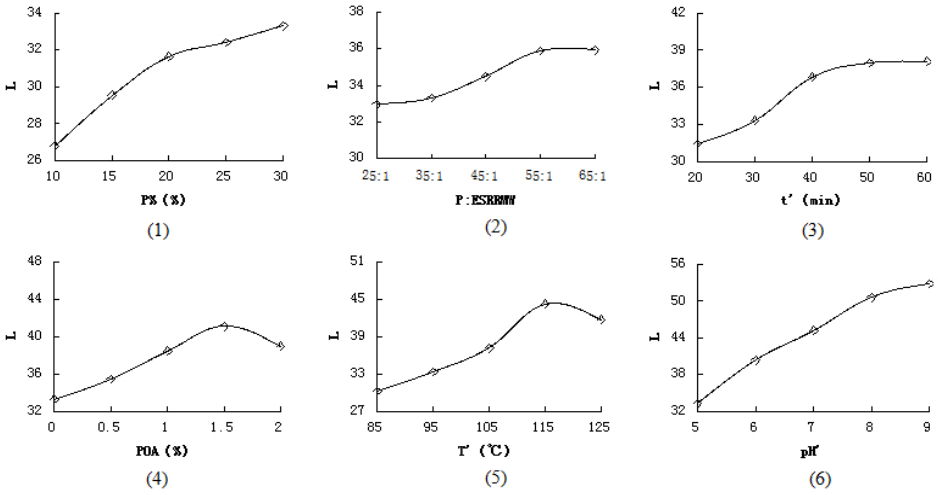
The determination method of chromaticity of montan wax.

The test sample was prepared according to the requirements of the test, and then relevant operations of color-difference meter were carried out. Differences between black and white degree of montan wax were judged by the value of L. The Lab system was chosen as the test system (Larger value of L denote more brightness and more tendence to white).

RESULTS AND DISCUSSION

The single factor experiment of oxidation bleaching under the P (or Pa) system.

The chroma of the single factor experiment of oxidation bleaching under the P (or Pa) system was shown in Fig.1.



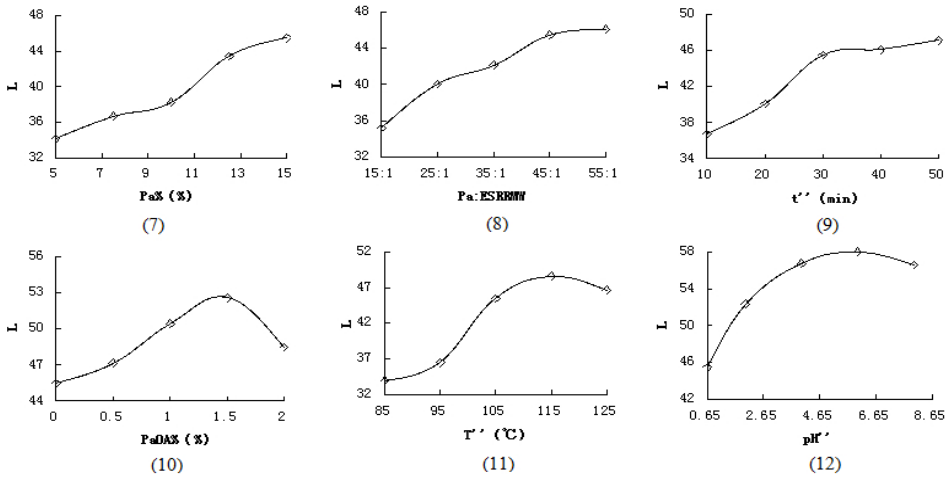


Fig.1 The chroma of the single factor experiment of oxidation bleaching under the P (or Pa) system

From Fig.1(1), along with the increasing of P %, L also increased. While P % was 30% of maximum setting and still presenting a trend of increasing, it was showed that the oxidation bleaching ability was proportional to P%.

From Fig.1(2), along with the increasing of P:ESRRMW (RRMW of E'shan from Yunnan province in China), L also increased. But when L increased slowly after P:ESRRMW was 55:1, it was indicated that colored substances or groups which could be oxidized by P were fully oxidized.

From Fig.1(3), along with the increasing of t', L also increased. But when L increased slowly after t' was 50min, it was indicated that t' increased with the unit content of P decreased and colored substances or groups were reduced which could continue to be oxidized.

From Fig.1(4), along with the increasing of POA%, L first increased and then decreased. L was maximum when POA% was 1.5%, it was indicated that the oxidative capacity of P enhanced with the increasing of POA% within a certain range. But P was decomposed too fast when POA% exceeded the best value and eventually led to decreasing of the bleaching capacity.

From Fig.1(5), along with the increasing of T', L first increased and then decreased. L was maximum when T' was 115 □, so it was indicated that the oxidation capacity of P was proportional to T' within a certain range. But P was decomposed too fast when T' exceeded the best value and eventually led to decreasing of the bleaching capacity.

From Fig.1(6), along with the increasing of pH', L also increased. But with the increasing of pH', the saponification reaction became more obvious. Meanwhile, the more and more intense reaction led to the difficult controlment of the bubbles, thus resulting to the obvious change of the physical and chemical properties of montan wax. Therefore, in order to ensure the basic properties of montan wax, high pH' value is inappropriate.

From Fig.1(7), along with the increasing of Pa %, L also increased. While Pa% was 15% of maximum setting and still presenting a trend of increasing, it was showed that the oxidation bleaching ability was proportional to Pa%.

From Fig.1(8), along with the increasing of Pa:ESRRMW, L also increased. But when L increased slowly after Pa:ESRRMW was 55:1, it was indicated that colored substances or groups which could be oxidized by Pa were fully oxidized.

From Fig.1(9), along with the increasing of t", L also increased. But when L increased slowly after t" was 30min, it was indicated that t" increased with the unit content of Pa decreased and colored substances or groups were reduced which could continue to be oxidized.

From Fig.1(10), along with the increasing of PaOA%, L first increased and then decreased. L was maximum when PaOA% was 1.5%, it was indicated that the oxidative capacity of Pa enhanced with the increasing of PaOA% within

a certain range. But P was decomposed too fast when PaOA% exceeded the best value and eventually led to decreasing of the bleaching capacity.

From Fig.1(11), along with the increasing of T", L first increased and then decreased. L was maximum when T" was 115℃, so it was indicated that the oxidation capacity of Pa was proportional to T" within a certain range. But Pa was decomposed too fast when T" exceeded the best value and eventually led to decreasing of the bleaching capacity.

From Fig.1(12), along with the increasing of pH", L also increased. But with the increasing of pH", the saponification reaction became more obvious. Meanwhile, the more and more intense reaction led to the difficult controlment of the bubbles, thus resulting to the obvious change of the physical and chemical properties of montan wax. Therefore, in order to ensure the basic properties of montan wax, high pH" value is inappropriate.

The experiment of P and Pa oxidation bleaching under better condition.

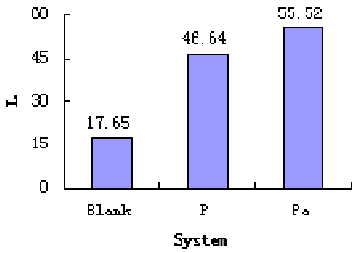


Fig.2 The chroma of experiments of P and Pa combination methods of P& Pa

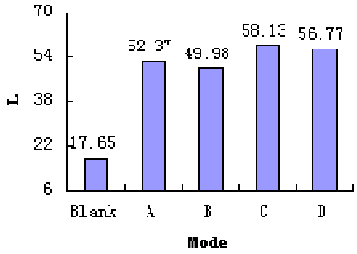


Fig.3 The chroma of Selection experiments of oxidation bleaching under better condition

A better condition of P system was: P%-30%, P:ESRRMW-55:1, POA%-1.5%, t-50min, T-115℃, pH-5.0; a better condition of Pa system was: Pa%-15%, Pa:ESRRMW-45:1, t-30min, PaOA%-1.5%, T-115℃, pH-0.65. From Fig.2, it was showed that Pa's bleaching effect is better than that of P, which has something to do with the more and stronger oxidation ability peroxide ions that has been produced by Pa.

The condition of P system was: P%-30%, P:ESRRMW-30:1, POA%-1.5%, t'-40min, T'-115℃, pH'-5.0; The condition of Pa system was: Pa%-15%, Pa:ESRRMW-15:1, t" -20min, PaOA%-1.5%, T"-115℃, pH"-0.65. From Fig.3, the effect of oxidation bleaching can be sorted as: C>D>A>B.

The reason why Mode C was the best bleaching effect may be related to the following reaction: Pa→HAc+H_2O, HAc+P→Pa, thus guaranteeing that the effective unit content of Pa was the slowest decayed over time. In addition, the consumption of Pa was only 1/3 of Pa oxidation bleaching under better condition, it was meant that the cost was reduced in a certain extent.

As the little difference between D and C was considered, D may be preferred to simplify the operation of industrial production, while C be preferred on the laboratory stage.

Optimization tests of oxidation bleaching under mode C.

Though the single factor experiment of oxidation bleaching under mode C. The chroma of optimization tests of oxidation bleaching under mode C was shown in Fig.4. As the two key factors, brightness enhancement and cost reduction, were considered, the response surface optimization range should be: Pa:ESRRMW-5:1~20:1, P:ESRRMW-20:1~40:1, T-105~125℃, t-40~80min.

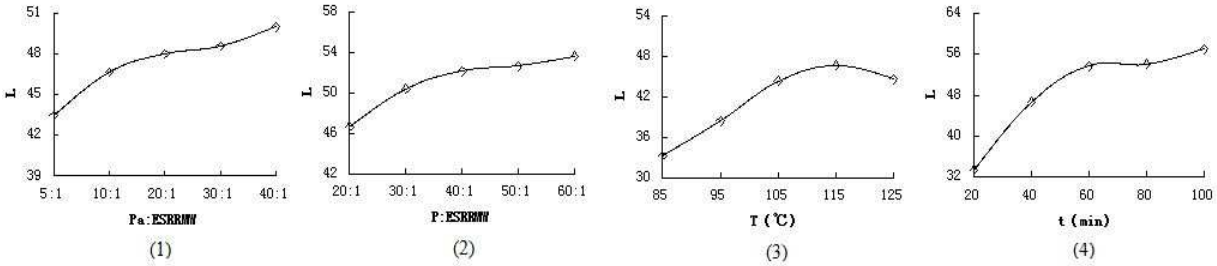


Fig.4 The chroma of optimization tests of oxidation bleaching under mode C

The response surface method analysis of oxidation bleaching under mode C.

Levels and factors of the test were shown in Table 1 according to Box-Benhnken's design principles. The test of response surface analysis was designed by the statistical software Design Expert 8.0.6, and the scheme and test results were shown in Table 2; Variance analysis results were shown in Table 3.

Table 1 Factors and levels of response surface design

Factors	Levels		
	-1	0	+1
Pa:ESRRMW (A)	5:1	12.5:1	20:1
P:ESRRMW (B)	20:1	30:1	40:1
T（℃） (C)	105	115	125
t（min） (D)	40	60	80

Table 2 The scheme and test results of response surface design

Trial No.	Pa:ESRRMW	P:ESRRMW	T(℃)	t(min)	L
1	12.5:1	40:1	105	60	44.10
2	12.5:1	40:1	125	60	52.11
3	5:1	30:1	115	80	48.00
4	5:1	30:1	125	60	47.30
5	12.5:1	30:1	115	60	58.96
6	12.5:1	30:1	105	80	44.04
7	12.5:1	30:1	115	60	58.78
8	12.5:1	20:1	125	60	47.50
9	20:1	40:1	115	60	59.89
10	5:1	40:1	115	60	49.16
11	20:1	30:1	115	80	61.59
12	20:1	30:1	115	40	55.78
13	12.5:1	40:1	115	80	59.01
14	20:1	30:1	125	60	53.85
15	20:1	30:1	105	60	46.38
16	12.5:1	30:1	125	80	55.78
17	12.5:1	20:1	105	60	43.59
18	5:1	20:1	115	60	46.41
19	12.5:1	30:1	125	40	48.72
20	20:1	20:1	115	60	54.32
21	5:1	30:1	105	60	39.30
22	12.5:1	40:1	115	40	52.74
23	12.5:1	20:1	115	40	49.23
24	12.5:1	30:1	105	40	42.22
25	12.5:1	20:1	115	80	55.31
26	12.5:1	30:1	115	60	50.94
27	5:1	30:1	115	40	46.87
28	12.5:1	30:1	115	60	58.92
29	12.5:1	30:1	115	60	58.78

Table 3 Results of the analysis of variance regression model of L

Sources	Sum of squares	df	Mean square	F value	P value	Significance
model	986.33	14	70.45	13.88	<0.0001	**
A	249.98	1	249.98	49.26	<0.0001	**
B	35.54	1	35.54	7.00	0.0192	
C	173.51	1	173.51	34.19	< 0.0001	**
D	66.13	1	66.13	13.03	0.0028	
AB	1.99	1	1.99	0.39	0.5414	
AC	0.07	1	0.07	0.014	0.908	
AD	5.48	1	5.48	1.08	0.3165	
BC	4.20	1	4.20	0.83	0.3782	
BD	$9.03E^{-03}$	1	$9.03E^{-03}$	$1.78E^{-03}$	0.967	
CD	6.86	1	6.86	1.35	0.2642	
A^2	46.07	1	46.07	9.08	0.0093	
B^2	28.61	1	28.61	5.64	0.0324	
C^2	431.92	1	431.92	85.11	< 0.0001	**
D^2	12.00	1	12.00	2.36	0.1464	
residual	71.04	14	5.07			
lack of fit	20.84	10	2.08	0.17	0.9902	
pure error	50.21	4	12.55			
cor total	1057.37	28				

According to the relevant experimental data in Table 2, Design Expert software was used for regression analysis, and then the quadratic multinomial regression model of A, B, C, D was fitted as:

$$L=57.28+4.56*A+1.72*B+3.80*C+2.35*D+0.70*A*B-0.13*A*C+1.17*A*D+1.03*B*C+0.047*B*D+1.31*C*D-2.67*A^2-2.10*B^2-8.16*C^2-1.36*D^2$$

From Table 3, A and C of above models were remarkable, while B and D were not obvious; C^2 was extremely notable, while A^2, B^2, D^2 were not significant; All interaction terms were not notable. That the F value of the model was 13.88 and the overall model significance level was $p<0.0001$ showed that the model was significant. That R^2 of the model was 0.9328 indicated that the degree of fit of the regression equation was good and the lack of fit was small. Therefore, the real test points can be replaced by the equation to analyze.The response surface plot in Fig.5 was drawn according to the mathematical model.

Within the scope of the above factor values and in accordance with the fitting, the optimum conditions were determined as follows: Pa:ESRRMW-20:1, P:ESRRMW-36.72:1, t-80min, T-118.49℃; An average value of L of three times verification testing was 62.02 under this condition, which was proved better than any of the conditions previously set. And it was also very close to the bleaching effect of the Cr^{6+} oxidation method (An average value of L was 62.58).

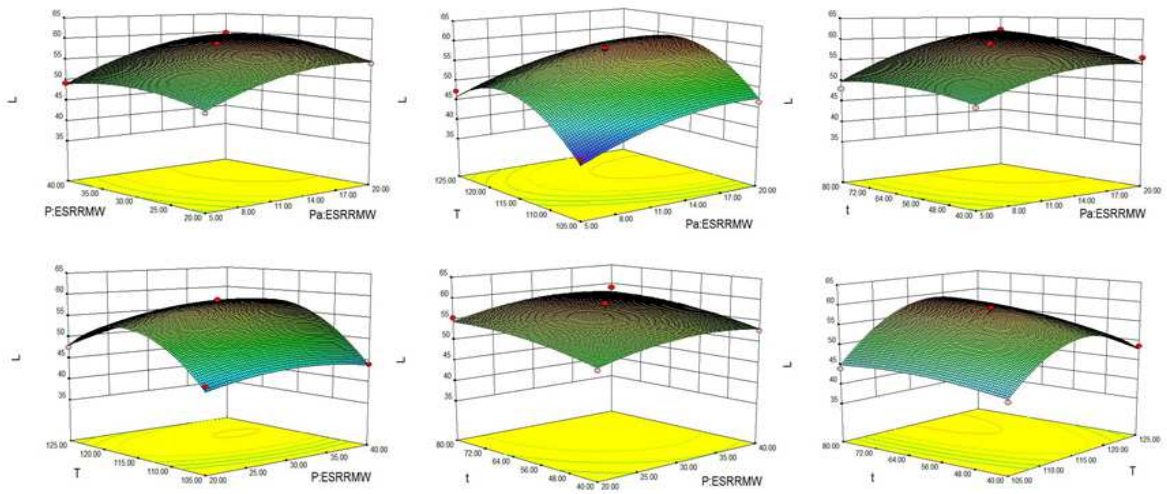


Fig.5 Response surface graphs

CONCLUSION

Both P and Pa oxidation system had some bleaching effect on montan wax of removed resin, but neither of them was as good as the combination of P and Pa system. And the bleaching effect of C (Pa-P) in the combination system was the best, which was selected as the best way.

Through the response surface analysis of the four key factors in mode C, the optimal conditions determined within the optimization range were: Pa:ESRRMW-20:1, P:ESRRMW-36.72:1, t-80min, T-118.49℃. Under this condition, the L value of the product was 62.02, which was almost consistent with the model prediction, and it was also very close to the bleaching effect of the Cr^{6+} oxidation method, therefore, it has potential prospects to replace the Cr^{6+} oxidation method.

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