Extraction of chromated copper arsenate from wood wastes using green solvent supercritical carbon dioxide

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Abstract

To provide a green method to remove chromated copper arsenate (CCA) in the wood before its dumping, incineration, reuse or disposal, extraction of CCA from wood wastes using supercritical carbon dioxide ($ScCO_2$) containing an organophosphorus reagent, Cyanex 302, was investigated. The majority of copper metal was removed using Cyanex 302 in supercritical fluid extraction (SFE). The order of extraction efficiency was found to be $Cu \gg As > Cr$. Factors that affected SFE efficiencies, such as matrices, oxidation state of metal species [Cr(III), Cr(VI), As(III), and As(V)], and SFE pressure, were studied. Using this *in situ* chelation/SFE technique to remove leachable metals from the CCA-treated wood was found to significantly reduce the risk of leaching metals into the environment during storage, or waste disposal.
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1. Introduction

Chromated copper arsenate, or CCA, has been used extensively as a wood preservative since 1940s [1]. CCA is composed of copper, arsenic and chromium. The copper acts primarily to protect the wood against decay fungi and bacteria, while the arsenic is the main insecticidal component of CCA. The chromium acts as a chemical fixing agent and has little or no preserving properties; it helps the other chemicals to fix in the timber, binding them through chemical complexes to the wood's cellulose and lignin. CCA is used to protect wood from dry rot, fungi, molds, termites, and other pests that can threaten the integrity of wood products. In the production process, CCA is injected into the wood using a high pressure to saturate wood products. The fixation of CCA inside the wood is a chemically complex process. The preservative is chemically bound to the wood fibers by reaction with wood sugars to form insoluble arsenate precipitates [2]. This process greatly reduces the potential for loss of CCA on the

surface of the wood. Retention levels in CCA-treated wood range from $4.0 \, kg/m^3$ for above ground contact to $40 \, kg/m^3$ for marine piling. The average retention of CCA for all products treated in the USA was estimated to be $5.6 \, kg/m^3$ in 1990 [3]. Applying wood preservatives can extend the productive life of wood and can help reducing the demand for forest resources. CCA-treated wood is primarily used for outdoor settings, including deck and fence, highway sign posts, telephone poles, etc.

However, during the period of service or storage of these woods, partial amount of CCA in the wood will leach out into the surrounding soil with time, and due to its high toxicity to non-target organisms, CCA-treated wood has caused environmental hazard. Current maximum contamination levels (MCL) for Cu, Cr, and As in the Safe Drinking Water Act Amendments of 1996 are 1.0, 0.1, and 0.010 mg/L (0.010 mg/L as of 23 January 2006), respectively [4]. The regulation of the MCL implies that contaminated wood preserved with CCA has become a big issue and has drawn great attention in scientific communities. The risks of exposing to those woods consist of being absorbed through the skin, inhalation, and ingestion either directly or indirectly. The degree of potential risk on the environment varies with different exposure status, i.e., the amount

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of CCA being leached out from treated wood into the aquatic ecosystem, being released into the air from burned ash [e.g., arsine gas (AsH_3)]. As reported in the literature [5], arsenic species in the wood turns to volatile compound (AsH_3) at the beginning of incineration, and the preservative chemicals concentrate and release in the ash and the smoke of a fire. Moreover, when the woods were dumped into landfills instead of incineration, heavy metals will leach out, which contaminate both soil and groundwater [5,6]. Besides, when the wood is reused, the toxic contents can likewise harm human health. Consequently, in order to have safer dumping, incineration or reuse of those CCA-treated woods, the most possible approach is to reduce the content of CCA in the wood before its sequent treatments, i.e., dumping, incineration or reuse. The feasible approach to reduce the content of CCA in the wood is to remove them.

Several approaches for the removal of CCA from wood wastes have been reported in the literature [7–16]. Metals in the CCA-impregnated wood was removed by using sulfuric acid and heated for 5 h (>95%) [15]. At high temperature (>1000 °C), the preservatives and metal components in the wood were separated effectively by high-speed thermal decomposition [16]. Hydrogen peroxide (H_2O_2) extraction [7,10], dialytic and electrodialytic process [11], EDTA extraction [12], oxalic extraction, steam explosion, and bacterial fermentation [13] were also applied for the removal of CCA from CCA-treated wood. Recently, a number of studies regarding the decontamination of CCA-treated wood using green solvent, supercritical carbon dioxide ($ScCO_2$) have been reported [17,18]. Takeshita et al. [17] described that with a continuous addition of acetylacetone in $ScCO_2$, copper can be successfully extracted from CCA-treated wood. $ScCO_2$ is very attractive for environmental remediation in consequence of its nontoxic, nonflammable, and possessing the potential for recycling. El-Fatah et al. reported that hazardous metals in CCA-treated wood can be extracted out using $ScCO_2$ by different chelating agents, among them Cyanex 302 was the best ligand [14]. However, those methods which using $ScCO_2$ as the medium to remove CCA in the wood are either having lower extraction efficiency or being failure to discuss the influence of the different species of Cu, Cr, As in the wood on the mechanism of extraction, this is because various species may present different extraction efficiencies while under the identical extraction condition. Hence, the aim of this work is to present a procedure which can increase the extraction efficiency by using green solvent $ScCO_2$. Besides, in order to treat a large quantity of wood, a combination of chelating agent/MeOH with a wood containing cell was assayed for a more efficient process. Metal ions can be successfully extracted using different chelating agents such as dithiocarbamates, β-diketones and ionizable crown ethers in $ScCO_2$ [19–22]. In this study, SFE of Cr, Cu, and As from wood wastes using an organophosphorus reagent, Cyanex 302, in $ScCO_2$ are surveyed, and the extraction efficiencies of CCA with other chelating agents are also compared. The results indicated that the extraction efficiency is enhanced, both the different oxidation of metal and the matrix effect influence the extraction mechanism.

2. Experimental

2.1. Reagent and materials

Bis(2,4,4-trimethylpenthyl) monothiophosphinic acid (Cyanex 302, Cytec, Canada, Inc.) was used as supplied. Gaseous CO_2 (Air Products, SFE/SFC grade) and SFC-grade of CO_2 modified with 5% methanol (Scott Specialty Gases, Plumsteadville, PA) were used through this research. Nitric acid was Ultrex-grade ultra-pure reagent from J.T. Baker Inc. Sodium diethyldithiocarbamate (NaDDC) was also purchased from J.T. Baker Inc. Dibutyldithiocarbamate ammonium salt (DBDC) was synthesized in our laboratory according to the literature [23]. Other reagents and solvents used in this study were of analytical grade and were obtained from Aldrich Chemical Company or Baxter Scientific (McGaw Park, IL). De-ionized water from a Millipore Milli-Q system (Bedford, MA) was used for the preparation of all aqueous solutions. Wood samples (a weathered telephone pole), containing CCA from wood treatment processes, were obtained from a forest product laboratory, Department of Forestry, University of Idaho, USA. The sample was dried, ground, and homogenized. The size of CCA-treated wood sawdust was around 40 mesh. Triplicate runs of all SFE samples were undertaken in this study.

2.2. Apparatus

The schematic diagram of SFE system used is shown in Fig. 1. The experiments were performed with an extraction cell (9 mL, ISCO, Lincoln, NE) placed in an extractor (SX2-10 ISCO, Lincoln, NE). The extraction vessel was maintained at the desired temperature in the thermostatic oven. At the oven exit, a 20 cm of stainless steel tubing (316 SS, 1/16 in. O.D., 0.030 in. I.D.) was used as pressure restrictor for the exit of CO_2. SFC-grade CO_2 or 5% MeOH modified CO_2 was supplied to a syringe pump (model 260D, ISCO, Lincoln, NE), the pump head was cooled with a circulating ice-water bath (0–5 °C). The flow rate was controlled around 0.5–1.0 mL/min by adjusting the outlet valve. A high performance liquid chromatography (HPLC) pump was used as a supplier of Cyanex 302/MeOH solution (0.02 M).
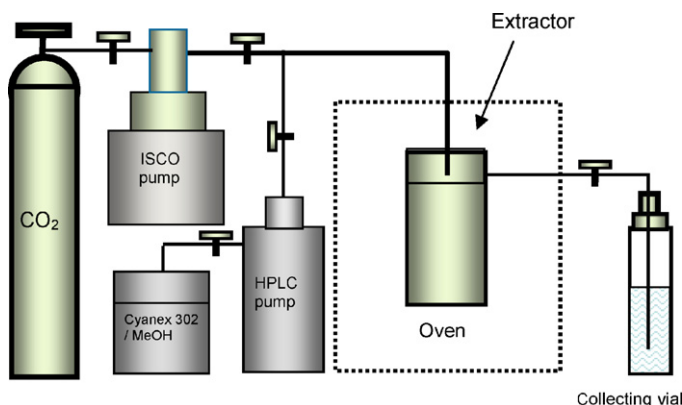

Fig. 1. Schematic diagram of the extraction apparatus used in *in situ* chelation/SFE.

A 1 MW TRIGA nuclear reactor (Washington State University, Pullman, WA, USA) at a steady flux of 6×10^{12} n cm^{-2} s^{-1} was used as the neutron source for the activation of CCA and standards. A large-volume ORTEC Ge(Li) detector with a resolution (FWHM) of 2.3 keV at the 1332 keV ^{60}Co peak was used for the measurement of As, Cr. The detector has an efficiency of 15% relative to a 3×3 NaI crystal. A Perkin Elmer Optima 3000XL ICP-AES with an axially mounted torch was used to measure the amounts of Cu, Pb, and Zn extracted.

2.3. Extraction procedure

Three different modes of extraction were carried out. The collection of extracted metals was simply venting the CO_2 into atmosphere and leaving solutes behind can easily separate the solutes that dissolved in the ScCO$_2$.

2.3.1. Single batch SFE

Fifty milligrams of ground wood sample was loaded into the extractor and 1 g of Cyanex 302 was loaded in a small boat-like glass container upstream as that depicted in Fig. 1. The extraction included 20 min static extraction followed by 40 min dynamic extraction, 5% MeOH modified CO_2 was used as the fluid, and keeping the pressure at 200 atm, temperature at 60 °C. The eluent released from SFE system was trapped in a 30 mL vial with 10-mL of methanol inside. After extraction, the vial along with the methanol was dried completely in an oven at 80 °C for 24 h, the residue at the bottom of the vial was thought to be the CCA. Ten milligrams sample residues and the standards with the same mass (without SFE) were analyzed by neutron activation analysis (NAA).

2.3.2. Multiple batchwise SFE

Fifty milligrams of ground wood, as sample, was placed in the extraction cell, and 1 g of Cyanex 302 was loaded in a small boat-like glass container upstream as that in Fig. 1. After 200 μL of water was added to the sample, the extraction cell was mounted in the oven and pressurized, 5% MeOH modified CO_2 was applied for extraction. Sample was subject to repeated batchwise SFE extractions and each experiment was carried out with a 10-min static extraction followed by a 30-min dynamic extraction at 200 atm and 60 °C. The extracted complexes were later trapped in a glass vial containing MeOH. The sample was extracted six additional times under the same conditions to remove remaining amounts of metals.

2.3.3. Dynamic extraction only

As described in the previous section, 50 mg of ground wood sample was placed in the extraction cell, neat CO_2 was charged in. Two hundred microliters of water were added to the wood sample prior to SFE. Cyanex 302 (chelating agent, 3.06 g) was dissolved in 500 mL of MeOH, this led the concentration of Cyanex 302 being 0.02 M (Cyanex 302/MeOH). A 3.5 mL stainless steel extraction cell filled with Cyanex 302/MeOH solution was installed between the outlet of the HPLC pump and the inlet of the SFE system to avoid the pressure unbalance which will cause CO_2 entering into the HPLC pump. Flow rate of the HPLC pump was set at 0.22 mL/min.

2.4. Analytical procedures

The amount of chromated copper arsenate was analyzed by NAA. Solution from the collecting vial was moved to a 2/5-dram polyethylene vial, evaporated to dryness and heat-sealed for neutron irradiation. Standards were prepared in the identical manner. Samples along with the standards were irradiated in a 1 MW TRIGA nuclear reactor for 1 h. The energy of irradiation will bring the elements to the state of unstable radioactive nuclides. The radionuclides, including both the activated samples and standards, will emit γ-rays with characteristic energies that can be measured by Ge(Li) detector. The amount of each metal was determined by calibration of the detector with the standard solutions stated above. The rate that γ-rays emitted from an element in the sample is directly proportional to its amount (concentration). Quantitative results can be calculated by comparing with the known values of the standards. The γ-rays of Cr, Sb and As emit at 320, 564, and 559 keV, with half lives of 27.8, 2.74, and 1.10 days, was used for the identification of these metals, respectively (note that a small amount of Sb was also present in SFE wood samples). Detection limit of NAA varies with different elements, because the production of radioactive nuclides depends on the cross-section of a specific element. Generally, element that has large cross-section will have lower detection limits. Arsenic, antimony, and chromium are very sensitive to NAA analysis and detection limits are 0.01, 0.035, and 0.5 ppm, respectively. Standard deviations are less than 4% for all samples.

Calibration standards for ICP-AES were prepared using certified standards of individual elements acquired from Aldrich Chemical Co. and Fisher Scientific. Sets of three to five different concentrations of the standards were used to establish calibration curves. To minimize matrix effects, blank and standard solutions were closely matched with the samples. Blanks and standards of known concentrations were run periodically through the ICP-AES analyses as quality control checks. Detection limits for this method are 0.1 (Cu), 0.5 (Pb), and 0.1 (Zn) ppm, respectively. Standard deviations are less than 6%. The whole set of metals can also be measured by using ICP-AES, if needed.

3. Results and discussion

3.1. Extraction efficiencies for CCA

The results indicated, without addition of chelating agents, no CCA were extracted from wood sample. This suggests that there is no organometallic species of these metals in the matrix; however, as 5% MeOH modified CO_2 which containing 1 g of Cyanex 302 was applied (added to the extraction cell upstream of the wood sample prior to each SFE), CCA were able to be extracted at 200 atm and 60 °C with 10-min static followed by 30-min dynamic extraction.

Initial concentration of Cu, As and Cr in the wood sample are 9420 ± 180, $20{,}050 \pm 290$ and $18{,}220 \pm 250$ ppm, respec-
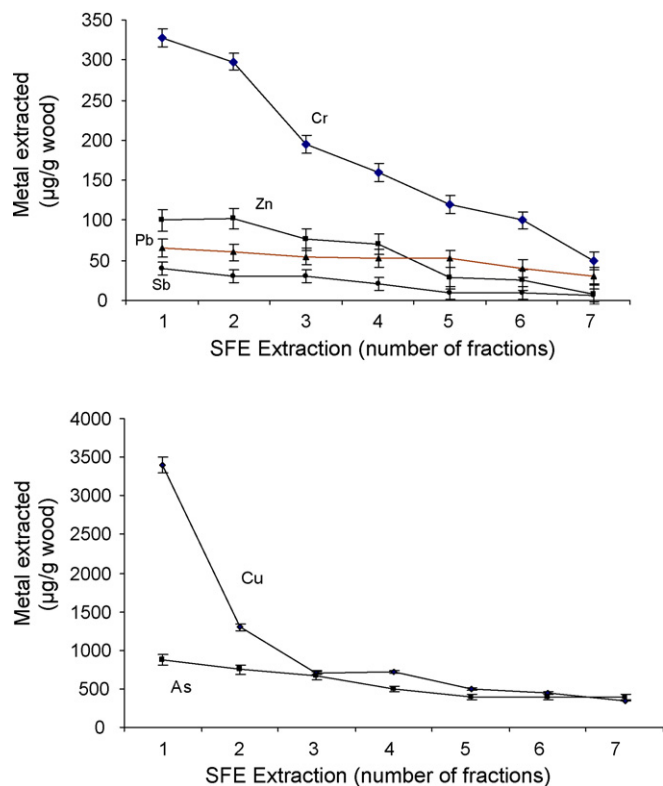
Fig. 2. SFE of heavy metals from wood sample which containing As, Cr, Cu, Pb, Sb and Zn. Samples were extracted at 200 atm and 60 °C using 5% MeOH modified CO_2. One gram of Cyanex 302 was added to the extraction cell upstream prior to each extraction. Each SFE extraction was carried out in 10-min static extraction followed by 30-min dynamic extraction. Fifty milligrams of wood sample were subjected to consecutive seven batchwise extractions.

tively, according to the elemental analyses by ICP-AES. Other metal species such as Pb, Sb, and Zn are much less concentration in the wood. As can be seen in Fig. 2, higher SFE efficiencies occurred in the first three extractions followed by much lower extraction efficiencies in the subsequent runs. The first batch showed the highest extraction efficiencies, i.e., 3500 ppm for Cu, 900 ppm for As and 340 ppm for Cr, respectively. The quantities of other elements (Pb, Sb, and Zn) extracted from the wood in the first batch SFE were less than 100 ppm. After seven consecutive batchwise extractions, the cumulative quantities for Cu, As and Cr extracted were approximately 7500, 4000, and 1300 ppm, respectively, i.e., Cu, As and Cr had been removed with 80%, 20% and 7%, respectively. The order of extraction efficiencies was Cu ≫ As > Cr, i.e., copper was primarily removed, followed by arsenic and chromium. This situation is probably due to the higher solubility of Cu-Cyanex 302 complex in comparison with those of other metal complexes. Our previous results indicated that the metal complexes formed by Cyanex 302 have good solubilities in ScCO$_2$ with reasonable formation constants [24]. The solubilities of Cu-Cyanex 302 are 2.4×10^{-3} M and 2.1×10^{-2} M at pressures of 200 and 300 atm, at 60 °C, respectively [20]. As can be seen in Fig. 2, the amount of Cr, Cu, and As, after multi-extractions (static plus dynamic), have reduced to 60, 500, and 500 ppm, respectively. The extraction profile reached plateau after several extractions, suggesting that leachable met-

als were represented from the matrix under the experimental conditions.

The nature of real sample may not be the same as spiked samples in the same matrix. The active sites and natural ligands presented in real samples may bind strongly to certain metal ions resulting in hindering their complexation with added ligands. However, our experiments demonstrate that quite a few CCA metals could be removed from the wood matrix using the Cyanex 302 in ScCO$_2$.

3.2. Extraction efficiencies between different extraction modes

Typical experiments were carried out at 200 atm and 60 °C in which Cyanex 302/MeOH solution (0.02 M), as chelating agent, was delivered using a HPLC pump, with dynamic extraction only and the extractions were undertaken for 2 h. Every 15 min, a portion of the sample was collected, with a total of eight portions collected. As can be seen in Fig. 3, the efficiencies from dynamic extraction were 5% for Cr, 10% for As and 65% for Cu, respectively. The results clearly indicate that using dynamic extraction only was not as effective as that of conventional SFE mode (static plus dynamic extraction). Comparing Figs. 2 and 3, the results indicate that conventional SFE has higher extraction efficiency.
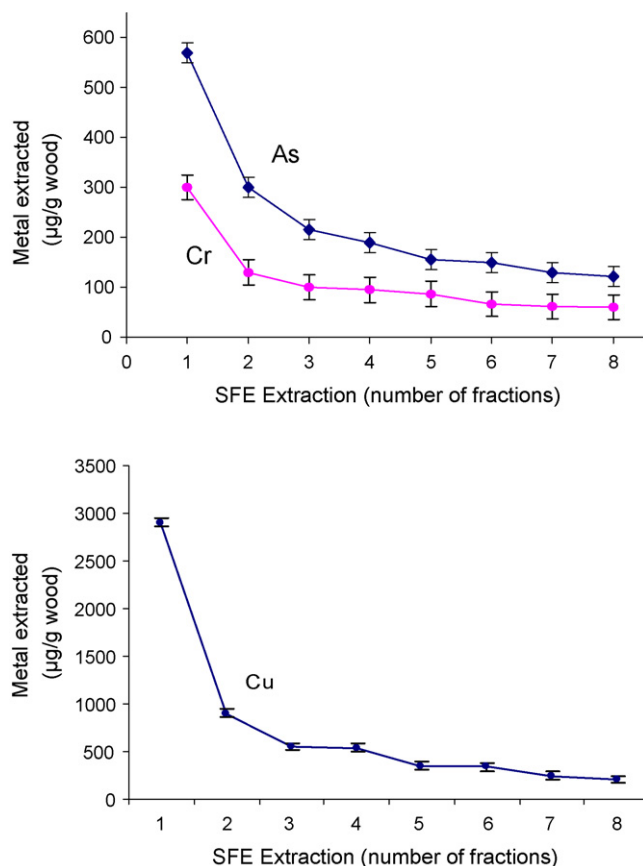

Fig. 3. SFE of Cr, Cu, and As from a wood sample using dynamic extraction. Samples were extracted using dynamic extraction at conditions of 200 atm, 60 °C, neat CO_2 and 0.02 M Cyanex 302/MeOH solution. Samples were collected in every 15 min, with a total of eight portions collected.

The static extraction increases the opportunities of interaction and the contact time between solvent and solutes. The solubility of chelating agents and metal complexes in CO_2 is the key controlling factor in determining the extraction efficiency of metal chelates. According to our previous research, the solubility of Cyanex 302 at 200 atm and 60 °C in $ScCO_2$ is 40 g/L [20], duo to this large solubility in $ScCO_2$, the chelating agent probably does not have enough time to interact with metal ions, hence it will elute directly from SFE system, if only dynamic extraction is applied.

Apparently, SFE with a static plus dynamic extraction shows better extraction efficiencies. However, for industrial scale operation, dynamic extraction may be suitable for the extraction of CCA, because the chelating agent can be reused, recycled and continuously provided in the system. Besides, due to its recyclability, CO_2 can be served as a green solvent as long as the chelating agents can be continuously supplied.

From the viewpoint of green approach, in comparison with other extraction approaches, for instance, bio-remediation, CCA could be removed from CCA-treated sawdust onto Chitosan (a biopolymer) about 57% (Cu), 43% (Cr) and 30% (As), respectively, in 10 days [25]. Hydrogen peroxide (H_2O_2), a strong oxidizing agent, was used to evaluate the extraction efficiencies of Cr, Cu and As from CCA-treated wood by different authors [7,10]. CCA can also be leached from CCA-treated wood via acid digestion according to US EPA method 3010 [26]. This method requires the addition of concentrated HNO_3 and HCl. Under room temperature, with 10% H_2O_2 and a 36 h extraction time, the extraction efficiencies could reach 51% (Cr), 51% (Cu), and 47% (As), respectively [10]; by 10% H_2O_2 at 50 °C and in 6 h, CCA components could be extracted with the average extraction efficiencies of 95% (Cr), 94% (Cu), and 98% (As), respectively [7]. This indicates that temperature probably plays a major role in the extraction process. Using 1% EDTA solution for 24 h at room temperature, the extraction efficiencies of CCA in CCA-treated sawdust were 60% (Cu), 13% (Cr), and 25% (As) from treated chips, and 93% (Cu), 36% (Cr), and 38% (As) from treated sawdust [12].

Although these approaches, which mentioned above, can remove CCA from wood wastes with considerable efficiencies; however, they will generate large quantities of chemical and acid wastes. On the contrary, extraction of CCA using $ScCO_2$ as a green solvent can provide an alternative way to minimize the liquid waste generation.

3.3. Influence of pressure and temperature

As mentioned in the previous statement, temperature may be the important factor for the higher extraction efficiencies. Fig. 4 demonstrates the SFE profile of removing Cr, Cu, and As from wood samples at 300 atm and 60 °C using dynamic extraction. The extraction curves show that the accumulated amount of extracted metal species in different extraction times. Two hundred microliters of 1 M HNO_3 was added to the sample prior to the experiment, and 0.02 M Cyanex 302/MeOH solution was delivered into SFE system by HPLC pump in the SFE process. The extracted metal species were collected in every 15-min
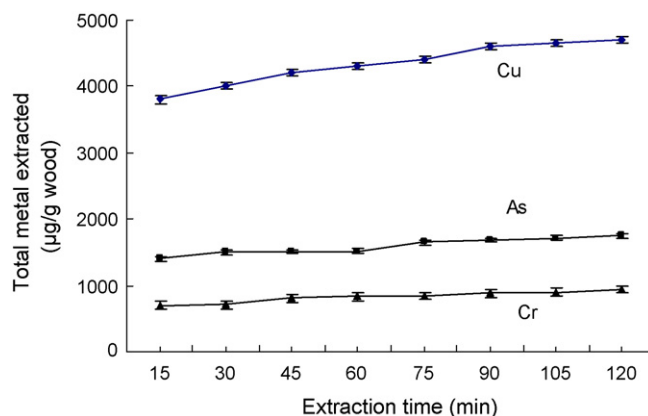

Fig. 4. Metals extracted in dynamic extraction of CCA-treated wood. The concentration of recovered solution was calculated in accumulation with previous fractions. Samples were extracted at 300 atm and 60 °C using neat CO_2 and 0.02 M Cyanex 302/MeOH solution.

interval. It was found that the heavy metals could be extracted continuously from CCA-treated wood. As can be seen in Fig. 4, After 2 h, almost all extractable metals were removed; this could be evidenced by the near plateau reached by CCA profile. The extraction profiles at 200 and 100 atm (not shown) were similar to that in Fig. 4 (300 atm) except for correspondingly low recoveries of metal species.

Solubility of chelating reagent and its complex can be enhanced by the increase of CO_2 density. At higher pressures, thus higher the density of $ScCO_2$, the solvation strength of the fluid will increase accordingly. This facilitates the interactions between solutes and solvents, and enhances their solubilities in $ScCO_2$, and thus leads to higher extraction efficiencies [20–22]. Different pressures can affect extraction efficiencies of copper significantly, whereas arsenic and chromium have less influence by the variation of pressure. The order of SFE efficiency for CCA is as follows: Cu ≫ As > Cr, similar to the trend obtained by the other authors in different methods [7–9,14–16,25,26]. This can also be observed from continuous extractions of CCA from wood samples at different pressures including 100, 200, and 300 atm (Fig. 5). The experiment was carried out in dynamic extraction by pumping 0.02 M Cyanex 302/MeOH solution in high-pressure system. The curves show the total amount of recovered metal species collected in 2 h. Samples were collected every 15 min with total 8 fractions. At 300 atm, in the first 15 min, about 3800, 1600, and 750 ppm of Cu, As, and Cr were extracted, i.e., about 190, 80, and 37.5 µg of Cu, As and Cr were removed, respectively. Accumulatively, about 4900, 3500, and 2300 ppm, i.e., 245, 175 and 115 µg of copper can be extracted at the pressure of 300, 200, and 100 atm, respectively. At 300 atm, accumulatively, 53%, 10%, and 5% of Cu, As and Cr can be extracted in the dynamic extraction as shown in Fig. 5. At 100 atm, the extraction efficiencies of Cu, As and Cr were 24%, 3%, and 1%, respectively.

The solvation strength of $ScCO_2$ can also be adjusted by manipulating the temperature. Increasing temperature can promote the diffusivities of solvents and solutes, besides, the solutes, extractants, and solvent can interact effectively, thus
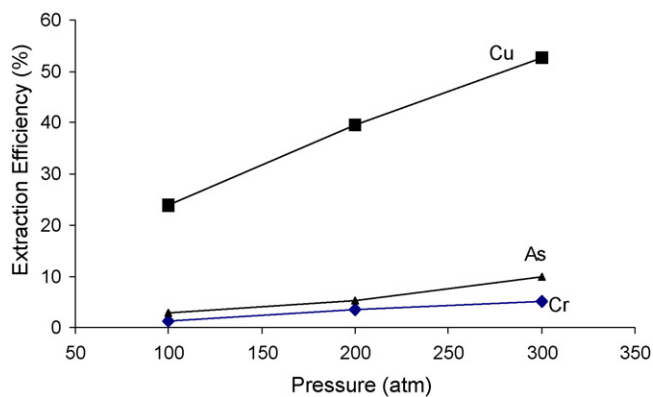
Fig. 5. Extraction efficiencies of Cr, Cu and As from a wood sample at different pressures using dynamic extraction by pumping 0.02 M Cyanex 302/MeOH in CO_2 phase. The extraction percentage was calculated from the final concentrations of accumulated trapped solution divided by the concentrations of CCA in wood.

enhancing the extraction efficiencies. However, unlike organic solvents, when keeping the pressure constant, the density of CO_2 decreases as the temperature increasing. This will in turn decrease the salvation strength, thus reducing the extraction efficiencies. As a consequence, we employed 60 °C as the extraction temperature through this study.

3.4. Influence of different oxidation states on the extraction efficiencies

Both As and Cr have different oxidation states, e.g., As(III), As(V), Cr(III), and Cr(VI) they might exist in the CCA-treated wood while exposing to the environment, and those species may present different extraction efficiencies under the identical extraction condition. In order to understand the chemistry of As and Cr in ScCO$_2$, investigation of the behavior of As(III), As(V), Cr(III), and Cr(VI) was carried out by using dithiocarbamate salts and Cyanex 302. A 10 μL aliquot of 1000 ppm of these two metal species in different oxidation states was spiked onto filter papers individually. The results indicated that both As(III) and As(V) can be extracted using 5% MeOH modified CO_2, but in neat CO_2 only As(III) can be extracted. When 5%

MeOH modified CO_2 was used in SFE system, As(V) turned to be extractable since As(V) has reduced to As(III) by methanol according to our experimental results. Methanol acts as both a modifier of CO_2 and a reducing agent in SFE system. For Cr species, Cr(III) and Cr(VI) can be extracted in both neat CO_2 and MeOH modified CO_2, but the extraction efficiency of Cr(III) is much lower than that of Cr(VI). In traditional solvent extraction, As(III) can be extracted by NaDDC, a chelating agent, whereas As(V) is non-extractable [27]. Cr(III) can be extracted by dithiocarbamate at higher pH but with lower efficiency [27]. The poor extractability of Cr(III) is due to the fact that Cr(III) is strongly hydrated in which a displacement of the coordinated water molecules by the ligand is difficult. Strong hydration of Cr(III) hinders the access of ligands to the central metal ion [28].

Matrix effects and different oxidation states of metals have led SFE extraction of CCA to a complicated status. The binding capacity between metal oxide anions and matrix (wood) can be different from metal to metal. Even for the same metal, these binding capacities can be various from different oxidation states and from the completeness of CCA fixation into wood. Complication of the chemistry of As and Cr is probably another factor causing low SFE efficiency.

3.5. Extraction efficiencies of different chelating agents

With identical conditions described in the previous sections, i.e., 30-min static plus 40-min dynamic extraction, pressure of 300 atm and temperature of 60 °C, various chelating agents, i.e., Cyanex 302, DBDC, and NaDDC, were tested in search of the difference of extraction efficiencies between them. After eight successively batchwise SFE, the extraction efficiencies are 95% for Cu, 66% for As, and 50% for Cr, using Cyanex 302. Cyanex 302 showed higher outcomes in comparison with those of DBDC and NaDDC under the same mole numbers as shown in Table 1. This is probably due to the fact that dithiocarbamate chelating agents and their complexes decompose easily in acidic medium of ScCO$_2$. A previous report indicated that under normal SFE condition, the pH of the water equilibrated with CO_2 is around 2.9 due to the formation and dissociation of carbonic acid [29]. When dithiocarbamate was used as chelating agent, it survives

Table 1
Extraction efficiencies of CCA from wood samples using different chelating agents

Ligand	Extraction efficiency (*E*%) of CCA with different ligands						
	SFE mode	Amt (mg)	MW (g/mol)	Mol	Cr (*E*%)	Cu (*E*%)	As (*E*%)
DBDC	SFE1–3	435	446	9.75×10^{-4}	11.5	28.5	21.2
DBDC	SFE1–6	435	446	9.75×10^{-4}	15.4	46.8	31.7
DBDC	SFE1–8	435	446	9.75×10^{-4}	20.1	84.4	33.8
NaDDC	SFE1–3	220	224	9.82×10^{-4}	10.2	27.4	22.4
NaDDC	SFE1–6	220	224	9.82×10^{-4}	16.1	44.8	30.0
NaDDC	SFE1–8	220	224	9.82×10^{-4}	17.9	85.3	32.5
Cyanex 302	SFE1–3	300	306	9.80×10^{-4}	17.7	81.7	30.5
Cyanex 302	SFE1–6	300	306	9.80×10^{-4}	28.8	87.3	42.0
Cyanex 302	SFE1–8	300	306	9.80×10^{-4}	50.3	94.7	66.3

SFE conditions: 30-min static and 40-min dynamic extraction, 300 atm and 60 °C, 5% MeOH modified CO_2, 200 μL of H_2O, trapped in $CHCl_3$, 50 mg of wood sample, data are based on trapped solutions, standard deviation: ±3 ~ ±5%.

in acidic condition for a very short time; however, organophosphorous (Cyanex 302) can act as a good chelating agent in the acidic condition. The former, i.e., dithiocarbamate, is a common chelating agent and commercially available, which is widely used in solvent extraction processes. For Cyanex 302, its major content is bis(2,4,4-trimethylpentyl) monophosphinic acid, and it varies from lot to lot production. Cyanex 302 has high solubility in $ScCO_2$ and can be sustained in a relatively acidic medium without decomposition. More importantly, Cyanex 302 is particularly favorable for the extraction of copper. In addition, for the spiked metal ions, DBDC and NaDDC may exhibit better extraction efficiencies [19,21]. However, if real samples were applied, complication of chemistry, such as the effects of different oxidation states of the native metal species and matrix effect, makes SFE more intricate. In addition to Cyanex 302, other organophosphorous reagents, such as Cyanex 301, Cyanex 272 and D2EHTPA are typical for the extraction of copper with high extraction efficiencies from various matrices including clay, soils, and wood samples [20]. This type of extractants would have potential applications for decontamination of metals, especially for copper, in various environmental samples.

4. Conclusions

Chromium, Cu, and As in CCA-treated wood can be extracted by $ScCO_2$ containing organophosphorus reagent, Cyanex 302. The extraction efficiencies of CCA by using Cyanex 302 are higher than the other chelating agents, due to the high solubilities of this chelating agent and its metal complex. The extraction efficiencies for the extraction of CCA are in the order of Cu ≫ As > Cr. The extraction profiles descend rapidly, followed by a plateau of metal extractions, suggesting that the process is limited to the leachable toxic heavy metals. By the alternation of extraction conditions, such as increase of pressure and extension of static extraction time, the efficiencies can promote to 95% (Cu), 66% (As) and 50% (Cr), respectively, after eight successive batchwise extractions. In comparison with other extraction methods, the green solvent $ScCO_2$ in SFE can significantly reduce acid and organic solvent waste generation, and may present a potential use in large-scale industrial applications. A tremendous advantage of $ScCO_2$ is that the solvent characteristics can be adjusted over a wide range by varying the density (i.e., pressure) of the fluid, thus controlling the solvent–solute interaction of CCA-treated wood sample. The *in situ* chelation/SFE presented here shows advantages over conventional solvent extraction, in which it greatly minimizes the generation of secondary wastes in decontamination processes and helps alleviate the land filling and potential CCA contamination problems. The results suggest that leachable metal species in CCA-treated wood wastes can be extracted in $ScCO_2$ containing an organophosphorus reagent that significantly reduce the risk of leaching toxic metals into the environment.

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