

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 impregnated with CCA. However, in these studies, it is 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 caused by DES solutions in wood samples were investigated. DES solutions, glycerol (GL) as hydrogen bond donor (HBD) and choline chloride as hydrogen bond acceptor (HBA) were used. According to the results obtained, it was seen that the DES prepared with GL:CL was low effective in the remediation process and 65.5% Cu, 30% Cr and 10% As were removed. It was obtained 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 wood samples treated with GL:CL decreased significantly.

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

1. Introduction

The use of toxic and harmful chemical solvents in industry and in laboratories is dangerous for those working there and for the environment. Volatile organic solvents cause environmental pollution. In addition, many are harmful to health if inhaled. For this reason, the “Green Chemistry” concept has emerged along with increased interest in “green” solvents. Green solvents can be classified as supercritical fluids (SCF), ionic liquids (IL), and deep eutectic solvents (DES), and the latter two have attracted much attention recently. In order to eliminate disadvantages such as the toxicity and high price of ionic liquids (98% pure 1-butyl-3-methylimidazolium chloride is ~360 €/250 g, whereas 99.9% pure toluene is ~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. Like ionic liquids, deep eutectic solvents have low vapor pressure and high thermal stability. However, unlike ionic liquids, they are inexpensive, easy to prepare, and biodegradable.

Many DESs 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 synthetic compounds, DESs 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]. 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

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energy. The use of DES systems in many different sectors is due to the advantages they possess [4].

A review of the literature determined that DESs have not yet been used to recover the active substances from copper-based impregnation materials 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 recovery of active substances. However, the chemicals that have been used in the remediation process are not environmentally friendly, and problems in recycling the used chemicals have necessitated the use of new natural substances. Copper/chrome/arsenic (CCA) impregnation uses a water-soluble impregnation substance 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 material has 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 taken by the US Environmental Protection Agency (EPA), since 2004, applications using wood materials containing CCA impregnated using pressure cannot be used in housing (residences), children's playground elements, picnic tables, flooring material, landscaping applications, fences, etc. in North America. European countries have also begun to implement this ban, and the usage areas of CCA impregnation material have become limited. The wood materials impregnated with 3-4 million m³ CCA in the USA and Canada are at the end of their service life and 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 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 are 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 traditional solvent systems with known toxic effects. In this study, DESs were used for the removal (remediation) of the chromium, copper, and arsenic from CCA-impregnated wood material.

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 prepared for testing. Choline chloride (CL) (99%, 139.62 g/mol, ACROS), Glycerol (GL) (92.09 g/mol, MERC) were used in the remediation process. Copper/chromium/arsenic (CCA) at 5% concentration was used as 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. A retention value of 20.85 kg/m³ was obtained in the samples after the impregnation process.

2.2. DES Preparation Process

It was prepared at 80 °C by mixing glycerol (GL) as hydrogen bond donor and choline chloride (CL) as 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 the mixtures were brought to room temperature. This was an indication that the DES mixtures had been successfully prepared.

2.3. DES Characterization

The viscosity of all the DES samples were measured using a HAAKE MARS III rheometer (Thermo Fisher Scientific) with cone/plate geometry (35 mm, 1°, 0.052-mm gap) at 25 °C. The density 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 process 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 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 Bartın 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, measurements were made with the ATR method from solid samples.

The X-ray diffraction (XRD) analysis was performed with a high-resolution XRD spectroscope equipped with a Ni-filter Cu K α (1.540562 Å) radiation source (X'Pert PRO, Philips PANalytical, The Netherlands) 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 the ESEM Phillips Electroscan 2020 device. During the examination, images were taken at different kilovolts (kV).

3. Results and Discussion

The impregnated Scots pine wood samples contained 0.8% CuO, 2.08% CrO₃, and 1.33% As₂O₅ at 20 kg/m³ retention level. The initial retention level was one of the factors affecting the removal of Cu, Cr, and As from 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 sample used, the lignin rate decreased to 28.75%, and after the remediation process with GL:CL, the lignin rate decreased to 22.50% (Table 1).

Table 1. Density (g/cm³)-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 SEM analysis images of wood samples treated with DES. All variations include images with 500x magnification. No significant change in wood structure was observed after CCA impregnation. However, it seems that there are significant changes in the structure of wood samples after treatment with DES. Fragments of the wood mid-lamella appear to have occurred with DES treatment.

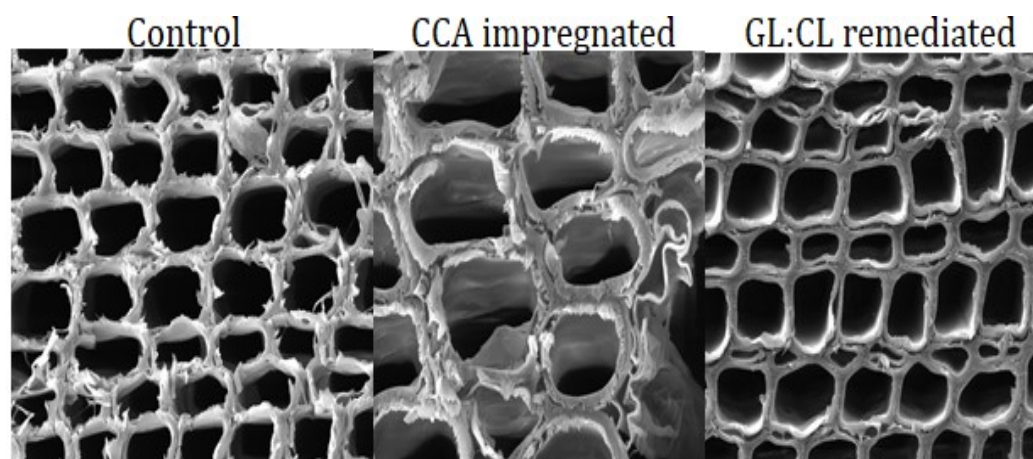


Figure 1. SEM analysis results of test and control samples.

X-Ray Diffraction (XRD) analysis was performed to determine the presence of the crystal structure of the wood samples after the impregnation and remediation process. Detection of crystalline materials will provide further insight into the chemical bonds and molecular structures of the CCA elements found in wood. This information can add to the characterization value and facilitate the remediation process. CCA impregnated samples produced similar peaks compared to the control sample. Overall, no significant difference was found between the CCA-impregnated and 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. A similar result was obtained in the study conducted by [14]. Figure 2 shows the XRD plot of (left) control, CCA impregnated and GL:CL remediated samples. There are two important peaks in the XRD spectra of 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 impregnation with CCA, it decreased after remediation.

FTIR analysis was performed on test and 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 lignin, and the change in the crystalline and amorphous content of cellulose. The peaks of carbonyl and acetyl groups in xylan in scotch pine wood samples are seen at 1740 cm^{-1} . In the wood samples used in the present study, this peak was observed at 1710 cm^{-1} . Wood samples impregnated with CCA and remediated with GL:CL gave peaks similar to the control samples. $1630\text{--}1660\text{ cm}^{-1}$ band stated that it is associated with --C=O bound aryl ketones, unbound C=C and water band. The intensity of absorption at $1630\text{--}1660\text{ cm}^{-1}$ indicates paired $\alpha\text{-C=O}$ bonds with para-hydroxyphenyl groups. 1610 cm^{-1} peak indicates that it is associated with the unbound C=C and 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 water in carbohydrates after pretreatment, increases. Water absorption increases due to the increased hydroxyl group with the deformation of the H-O-H bond [15–17]. The peaks at $1595, 1510, 1470\text{ cm}^{-1}$ are associated with aromatic rings. The peak in

the 1595 cm^{-1} band is associated with an aromatic ring tension strongly correlated with the aromatic C-O tension state. The peaks in the range of 1506-1510 cm^{-1} are characteristic peaks for lignin components due to 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 wood samples 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 1230-1270 cm^{-1} peaks indicate the C=O tension in lignin. The decrease or disappearance of the peaks gap indicates delignification and degradation of aromatic rings [21,22].

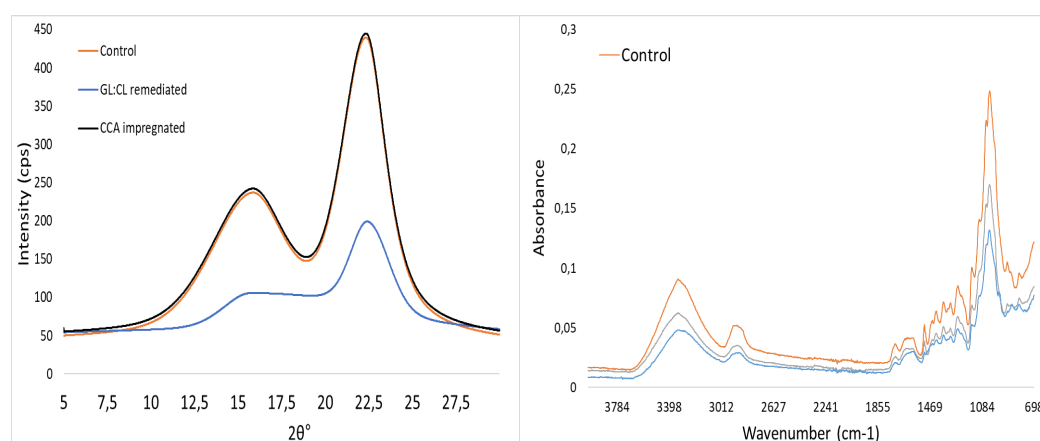


Figure 2. XRD (left) and FTIR (right) analysis results of test and control samples.

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 impregnated wood samples with GL:CL, low amounts of As, Cu, Cr were removed. Ace removal remained around 10%. Cr was removed at the rate of 30% and Cu at the rate of 65%. pH, wood type, retention level, chemicals, wood type, removal process, time, chemical concentration are the factors affecting Cu, Cr and As removal from wood. In the literature studies, 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 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 Scots pine wood samples. For this purpose, DES solutions were prepared in 1:1 mole ratios of glycerol and clone chloride. After the treatment of scotch pine wood samples 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 prepared with glycerol was ineffective in the remediation process. Changes in the chemical structures of wood samples 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 DES treatment. Many different chemicals are used in the remediation process. However, the fact that these chemicals used are harmful and cause environmental pollution, and that the chemicals used in green chemistry can also be used in the remediation process, it has been revealed with this project. By using different DES chemicals, which chemical is more effective in the remediation process should be revealed in future studies.

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