

Removal of Copper, Chromium, and Arsenic from CCA-Treated Wood Using Glycerol/Choline Chloride Deep Eutectic Solvent [†]

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Abstract: Many chemicals and methods have been used to remove copper, chromium, and arsenic from wood that is impregnated with CCA. However, in these studies, it can be seen that deep eutectic solvents (DES) are not used in the removal of copper, chromium, and arsenic. In this study, the effect of DES on the removal of copper, chromium, and arsenic from CCA-impregnated wood and the changes that are caused by DES solutions in wood samples were investigated. DES solutions, glycerol (GL) as a hydrogen bond donor (HBD), and choline chloride as a hydrogen bond acceptor (HBA), were used. According to the results that have been obtained, it can be seen that the DES that was prepared with GL:CL was less effective in the remediation process, and 65.5% Cu, 30% Cr, and 10% As, were removed. It was found in FTIR analysis and lignin determination that the lignin ratio of the wood samples decreased after the remediation process. It seems that the crystallinity ratio of the wood samples that were treated with GL:CL decreased significantly.

Keywords: deep eutectic solvent; chromium copper arsenic (CCA); remediation; chemical characterization



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1. Introduction

The use of toxic and harmful chemical solvents in industry and in laboratories is dangerous for those who are working there and for the environment. Volatile organic solvents cause environmental pollution. In addition, many are harmful to health if they are inhaled. For this reason, the “Green Chemistry” concept has emerged, along with an increased interest in “green” solvents. Green solvents can be classified as supercritical fluids (SCF), as ionic liquids (IL), and as deep eutectic solvents (DES), and the latter two have attracted much attention recently. In order to eliminate the disadvantages, such as the toxicity and the high price of ionic liquids (98% pure 1-butyl-3-methylimidazolium chloride is ~EUR 360/250 g, whereas 99.9% pure toluene is ~EUR 71/250 g), new-generation solvents have emerged [1]. These new-generation deep eutectic solvents are formed by the bond between ammonium or phosphonium organic salts and a hydrogen bond donor (HBD), such as alcohol, an acid, or an amide. The disadvantages of ionic liquids have been overcome, while maintaining their advantageous properties. Similarly to ionic liquids, deep eutectic solvents have a low vapor pressure and a high thermal stability. However, unlike ionic liquids, they are inexpensive, are easy to prepare, and they are biodegradable.

Many DESs that have been synthesized to date are in liquid form below 70 °C, and many have been synthesized using sugar, alcohol, acids, amides, and amines as HBDs [1]. In addition to the synthetic compounds, the DESs that are formed with natural compounds, such as organic acids, sugars, and choline, are called natural deep eutectic solvents (NADES) [2]. Choline chloride (ChCl) is the most frequently used cationic salt [3]. The number of publications on DES solutions began to increase after 2004. To date, the greatest

number of studies (approximately 190 articles) have been conducted in the fields of electrochemical, radiation, and thermal energy. The use of DES systems in many different sectors is due to the advantages that they possess [4].

A review of the literature has determined that DESs have not yet been used to recover the active substances from the copper-based impregnation materials that are used in wood. To date, many chemicals and methods have been tested in the remediation process. Some of these approaches have been successful in terms of the recovery of active substances. However, the chemicals that have been used in the remediation process are not environmentally friendly, and problems in the recycling of the used chemicals have necessitated the use of new natural substances. Copper/chrome/arsenic (CCA) impregnation uses a water-soluble impregnation substance, which is bonded to the wood by reacting with the wood structure or by precipitation as a result of the impregnation processes. Because of these reactions, the wood becomes resistant to leaching, resulting in fixation. Although CCA impregnation materials have been used for many years in almost every country in the world, in recent years, its use has been banned or limited in many countries. Within the framework of the decision that was taken by the US Environmental Protection Agency (EPA), since 2004, applications using wood materials containing CCA that is impregnated using pressure cannot be used in housing (residences), in children's playground elements, in picnic tables, in flooring material, in landscaping applications, in fences, etc., in North America. European countries have also begun to implement this ban, and the usage areas of CCA impregnation materials have become limited. The wood materials that have been impregnated with 3–4 million m³ CCA in the USA and Canada are at the end of their service life and, therefore, they must be removed [5]. Gezer et al. [6] reported that there are 8 million wooden utility poles in Turkey, whereas their number is 110–132 million in the USA, and 5.4 million in Australia. It was stated that this number was 117,000 units (approximately 38,924 m³) in 2010 alone. Although the service life of impregnated utility poles varies from 40 to 50 years, this period decreases to 10–15 years in areas such as the Eastern Black Sea Region in Turkey, where the decay index is high and the impregnated utility poles require maintenance [7]. Various methods have been used to date in order to dispose of or recycle the impregnated materials from installations that have reached the end of their service life. These methods have been classified in many studies [8–13].

One of the topics on which green chemistry focuses is the development of new-generation solvent alternatives that are environmentally friendly and can be used in many chemical processes instead of the traditional solvent systems with known toxic effects. In this study, DESs were used for the removal (remediation) of chromium, copper, and arsenic from CCA-impregnated wood materials.

2. Materials and Methods

Scotch pine (*Pinus sylvestris* L.) (density 0.42 g/cm³) samples were cut from the sapwood part of 5 (Radial, R) × 15 (Tangential, T) × 30 (Longitudinal, L) mm³ and were prepared for testing. Choline chloride (CL) (99%, 139.62 g/mol, ACROS) and glycerol (GL) (92.09 g/mol, MERC) were used in the remediation process. Copper/chromium/arsenic (CCA) at 5% concentration was used as the impregnation material.

2.1. Impregnation of Wood

The wood samples were impregnated with CCA solution prepared at 5% concentration by applying vacuum pressure. During the procedure, after a pre-vacuum treatment at 650 mm Hg for 30 min, 5 bar pressure was applied for 1 h. The samples were removed from the impregnation solution and cleaned of the impregnation materials. The retention values of the wood samples were then calculated and a retention value of 20.85 kg/m³ was obtained in the samples after the impregnation process.

2.2. DES Preparation Process

The DES was prepared at 80 °C by mixing glycerol (GL) as a hydrogen bond donor and choline chloride (CL) as a hydrogen bond acceptor at 1:1 mole ratio for 2 h. All mixtures were shown to be homogeneous and clear liquids. No precipitation was observed when all of the mixtures were brought to room temperature. This was an indication that the DES mixtures had been successfully prepared.

2.3. DES Characterization

The viscosities of all of the DES samples were measured using a HAAKE MARS III rheometer (Victoria, Australia) with cone/plate geometry (35 mm, 1°, 0.052-mm gap) at 25 °C. The densities of the four DES solutions were calculated by measuring the mass of a given volume.

2.4. Treatment of Wood Samples with DES

Each 5 × 15 × 30 mm wood sample was kept separately in a beaker of 50 g of DES solution for 2 h at 150 °C. No mixing process was applied during this period. After the modification period of 2 h, the samples were washed with an ethanol/water mixture (15 mL 1:1 mole ratio) to ensure that the DES solution was completely removed from the samples. This process was repeated three times and the samples were then dried under vacuum.

2.5. Characterization of DES-Treated Wood

The chemical composition of each sample was determined by analyzing the characteristic X-rays that were obtained after the sample was subjected to XRF (X-ray fluorescence). A special sample preparation process was not needed, and the analysis was carried out at the ppm level. The XRF analysis was performed to measure the amount of copper, chromium, and arsenic in the powder samples.

The Klason method specified in the TAPPI T 222 om-02 standard was used for the determination of lignin.

Measurements were taken using the Shimadzu Fourier-transform infrared (FTIR) spectrometer at the Barts University Department of Forestry Industrial Engineering. The spectra of each sample were measured at a resolution of 4 cm⁻¹ and a scanning range of 600–4000 cm⁻¹. In the study, the measurements were made with the ATR method from the solid samples.

The X-ray diffraction (XRD) analysis was performed with a high-resolution XRD spectroscopy equipped with a Ni-filter Cu K α (1.540562 Å) radiation source (X'Pert PRO, Philips PANalytical, EA Almelo, The Netherlands), which was used at 45 kV voltage and 40 mA electric current. The samples were scanned in the range of 2 θ (5°–40°) at incremental steps of 0.02°.

The surface morphology of the samples was examined via scanning electron microscopy (SEM) using an ESEM Phillips Electroscan 2020 device (LEUVEN, Belgium). During the examination, images were taken at different kilovolts (kV).

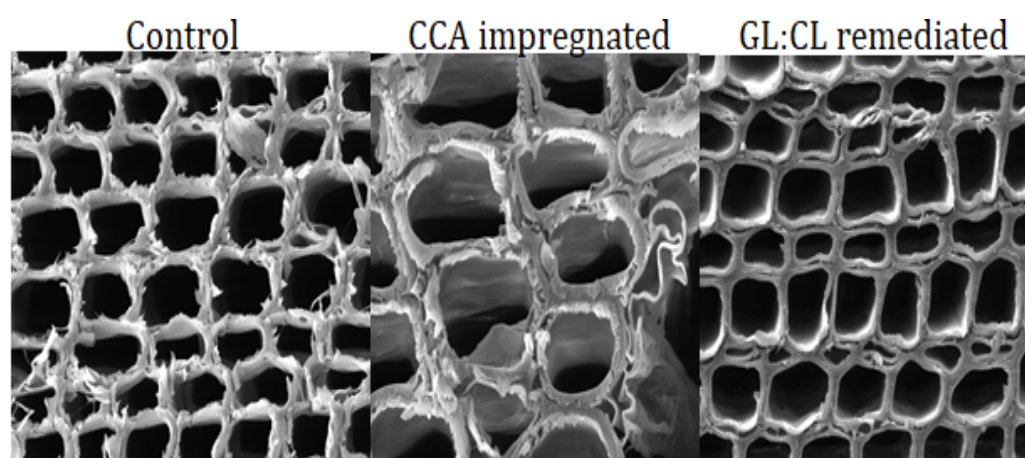
3. Results and Discussion

The impregnated Scotch pine wood (*Pinus sylvestris* L.) samples contained 0.8% CuO, 2.08% CrO₃, and 1.33% As₂O₅ at a 20 kg/m³ retention level. The initial retention level was one of the factors affecting the removal of Cu, Cr, and As from the CCA-impregnated wood. The density value of the prepared DES solution at 24 °C was 1.22 g/cm³, and the viscosity was measured as 210.21 cP. In the Scotch pine wood samples that were used, the lignin rate decreased to 28.75%, and after the remediation process with GL:CL, the lignin rate further decreased to 22.50% (Table 1).

Table 1. Density (g/cm^3)-24 °C, Viscosity (cP), and Lignin ratio (%) values of the samples.

	Density (g/cm^3)-24 °C	Viscosity (cP)	Lignin Ratio (%)
GL:CL	1.22	310.21	
Control			28.75
GL:CL remediated wood			22.5

Figure 1 shows the SEM analysis images of the wood samples that were treated with DES. All of the variations include images with $500\times$ magnification. No significant change in the wood structure was observed after CCA impregnation. However, it seems that there are significant changes in the structure of the wood samples after treatment with DES. Fragments of the wood mid-lamella appear to have occurred with DES treatment.


Figure 1. SEM analysis results of test and control samples.

The X-Ray diffraction (XRD) analysis was performed in order to determine the presence of the crystal structure of the wood samples after the impregnation and the remediation process. The detection of the crystalline materials will provide further insight into the chemical bonds and the molecular structures of the CCA elements that are found in wood. This information can add to the characterization value and can facilitate the remediation process. The CCA impregnated samples produced similar peaks compared to the control sample. Overall, no significant difference was found between the CCA-impregnated samples and the control samples and, therefore, phases could not be identified. This means that the CCA elements have minimal crystalline properties that can be distinguished from the control samples (Nico et al.), and a similar result was obtained in the study that was conducted by [14]. Figure 2 shows the XRD plot of the (left) control, the CCA impregnated, and the GL:CL remediated samples. There are two important peaks in the XRD spectra of the lignocellulosic biomass; the peak at 18.7° represents amorphous cellulose only, and at 22.5° it represents both amorphous and crystalline cellulose. According to Figure 2, while the peak at 22.5° did not change after the impregnation with CCA, it decreased after the remediation process.

The FTIR analysis was performed on the test samples and the control samples by scanning in the wave range of $4000\text{--}700\text{ cm}^{-1}$. These absorption peaks reflect the changes in the benzene rings, the main functional groups in the lignin, and the change in the crystalline and amorphous content of the cellulose. The peaks of carbonyl and acetyl groups in the xylan in the Scotch pine wood samples were observed at 1740 cm^{-1} . In the wood samples that have been used in the present study, this peak was observed at 1710 cm^{-1} . The wood samples that were impregnated with CCA and remediated with GL:CL showed peaks that were similar to the control samples. The $1630\text{--}1660\text{ cm}^{-1}$ band stated that it is associated with the --C=O bound aryl ketones, the unbound C=C , and the water band. The intensity

of absorption at $1630\text{--}1660\text{ cm}^{-1}$ indicates paired $\alpha\text{-C=O}$ bonds with para-hydroxyphenyl groups. The 1610 cm^{-1} peak indicates that it is associated with the unbound C=C and the water band. The absorption density at 1615 cm^{-1} indicates paired $\alpha\text{-C=O}$ bonds with para-hydroxyphenyl groups. In this case, it is thought that the H-O-H tension vibration, which absorbs the water in the carbohydrates after pretreatment, increases. The water absorption increases due to the increased hydroxyl group with the deformation of the H-O-H bond [15–17]. The peaks at 1595 , 1510 , and 1470 cm^{-1} are associated with the aromatic rings. The peak in the 1595 cm^{-1} band is associated with an aromatic ring tension that is strongly correlated with the aromatic C-O tension state. The peaks in the range of $1506\text{--}1510\text{ cm}^{-1}$ are characteristic peaks for the lignin components due to the C=O and COO-unsymmetrical tension vibrations in the aromatic rings in the lignin structure. Significant changes occur in the form of an increase in the 1510 cm^{-1} and 1595 cm^{-1} absorption peaks of the wood samples that were treated with copper compounds [18]. As a result of the changes in this band, it is understood that the ratio of the crystal zone increases as a result of the decrease in the amorphous structure of the cellulose [19,20]. The $1230\text{--}1270\text{ cm}^{-1}$ peaks indicate the C=O tension in the lignin. The decrease or the disappearance of the peaks' gap indicates the delignification and the degradation of the aromatic rings [21].

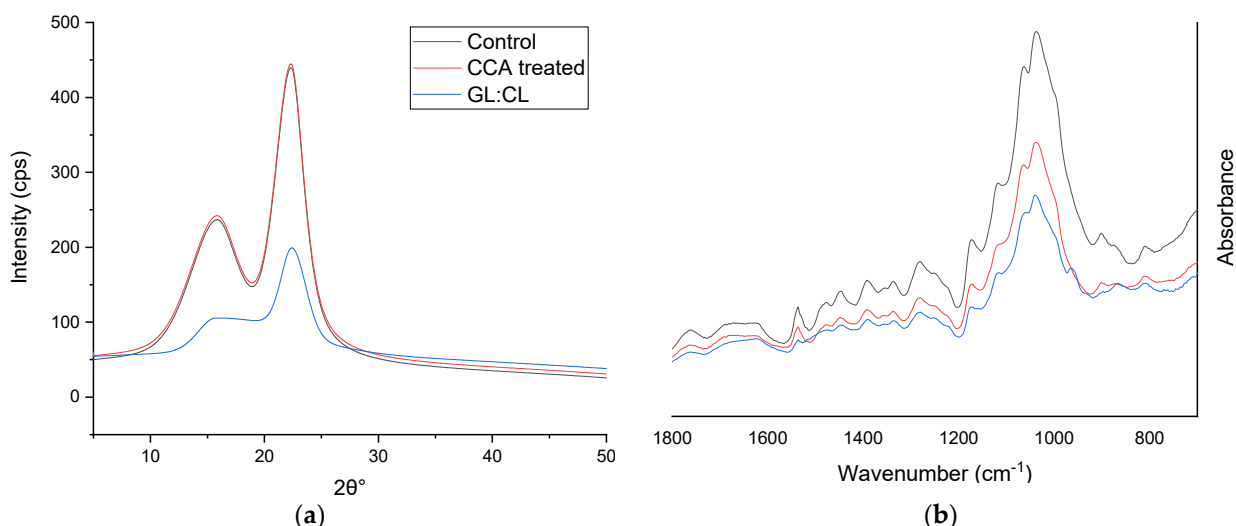


Figure 2. XRD (a) and FTIR (b) analysis results of test and control samples.

The first retention level is one of the factors affecting the removal of Cu, Cr, and As from CCA-impregnated wood. After the treatment of the impregnated wood samples with GL:CL, low amounts of As, Cu, and Cr were removed. The As removal remained around 10%. The Cr was removed at a rate of 30% and the Cu at a rate of 65%. The pH, the wood type, the retention level, the chemicals, the removal process, the time, and the chemical concentration are the factors affecting the Cu, Cr, and As removal from wood. In the literature, the effects of these factors on remediation were examined. However, in this study, the effects of deep eutectic solvents were investigated. Coniferous trees contain high levels of free phenyl OH groups, as well as a high lignin content. These groups seem to be the most likely reaction groups for Cr.

4. Conclusions

This study investigated the usability of deep eutectic solvents in the removal of chromium, copper, and arsenic from Scotch pine wood samples. For this purpose, DES solutions were prepared in 1:1 mole ratios of glycerol and choline chloride. After the treatment of the Scotch pine wood samples that were impregnated with 5% CCA with DES solutions, the rates of copper, chromium, and arsenic removed were examined and it was

determined that the DES solution that was prepared with glycerol was ineffective in the remediation process. The changes in the chemical structures of the wood samples that were treated with DES solutions were determined by XRD and FTIR analysis. In addition, with the lignin analysis, it was observed that the lignin ratio of the samples decreased after the DES treatment. Many different chemicals are used in the remediation process. However, the fact the chemicals that are used are harmful and cause environmental pollution, and that the chemicals that are used in green chemistry can also be used in the remediation process has been revealed with this project. By using different DES chemicals, finding out which chemical is more effective in the remediation process should be revealed in future studies.

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Conflicts of Interest: The authors declare no conflict of interest.

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