

Optimization of hydrogen peroxide extraction conditions for CCA removal from treated wood by response surface methodology

Gyu-Hyeok Kim*
Jong-Bum Ra*
Il-Gon Kong
Yun-Sang Song

Abstract

This research was performed to evaluate the effect of extraction conditions (time, temperature, and concentration of hydrogen peroxide) on extraction yield of copper, chromium, and arsenic from chromated copper arsenate (CCA)-treated wood. The quadratic regression models representing the extraction yield of each CCA component and total CCA at various conditions were fitted using response surface methodologies (RSM). The coefficients of determination of fitted models were above 0.97, meaning that the model can be highly accurate in predicting extraction yield at various conditions. The fitted RSM models allowed multiple solutions with any desirable extraction yield of CCA components. This research indicates that the use of an RSM model may offer considerable flexibility in controlling extraction variables for practical uses.

Chromated copper arsenate (CCA)-treated wood removed from service can be disposed of either by landfill or incineration. Most spent treated wood is currently placed in approved landfills, although a shortage of landfill space is anticipated with increasing removal of treated wood from service in the future. Public concern about environmental contamination from chemicals leaching from treated wood placed in landfills has been increasing. Incineration is generally not an acceptable means of disposal due to the potential toxicity of chemicals emitted from the treated wood and from

metals remaining in the ash. Thus, alternative methods for removing CCA from treated wood need to be developed to alleviate contamination concerns as well as to decrease the demand on landfill

space so that the preservative-free wood materials may be reused as furnish for wood composites.

Recovery of CCA components from spent treated wood by chemical extraction has been the focus of several international research groups (Kim et al. 2003, Shiau et al. 2000, Kamdem et al. 1998, Kazi and Cooper 1998, and Honda et al. 1991). Various organic and inorganic chemicals were reported to be effective in removing CCA. However, optimal extraction conditions, that is, reaction time, reaction temperature, and concentration of reagent, are highly reagent-dependent. It is therefore necessary to determine optimal extraction conditions for the removal of CCA components from spent CCA-treated wood.

In this study, hydrogen peroxide was used to extract CCA components from

The authors are, respectively, Professor, Division of Environmental Science and Ecological Engineering, Korea Univ., 5-1 Anam-Dong Sungbuk-Gu, Seoul 136-701, Republic of Korea; Assistant Professor, Dept. of Forest Products Engineering, 150 Chilam-dong Jinju, Jinju National Univ., Kyungsangnamdo South 660-758, Republic of Korea; and Former Graduate Research Assistant and Graduate Research Assistant, Division of Environmental Science and Ecological Engineering, Korea Univ. This research was supported by Korea Research Foundation Grant (2001-041-G00053). This paper was received for publication in June 2003. Article No. 9701.

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treated wood because of its proven ability to extract CCA components and its low toxicity compared to other organic or inorganic chemicals tested (Kim et al. 2003, Kazi and Cooper 1999). Response surface methodology (RSM) was used to develop a model for optimal extraction conditions, and the practical application of the fitted model is discussed in this paper.

Materials and methods

Radiata pine (*Pinus radiata* D. Don) sapwood samples, nominally 5 by 10 cm in cross section by 30 cm in length, were air-dried to approximately 15 percent moisture content (MC) and treated with 2 percent CCA-C (w/v) using a full-cell process. The treated samples were wrapped in plastic bags for 48 hours at 60°C, and then air-dried at room temperature for two weeks to allow complete fixation of CCA components. The treated samples were ground in a Wiley mill equipped with a 20-mesh screen. The ground CCA-C-treated wood was kept in plastic bags and used for extraction experiments under various conditions of reaction time, reaction temperature, and reagent concentration. The ground wood was digested by the AWP A7-93 procedure (AWPA 2001), and the initial amounts of CCA components in the ground wood were determined by an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) according to the AWP A21-00 procedure (AWPA 2001).

Two grams of the ground wood were placed in a volumetric flask and aqueous hydrogen peroxide solution was added. The ratio of ground wood to aqueous hydrogen peroxide solution was fixed at 1 to 20 in all experiments. The flasks were agitated in a shaking incubator according to the predetermined extraction conditions. At the end of each extraction, the ground wood was filtered, and the filtered ground wood was washed thoroughly using a sufficient quantity of distilled water to make sure that no leachate was left in the ground wood. Leachate was collected in a vial and kept in a refrigerator for future analysis.

Extraction experiments were designed to find the optimum solvent extracting conditions; 15 different combinations of extraction conditions were set according to the central composite design (Table 1). The treatment combinations were selected to fit a quadratic RSM model relating extraction yield,

Table 1. — Central composite design for extracting processes of chromium, copper, and arsenic from CCA-treated wood.

Actual factor values			Coded variables		
Time	Conc.	Temp.	Time	Conc.	Temp.
(hr.)	(%)	(°C)	(hr.)	(%)	(°C)
12	5	20	−1	−1	−1
36	5	20	+1	−1	−1
12	10	20	−1	+1	−1
36	10	20	+1	+1	−1
12	5	60	−1	−1	+1
36	5	60	+1	−1	+1
12	10	60	−1	+1	+1
36	10	60	+1	+1	+1
24	7.5	40	0	0	0
24	7.5	70	0	0	+1.5
24	7.5	10	0	0	−1.5
24	11.25	40	0	+1.5	0
24	3.75	40	0	−1.5	0
6	7.5	40	−1.5	0	0
42	7.5	40	+1.5	0	0

Table 2. — Summary of extraction efficiency of CCA components from CCA-treated wood under various extracting conditions.

Time	Conc.	Temp.	Extracting yield (%)			
			Chromium	Copper	Arsenic	Total
(hr.)	(%)	(°C)	(hr.)	(%)	(°C)	
12	5	20	13	25	19	17
36	5	20	25	41	33	31
12	10	20	29	36	30	30
36	10	20	51	51	47	50
12	5	60	92	82	90	89
36	5	60	97	81	100	95
12	10	60	100	86	98	97
36	10	60	100	83	100	97
24	7.5	40	91	88	90	90
24	7.5	70	100	85	99	97
24	7.5	10	21	21	19	20
24	11.25	40	100	84	100	97
24	3.75	40	67	79	72	71
6	7.5	40	54	69	58	58
42	7.5	40	97	83	98	95

and variables were coded by following methods:

$$C = \{R - [\max(R) + \min(R)]/2\} / \{[\max(R) - \min(R)]/3\}$$

where:

C = coded value and

R = actual value.

The experimental design consisted of eight equally spaced points: one point on a circle of radius $\sqrt{2}$, one point in the design center, and six points on a circle of

radius 1.5. Although the point with radius $\sqrt{2}$ offers more precise results for modeling, the value of 1.5 instead of $\sqrt{2}$ was chosen to provide easy control of the extraction variables in this experiment (Myers and Montgomery 1995). The leachate was analyzed using an ICP-AES at the end of each extraction experiment according to the AWP A21-97 procedure (AWPA 1997). Each treatment combination had three replicates.

Results and discussion

The extraction yield of chromium (Cr), copper (Cu), and arsenic (As) after the end of each extraction reaction is shown in **Table 2**. The efficiency of extraction with hydrogen peroxide increased greatly with increasing time, temperature, and concentration. Copper appeared to show the fastest extraction rates under mild extraction conditions (temperature < 40°C, concentration < 7.5%, time < 24 hours) compared to chromium and arsenic. Chromium and arsenic were totally removed from treated wood by an increase in the severity of extraction conditions, but copper was not completely extracted in any given extraction conditions.

The equations of extraction yield of CCA components in terms of the coded factors are:

$$\begin{aligned} \% \text{ Cr extraction} = & 93.63 - 8.67 x_1^2 - 15.33 x_2^2 - 5.19 x_3^2 + 8.27 x_1 + 31.04 x_2 + 8.17 x_3 - 3.92 x_2 x_3 - 3.58 x_3 x_1 \quad (r^2 = 0.97) \end{aligned}$$

$$\begin{aligned} \% \text{ Cu extraction} = & 89.96 - 7.03 x_1^2 - 16.96 x_2^2 - 4.36 x_3^2 + 3.81 x_1 + 21.81 x_2 + 2.75 x_3 - 4.42 x_1 x_2 - 1.83 x_2 x_3 - 0.17 x_3 x_1 \quad (r^2 = 0.99) \end{aligned}$$

$$\begin{aligned} \% \text{ As extraction} = & 92.76 - 7.45 x_1^2 - 15.67 x_2^2 - 3.89 x_3^2 + 8.17 x_1 + 30.32 x_2 + 6.04 x_3 \quad (r^2 = 0.97) \end{aligned}$$

$$\begin{aligned} \% \text{ Total extraction} = & 92.74 - 8.08 x_1^2 - 15.71 x_2^2 - 4.59 x_3^2 + 7.37 x_1 + 29.09 x_2 + 6.40 x_3 - 2.96 x_1 x_2 - 3.38 x_3 x_1 \quad (r^2 = 0.97) \end{aligned}$$

where:

x_1 = coded extraction time,
 x_2 = coded extraction temperature,
 x_3 = coded concentration of hydrogen peroxide, defined as:

$$x_1 = [t_i - \{\max(t) + \min(t)\}/2] / [\{\max(t) - \min(t)\}/3]$$

$i = 1, 2, 3$

$$x_2 = [T_i - \{\max(T) + \min(T)\}/2] / [\{\max(T) - \min(T)\}/3]$$

$$x_3 = [C_i - \{\max(C) + \min(C)\}/2] / [\{\max(C) - \min(C)\}/3]$$

where:

t = actual extraction time,
 T = extraction temperature, and
 C = concentration of hydrogen peroxide.

The equations should be changed in terms of real variables for the practical applications. The RSM models representing extraction yield of each CCA component and total CCA in terms of real variables are:

$$\begin{aligned} \% \text{ Cr extraction} = & -190.02 - 0.06t^2 - 0.038T^2 - 0.83C^2 + 4.18t + 5.56T + 18.85C - 0.02tT - 0.078TC \end{aligned}$$

$$\begin{aligned} \% \text{ Cu extraction} = & -134.41 - 0.05t^2 - 0.04T^2 - 0.70C^2 + 3.44t + 5.20T + 13.20C - 0.02tT - 0.04TC - 0.01tC \end{aligned}$$

$$\begin{aligned} \% \text{ As extraction} = & -129.88 - 0.05t^2 - 0.039T^2 - 0.62C^2 + 3.16t + 4.65T + 11.76C \end{aligned}$$

$$\begin{aligned} \% \text{ Total extraction} = & -167.97 - 0.06t^2 - 0.04T^2 - 0.73C^2 + 4.65t + 4.89T + 16.28C - 0.01tT - 0.11tC \end{aligned}$$

The fitted models showed a coefficient of determination (r^2) of above 0.97, meaning that they are highly accurate in reflecting the nature of the extraction process. The equations showed that the concentration of hydrogen peroxide affected the extraction of CCA components the most, followed by temperature and time, and that any other combinations ($t \times C$, $C \times T$, $T \times t$) of three extraction factors affected extraction yield to a lesser extent. The interaction effect of time and concentration on the extraction of total CCA chemicals was not found to be significant at the 0.05 percent level. The extraction yield of CCA components varied according to extraction conditions, and an increase in these conditions resulted in an overall increase of extraction yield of CCA components (**Fig. 1**).

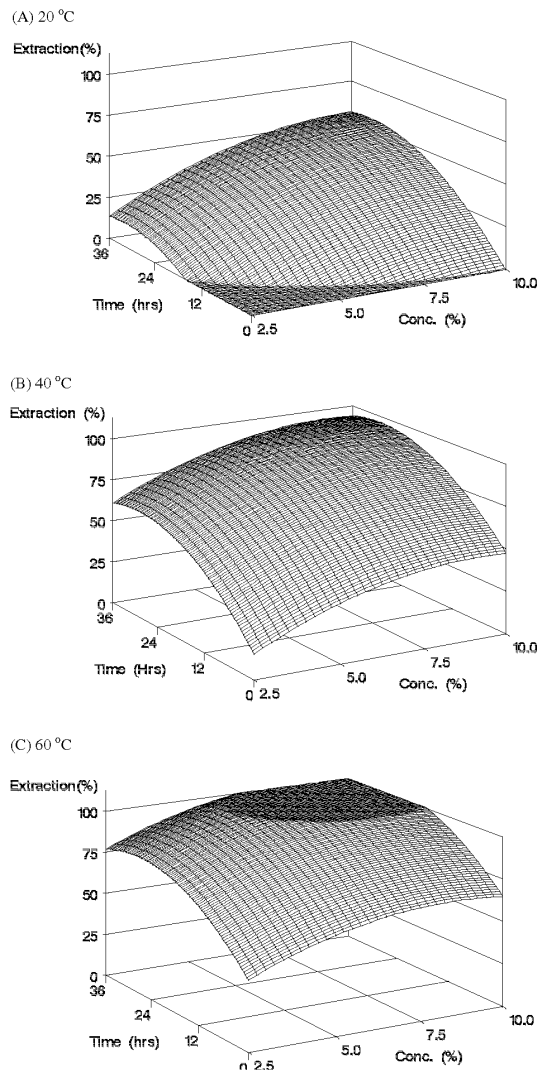


Figure 1. — Three-dimensional response surface plot expressing extraction yield (%) of total CCA components from treated wood at the various extraction conditions.

Figure 2 shows the contour plots with a change in the extraction ratio of total CCA components at various reaction temperatures (20°, 40°, and 60°C, respectively). The extraction yields of CCA increased initially and then slightly decreased with an increase in extraction time, especially at higher temperature conditions. The reason is as yet unclear, but this phenomenon may be explained by the decrease of copper extraction yields with additional extraction time. Previous research showed that if additional extraction time is applied after most of the copper has been extracted from the treated wood, the extraction yields of copper in hydrogen peroxide solution decreased (Kim et al. 2003).

The optimum extraction conditions could be solved for the stationary point of the fitted model, allowing the derivative to be set to zero. The optimized extraction conditions determined by the fitted model were a temperature of 57°C, an extraction time of 27 hours, and a hydrogen peroxide concentration of 8.7 percent. Besides the mathematically calculated optimum conditions, RSM offers multiple solutions for desirable extraction yields when the value of one extraction variable is fixed. The contour line in **Figure 2** represents the same extraction ratio, and any combination of reaction time and concentration of hydrogen peroxide in the circle of same contour line can be chosen as the optimized solution.

Conclusion

The RSM model developed in this study successfully represented the relationships between three extraction variables (time, temperature, and concentration of hydrogen peroxide) and the extraction yield of CCA components from CCA-treated wood. The quadratic RSM model showed that the extraction yield of CCA components was most sensitive to reagent concentration, and an increase in extraction conditions resulted in an overall increase of extraction yield. The model allowed multiple solutions for desirable extraction yields of CCA components. As a result, the model can offer considerable flexibility in controlling extraction variables for practical uses. Further study to investigate the effect of particle size on the extraction yield is suggested.

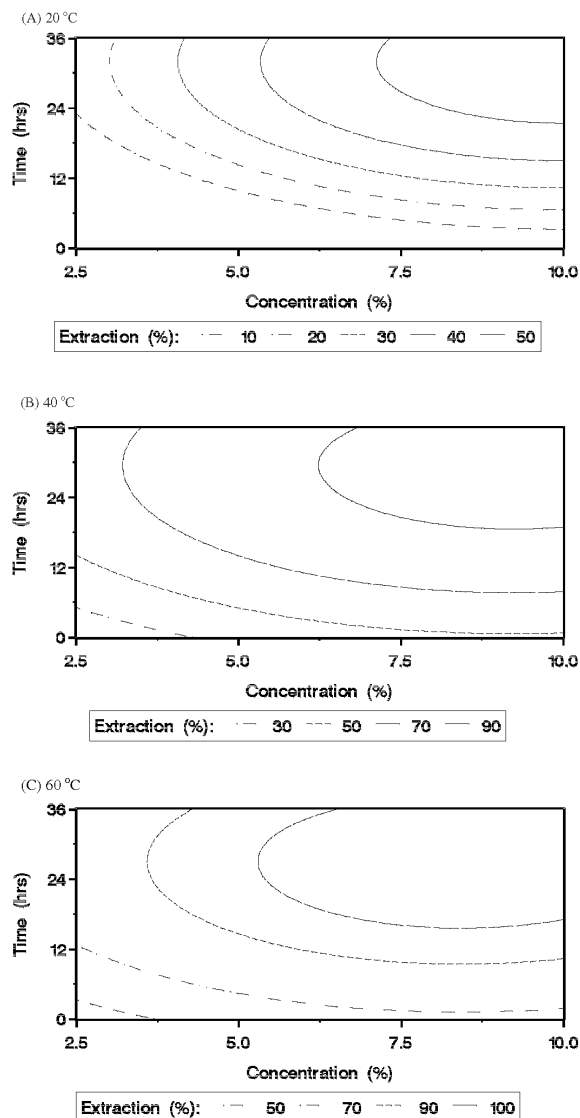


Figure 2. — Contour plot expressing the extraction yield (%) of total CCA components from treated wood at the various extraction conditions.

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