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Short Communication

Extraction of chromium, copper, and arsenic from CCA-treated wood by using wood vinegar

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HIGHLIGHTS

- ▶ Wood vinegar was applied to extract CCA elements from treated wood.
- ▶ Cu, As, and Cr were removed of up to 95.7%, 92.7%, and 86.3%, respectively.
- ▶ A notable extractability of Cu from ACQ- and CuAz-treated sawdust was also observed.

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ABSTRACT

In the present study, wood vinegar was used to extract chromium, copper, and arsenic from chromated copper arsenate (CCA)-treated wood. The extraction efficiency for CCA elements was evaluated using various concentrations of wood vinegar, extraction temperatures, and extraction periods. The extraction efficiency for CCA elements increased with increasing the concentration of wood vinegar and the extraction conditions, resulting in maximal removal rate of copper (95.7%), followed by arsenic (92.7%) and chromium (86.3%). Since wood vinegar afforded high levels of copper extraction, its use was extended to copper-based preservative-treated wood, wherein significant extraction of copper up to 97.6% and 95.7% was obtained from alkaline copper quats (ACQ)- and copper azole (CuAz)-treated sawdust, respectively. To the best of our knowledge, this is the first study on the application of wood vinegar for the extraction of metal elements from CCA-treated wood.

1. Introduction

The use of chromated copper arsenate (CCA)-treated wood has been banned or restricted in many countries throughout the world since it poses the risk of environmental contamination. However, considering its expected average service life, the quantity of spent CCA-treated wood will be removed from service within the next few decades. Therefore, safe disposal of CCA-treated wood is a matter of increasing concern because of the potential public health and ecological risks associated with the possible release of the toxic CCA components.

Currently, CCA-treated wood is disposed of either by landfill or incineration. Most spent treated wood is placed in approved landfills. However, there is growing public concern about hazardous CCA components that leach out from treated wood and result in the contamination of soil and groundwater. Incineration is generally not an acceptable means of disposal because the resulting ash containing toxic metals still needs to be landfilled. Complete recovery of CCA components from spent treated wood is thus needed to alleviate contamination concerns as well as to decrease the demand of landfill space.

Chemical extractions using acids and oxidants have been widely applied for removing CCA metals from treated wood waste (Clausen, 2004; Honda et al., 1991; Janin et al., 2009; Kakitani et al., 2006a,b, 2007; Kartal, 2003; Kartal and Kose, 2003; Kazi and Cooper, 1998; Kim et al., 2004; Kim and Kim 1993; Ko et al., 2010), even though they burden the environment with synthetic chemicals. Wood vinegar, a condensed liquid obtained from smoke produced by charcoal production, is a promising alternative to synthetic chemicals because it contains several organic acids as an organic fraction. Yatagai et al. (2002) reported that the main acids in wood vinegar are acetic acid, *n*-propionic acid, butanoic acid, and *n*-valeric acid. Acetic acid is

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Abbreviations: CCA, chromated copper arsenate; ACQ, alkaline copper quats; CuAz, copper azole; MC, moisture content; AWPA, America Wood Protection Association; ICP-AES, inductively coupled plasma-atomic emission spectrophotometer.

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Table 1
General characteristics of crude wood vinegar used in this study.

Baume gravity (Be)	Acid ratio (%)	Acidity (pH)	Dissolved tar (%)	Refraction index (% Brix)
4.2	4.6–5.5	<2.5	<4.0	>8.0

the largest component of the acid portion, and forms the largest fraction of all the organic components of wood vinegar.

The purpose of this study is to investigate the feasibility of wood vinegar to extract CCA metals from CCA-treated wood. The extraction efficiency for chromium, copper, and arsenic was evaluated at various concentrations of wood vinegar, extraction temperatures, and extraction periods, and the results were compared with the extraction efficiency with acetic acid.

2. Methods

Radiata pine (*Pinus radiata* D. Don) sapwood samples, nominally 5 × 10 cm in cross section and 30 cm in length, were air-dried to approximately 15% moisture content (MC), and treated with 2% CCA–C (hexavalent chromium as CrO_3, 44.5–50.5%; copper as CuO, 17.0–21.0%; arsenic as As_2O_5, 30.0–38.0%) using a full-cell process. After treatment, the treated samples were wrapped in plastic bags for 48 h at 60 °C, and then air-dried at room temperature for 2 weeks to allow complete fixation of CCA elements. The treated samples were ground in a Wiley mill equipped with a 20-mesh screen. The sawdust was digested by the America Wood Protection Association (AWPA) A7–04 procedure (AWPA, 2005a), and the initial amounts of CCA elements in the sawdust were determined by an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) according to the AWPA A21–00 procedure (AWPA, 2005b). The initial elemental content in the present sawdust sample was 3.34 mg/g for copper, 6.19 mg/g for chromium, and 4.89 mg/g for arsenic.

For metal extraction processes, CCA-treated sawdust was placed into teabags made from polyester fibers. Each bag containing 3 g of sawdust was placed in the flasks containing 100 ml of extracting solvent. In this study, crude wood vinegar solutions at 3:1, 1:1, 1:3 dilutions (wood vinegar:deionized water on a volume basis), including an undiluted solution, were used as the extracting solvents. The flasks were agitated at 150 rpm on a rotary shaker under various extracting conditions for different durations (12, 24, 36, and 48 h) and temperatures (20, 40, and 60 °C), respectively. The wood vinegar used in this study was prepared by a block-type kiln for carbonization of mixed chips of *Quercus* species, and its general characteristics are shown in Table 1.

At the end of each extraction, the sawdust was washed thoroughly by using sufficient quantity of deionized water to ensure that no leachate was left in the sawdust. Remediated sawdust was air-dried, and then analyzed for remaining CCA elements using ICP-AES as described above. The percent reduction of CCA elements in the sawdust was calculated based on the initial amount of elements in the samples.

3. Results and discussion

The percentages of copper, chromium, and arsenic removed from CCA treated sawdust samples following the end of each extraction are shown in Table 2. Values represent the average of triplicate samples. The extraction efficiency for CCA elements increased with the increasing extraction temperature, concentration of wood vinegar solution, and extraction duration. The order of the extractability was copper ≫ arsenic > chromium, regardless of the extraction temperature and concentration of wood vinegar solution.

3.1. Effect of concentration of wood vinegar solution

Fig. 1 shows the extraction efficiency for CCA elements as a function of wood vinegar concentration at the extraction temperature of 60 °C. The pH of wood vinegar solution was proportionally changed by dilution, from 2.24 (undiluted solution) to 2.62 (1:3 diluted solution).

Fig. 1(a) shows the extraction efficiency for copper at various concentrations of wood vinegar solution between 1:3 diluted solution and undiluted solution. High extraction efficiency was observed, even at very low concentrations of wood vinegar and short extraction period. The extraction efficiency for copper was 86.2%, 90.7%, 92.9%, and 94.2% with 1:3 diluted solution, 1:1 diluted solution, 3:1 diluted solution, and undiluted solution, respectively, after the 12-h extraction period. These results indicate that wood vinegar is a viable extraction solvent for the efficient removal of copper from CCA-treated sawdust at a wide range of concentrations. It is a noteworthy fact that copper has a very low resistance

Table 2
Percentage of metal extracted from CCA-treated sawdust by using wood vinegar at various extraction conditions[a].

Dilution[b]	Time (h)	20 °C			40 °C			60 °C		
		Copper	Chromium	Arsenic	Copper	Chromium	Arsenic	Copper	Chromium	Arsenic
1:3	12	73.7 (3.4)	12.5 (1.1)	14.3 (4.3)	81.3 (1.4)	13.3 (2.5)	14.3 (4.1)	86.2 (0.6)	28.8 (2.9)	39.3 (3.0)
	24	74.4 (1.8)	11.1 (2.3)	16.4 (2.0)	86.2 (1.0)	32.2 (6.1)	36.6 (5.6)	87.2 (0.3)	36.6 (0.8)	46.2 (0.8)
	36	80.0 (0.4)	20.8 (1.5)	25.0 (1.2)	85.8 (0.7)	34.0 (1.4)	37.3 (1.8)	87.6 (0.7)	48.2 (0.6)	50.4 (1.7)
	48	80.3 (1.5)	19.0 (3.1)	24.4 (2.8)	88.9 (0.6)	46.0 (4.3)	51.4 (3.8)	88.5 (0.8)	49.9 (2.9)	56.5 (1.5)
1:1	12	78.8 (1.2)	13.7 (1.3)	18.0 (1.8)	90.4 (1.0)	24.2 (1.4)	28.0 (5.2)	90.7 (0.2)	46.6 (0.9)	52.1 (1.2)
	24	81.9 (0.8)	15.8 (1.9)	20.2 (1.9)	91.9 (0.6)	46.2 (1.0)	48.6 (3.3)	91.4 (0.3)	56.2 (3.3)	63.0 (0.5)
	36	85.0 (0.4)	25.3 (0.6)	28.2 (0.9)	90.0 (0.4)	51.1 (0.3)	52.3 (2.0)	92.3 (0.1)	66.4 (0.1)	71.8 (3.6)
	48	85.1 (2.7)	27.3 (1.1)	32.0 (0.2)	91.3 (1.6)	59.1 (1.9)	61.8 (1.1)	92.3 (0.4)	69.6 (2.2)	77.2 (0.2)
3:1	12	82.9 (1.2)	18.2 (5.0)	23.0 (5.2)	93.3 (0.4)	39.7 (4.0)	39.9 (3.1)	92.9 (0.2)	54.0 (1.2)	63.1 (0.6)
	24	83.6 (2.0)	19.6 (1.5)	24.5 (1.8)	92.2 (0.8)	50.2 (5.1)	52.9 (4.6)	94.5 (0.1)	69.1 (1.3)	76.5 (1.7)
	36	87.1 (0.5)	28.7 (2.3)	31.6 (1.9)	91.7 (0.2)	53.2 (1.5)	54.6 (2.6)	94.2 (0.5)	75.5 (1.4)	84.1 (0.1)
	48	88.5 (0.7)	32.2 (2.6)	35.8 (1.4)	93.4 (1.0)	62.1 (5.8)	63.2 (6.1)	94.3 (0.5)	79.5 (1.0)	88.2 (0.1)
U[c]	12	84.5 (0.6)	19.3 (2.6)	23.6 (2.8)	92.3 (1.3)	49.0 (3.5)	50.6 (4.1)	94.2 (0.3)	66.5 (0.2)	74.6 (0.5)
	24	85.8 (0.2)	22.3 (1.9)	26.7 (3.9)	92.6 (0.7)	50.4 (1.5)	53.5 (1.9)	94.8 (0.2)	78.3 (1.8)	84.9 (1.6)
	36	89.0 (0.6)	32.8 (0.5)	35.9 (1.7)	93.1 (0.2)	57.2 (0.6)	58.1 (0.9)	95.7 (0.2)	83.9 (0.4)	91.6 (0.1)
	48	90.6 (0.5)	36.7 (3.4)	40.9 (0.3)	95.6 (0.0)	70.4 (2.1)	72.2 (1.4)	95.7 (0.3)	86.3 (1.2)	92.7 (0.4)

[a] Values are the mean of 3 replicates and ones in parentheses are the standard deviation.
[b] Dilution is wood vinegar:deionized water on volume basis.
[c] U: undiluted solution of wood vinegar.

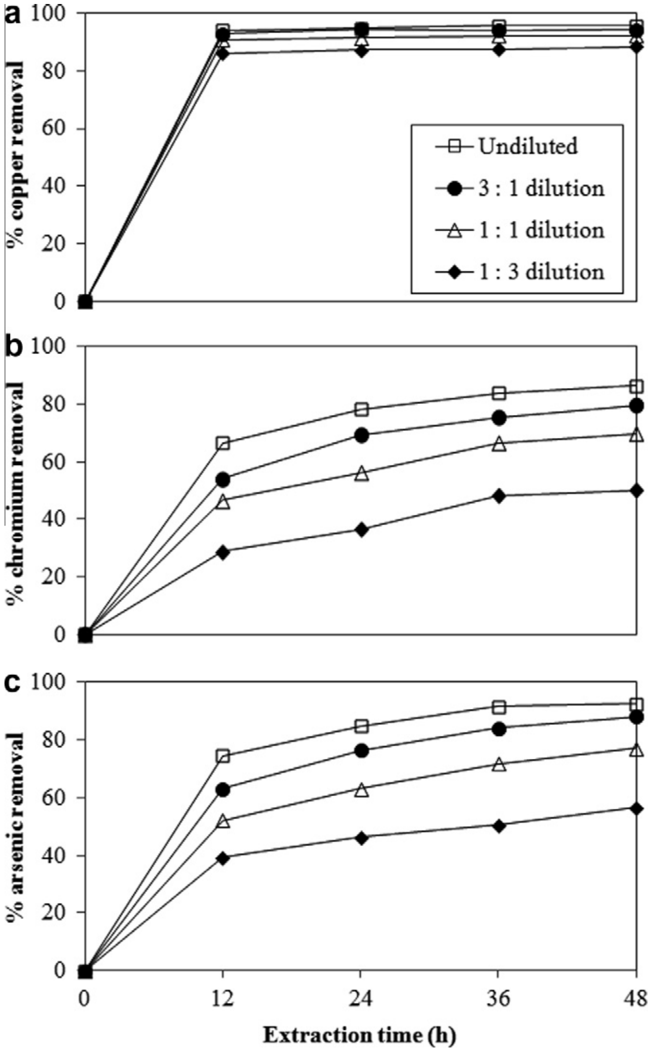

Fig. 1. Effect of solution concentration on the extraction efficiency for copper, chromium, and arsenic from CCA-treated wood sawdust by using wood vinegar at 60 °C. (a) Effect of concentration on the extractability of copper. (b) Effect of concentration on the extractability of chromium. (c) Effect of concentration on the extractability of arsenic.

Table 3
Percentage of copper extracted from ACQ- and CuAz-treated sawdust with undiluted wood vinegar solution after 24-h extraction period.

Preservatives	Extraction temperature		
	20 °C	40 °C	60 °C
ACQ-D	90.1 ± 0.3	92.6 ± 0.1	97.6 ± 0.1
CuAz-2	92.1 ± 1.5	95.2 ± 0.1	95.7 ± 0.5

to leaching with the wood vinegar solution, even at very low concentrations. Several studies have shown that the extraction efficiency for copper decreased with increase in extraction time, probably due to the accumulation of insoluble copper oxalates in the sample (Kartal and Kose, 2003; Kazi and Cooper, 1998). In the present study, however, the extraction efficiency for copper did not decrease with increasing duration of extraction, indicating no accumulation of insoluble copper oxalates with wood vinegar.

High levels of copper extraction with wood vinegar solution show that this extraction technique could be applied to the waterborne copper-based preservatives such as alkaline copper quats

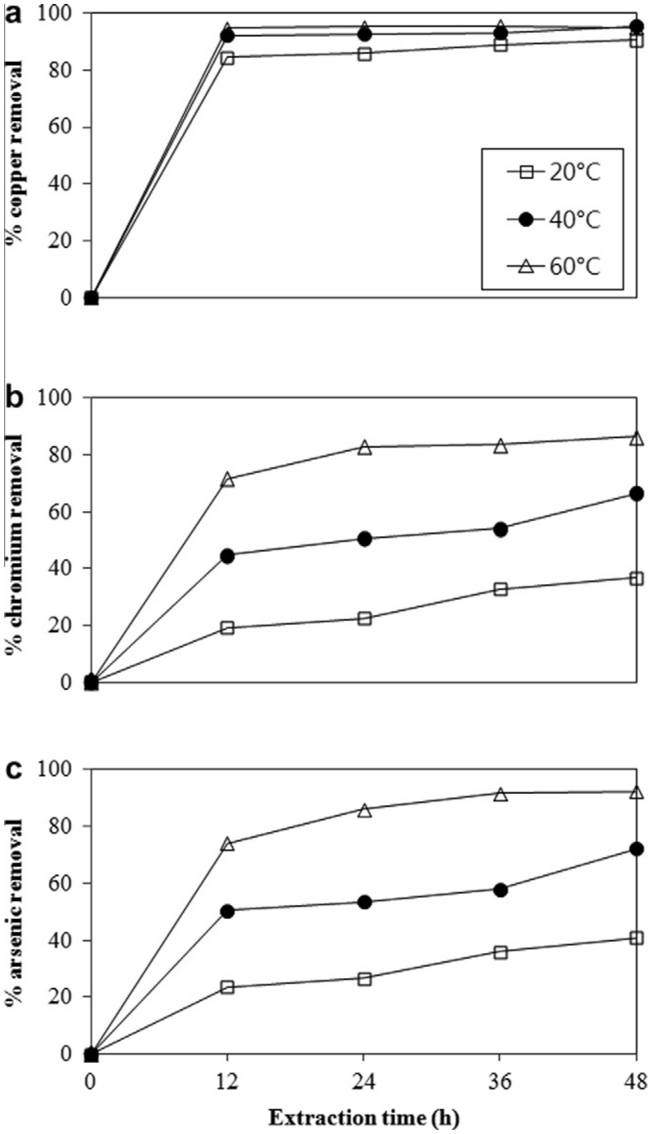

Fig. 2. Effect of extraction temperature on the extraction efficiency for copper, chromium, and arsenic from CCA-treated wood sawdust by using undiluted wood vinegar. (a) Effect of extraction temperature on the extractability of copper. (b) Effect of extraction temperature on the extractability of chromium. (c) Effect of extraction temperature on the extractability of arsenic.

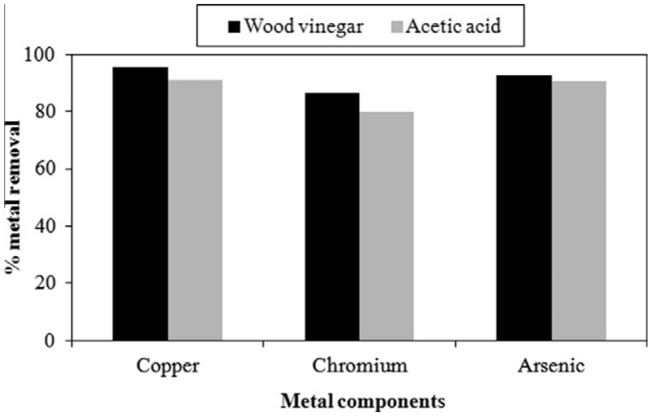

Fig. 3. Comparison of the extractability of CCA metals between wood vinegar solution and acetic acid.

(ACQ) and copper azole (CuAz). Consequently, undiluted wood vinegar solution was applied to extract copper from 6.25% ACQ (copper as CuO, 62–71%; didecyl dimethyl ammonium chloride, 29–38%)- and 2.78% CuAz (copper as CuO, 45–59%; boron as H_3BO_3, 40–46%; tebuconazole, 1.6–2.4%)-treated sawdust, and the results are shown in Table 3. The extractability of copper from ACQ- and CuAz-treated sawdust was similar to that from CCA-treated samples.

The extraction efficiency for chromium and arsenic are shown in Fig. 1(b) and (c), respectively; the removal rates of chromium and arsenic were lower than that of copper. The extraction efficiency for both CCA metals was similar, even though the extractability of chromium was slightly lower compared to arsenic. This result is probably due to the difference in bonding strength between these two metals and wood components such as lignin in CCA-treated wood (Pizzi, 1990a,b). The strong chromium–lignin affinity has reduced the extraction percentage of chromium with wood vinegar. Effective chromium removal ($\geqslant$80%) was obtained with undiluted solution after the 36-h extraction. The extraction efficiency for chromium was 86.3% after the 48-h extraction. In the case of arsenic extraction, effective removal was achieved with 3:1 diluted solution after the 36-h extraction and with undiluted solution after the 24-h extraction. The extraction efficiency for chromium was 92.7% with undiluted solution after the 48-h extraction.

3.2. Effect of temperature

As shown in Fig. 2, increased extraction temperature enhanced the extraction efficiency for all CCA elements from CCA-treated sawdust because the solubility of weakly soluble salts mainly depends on the temperature of extracting solvent. The removal of both chromium and arsenic was markedly enhanced with the increase in extraction temperature; however, the extraction efficiency for copper was not significantly influenced by increase in temperature because copper was easily removed at lower temperatures as compared to chromium and arsenic.

Fig. 2(a) clearly demonstrates the high extraction efficiency for copper at temperatures ranging from 20 to 60 °C. After 48 h of extraction with undiluted solution, the extraction efficiency was 90.6%, 95.6%, and 95.7% at 20, 40, and 60 °C, respectively, thus confirming that wood vinegar solution is highly effective for the extraction of copper under both low and high temperature conditions. As shown in Fig. 2(b) and (c), increase in temperature significantly enhanced the extraction efficiency for chromium and arsenic. The extraction efficiencies for chromium and arsenic after 48 h of extraction with undiluted solution were 36.7% and 40.9% at 20 °C, 70.4% and 72.2% at 40 °C, and 86.3% and 92.7% at 60 °C. Hence, the extraction efficiency for chromium and arsenic strongly depends on the extraction temperature. Therefore, temperature plays a very important role in the solubility of chromium and arsenic during their extraction from CCA-treated wood.

Based on the present study, in summary, the maximum extraction for CCA elements from CCA-treated sawdust was achieved using undiluted wood vinegar solution for 48 h at a temperature of 60 °C. Under this condition, the extraction efficiencies for copper, chromium, and arsenic were 95.7%, 86.3%, and 92.7%, respectively. Kakitani et al. (2006b) revealed that arsenic and chromium can totally be removed by using dual leaching process consisted of oxalic acid and sodium oxalate extraction, while copper can totally be removed by using oxalic acid and ethylenediaminetetraacetic acid (Kartal and Kose, 2003). Although extraction efficiency by using synthetic chemicals is somewhat higher than that by wood vinegar, usage of synthetic chemical can cause secondary environmental pollution. Thus, when considering the environmental aspect and acceptable extractability, wood vinegar might substitute for synthetic chemicals to extract metals from treated wood waste.

3.3. Comparison of extractability between wood vinegar solution and acetic acid

The extraction of CCA-treated sawdust using acetic acid, which is the largest component of the acid portion in wood vinegar, was performed additionally for comparative studies. The pH of acetic acid was adjusted by diluting with deionized water to same pH value as undiluted wood vinegar solution (pH 2.24). Fig. 3 shows interesting results that the removal rates of copper, chromium, and arsenic with undiluted wood vinegar solution was slightly higher than those with acetic acid. This result suggests that many other organic acids comprising of wood vinegar such as *n*-propionic and butanoic acid stimulated the extraction process.

4. Conclusions

The extraction of CCA elements using wood vinegar was significantly affected by the concentration of wood vinegar and the extraction conditions. The higher concentration of wood vinegar and the extraction conditions of increased severity increased the extraction efficiency, resulting in removal of up to 95.7%, 92.7%, and 86.3% copper, arsenic, and chromium from CCA-treated sawdust, respectively. The wood vinegar also showed a notable extractability of copper from ACQ- and CuAz-treated sawdust. Thus, wood vinegar might be a promising alternative to synthetic chemicals for removing metal elements from treated wood waste.

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