

Effect of Reusing Extraction Liquids from Microwave Extracted Spent CCA-Treated Wood and its Anti-fungal Activities

Xinan Zhang

Todd F. Shupe

Louisiana State University Agricultural Center
Baton Rouge, Louisiana

Chung Y. Hse

USDA Forest Service, Southern Research Station
Pineville, Louisiana

ABSTRACT

Acid extraction microwave treatment is a fast and effective method to remove copper (Cu), chromium (Cr), and arsenic (As) from CCA-treated waste wood. The extraction liquids contain these removed metals, but the concentration is low due to the washing and dilution process. In this study, preliminary research was done to investigate the effect of reusable extraction liquids. 2.75% phosphoric acid and 0.75% acetic acid were prepared and mixed at 50:50 proportions. 1 g of CCA-treated waste wood powder was then mixed with 20 ml of acid in each reaction vessel. After treatment, the extraction liquids were reused for the next cycle, the lost volume was made up with previously unreacted acid. The liquids were used for 12 cycles. The concentration of Cu, Cr, and As in the liquids of each cycle were determined by ICP. The wood residue after each extraction cycle was digested and the metal concentration in the solution was also tested by ICP. The anti-fungal function of the extraction liquid was investigated by a white rot fungi (*Trametes versicolor*) and a brown rot fungi (*Gloeophyllum trabeum*) in a Petris-dish based test.

INTRODUCTION

Chromated copper arsenate (CCA) is an inorganic waterborne wood preservative which has been widely used for approximately 70 years. In this preservative, copper (Cu) is an effective fungicide, arsenic (As) is both effective as an insecticide and fungicide, while chromium (Cr) is a fixing agent for these components (Kazi and Cooper, 2002). A wide range of wood products such as decks, fences, and other industrial products like poles, timbers, and marine piling are treated by CCA. Since January 1, 2004, the US and Canadian wood preservation industry voluntarily withdraw the use of CCA treated wood for residential uses.

Since CCA-treated wood has a relatively long service life, the amount of CCA-treated wood that will be removed from service should greatly expand. It has been estimated that CCA-treated wood being removed from service annually in the US and Canada would increase to 12 million m³ within the next 15 years (Copper 2003). Currently, American and Canadian environmental regulations allow the disposal of CCA-treated lumber in landfills, and most of the out-of-service treated wood ends up in landfills. Possible environmental contamination from treated wood is becoming an increasing public concern and how to manage used treated wood products coming out of service will be a concern for many years.

When CCA-treated wood is disposed of, the heavy metal should be separated from the waste wood in order to prevent the movement of toxins into the environment (Kakitani et al., 2006). CCA-treated wood can be decontaminated to a high degree by 10% aqueous hydrogen peroxide (H₂O₂). After a 50°C water bath for 6h, 95% Cr, 94% Cu, and 98% As were removed (Kazi and Cooper 2006). Kartal and Imamura (2005) found that exposing 3g of CCA-treated sawdust to a 200 ml solution containing 2.5 g chitin for 10 days removed 74% Cu, 62% Cr, and 63% As. Extraction of CCA-treated sawdust samples with 1% ethylenediaminetetracetic acid (EDTA) solution for 24 h resulted in 93% Cu, 36% Cr, and 38% As removal (Kartal 2003).

Clausen and Smith (1998) found that extraction with oxalic acid as a precursor to bacterial fermentation with *B. licheniformis* CC01 removed 90% Cu, 80% Cr, and 100% As from CCA-treated chips. Kazi and Cooper (2002) extracted CCA from sludge in three stages. In the first stage, after 2h of extraction-oxidation by 5.25% aqueous sodium hypochlorite at 100°C with a reagent:sludge ratio of 100:1, the total conversion was 51%. The remaining CCA salts were extracted by 2.5% phosphoric acid in the second stage and phosphoric acid leachate was oxidized by 5.25% aqueous sodium hypochlorite in the third stage. Treatment temperature has been found to be an important factor in acid extraction.

Chemical extraction has two benefits, the extracted CCA solution may be disposable or may be reused as a preservative, and the separated wood chips or wood power may be reused as a raw material for wood plastic composites or wood-based

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composites (Clausen et al., 2000; Munson and Kamden 1998; Li et al. 2004; Kamdem et al., 2004; Clausen et al., 2006), but this approach is limited because of environmental concerns in the manufacturing plant and possible cross contamination of untreated raw material.

Through the above literature, we could find that, for acid extraction of spent CCA-treated wood, treatment time and cost are the key points. The longest treatment time in previous efforts is 10 days, and some extraction requires multiple steps. If the treatment time can be reduced, it will be more industrial applicable. The acids are a major cost for the extraction. The total cost of the process will be reduced if the amount of chemical can be reduced. The concentration of Cu, Cr, and As is usually low in the high volume of extracted liquids, so reusing the process liquids will have financial benefits, and there is also an advantage that a smaller amount of soaking solution with a larger concentration of Cu, Cr, and As would be generated. This would make the handling of the liquids easier and the possible recovering of the metals more beneficial.

The objective of this study was to evaluate the possibility of reusing the process liquids to continue the acid extraction of heavy metals from CCA-treated wood. Microwave treatment was applied as a fast extraction method. Microwave energy can generate a condition of high temperature and relatively high pressure in a short time and could be a useful tool for metal extraction. The antifungal activities of recycled soaking solution against white-rot and brown-rot fungi were also investigated.

MATERIALS AND METHODS

Wood Particles Preparation

A decommissioned CCA-treated utility pole was obtained from a local utility company. The pole was initially cut into 2.4 m long sections and then into 2.5-cm thick lumber using a portable sawmill. After air-dried, the lumber was cut on a table saw into small pieces that were ground in a Wiley Mill. The wood particles which passed the 40-mesh sieve were collected for further microwave extraction.

Acid Extraction Through Microwave Treatment

Microwave treatment was used to enhance acid extraction of the treatment metals. Phosphoric acid and acetic acid were prepared at the concentration of 2.75% and 0.75% respectively, and then well mixed at 50:50 proportions as fresh acids. 1 g of CCA-treated waste wood particles were mixed with 20 ml of acid in a Teflon reaction vessel (3.8 cm in diameter and 9.8 cm in height). Each vessel was then sealed and placed in the microwave reactor (Milestone; Sheton, CT). The microwave treatment time was 20 min. and the reaction temperature was 145°C.

After treatment, the extraction liquids were vacuum-filtered through Whatman No.4 filter paper and collected for analysis and for reuse in the next cycle without any dilution. When the first cycle was complete, the volume of extraction liquid was measured and compared with the original volume of the previously unreacted acid. The lost volume was made up by the addition of previously unreacted acid, and then the liquid was reused in microwave treatment for the second cycle. This method was repeated for a total of twelve cycles.

Determination of Copper, Chromium and Arsenic Concentrations

After extraction, the wood residue from each cycle was rinsed with deionized (DI) water, oven dried, and then collected and digested according to American Wood Protection Standard A7-04 (AWPA 2010a). 1 g of wood residue and 15 ml nitric acid were mixed in a 100 ml test tube. After the initial reaction of brown fumes appeared, the test tubes were placed into an aluminum heating block and slowly warmed until the temperature reached 120 °C. The temperature was maintained until a transparent liquid was obtained, then the liquid was continually heated to a volume of 1 ml. The digestion liquid was transferred into a 25 ml volumetric flask and diluted into 25 ml solution with distilled water. Quantitative elemental analysis of copper, chromium, and arsenic was conducted according to American Wood Protection Association Standard A21-08 (AWPA 2010b). The extraction liquids of each cycle were also analyzed for CCA content by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

Evaluation of Antifungal Activities Against White-rot and Brown-rot Fungi

The antifungal activities were evaluated according to Gao et al. (2008) with slight modifications. The media was prepared by 2% malt extract, 1.5% agar and was sterilized for 15 min. A series of media with a Cu concentration ranging from 1.92 mg/L to 11.72 mg L⁻¹ were prepared.

White-rot fungi (*Trametes versicolor*) and brown-rot fungi (*Gloeophyllum trabeum*) were cultured from lab stock. White and brown rot fungus plugs from the edge of growing culture were transferred onto the center of the Petri dishes and incubated at room condition. The control Petri dishes only contain culture media. When the fungal mycelia reached the edges of the control Petri dishes, the diameters in all experimental dishes were recorded and the anti-fungal index (AI) expressed as % inhibition was calculated by equation 1 as follows,

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$$\% AI = \frac{D_2 - D_1}{D_1} \times 100\% \quad (1)$$

Where D_2 is the diameter growth in the control dishes and D_1 is diameter growth in the experimental Petri dishes with extraction liquids. The estimation of antifungal activities was carried out with 5 replications.

RESULTS AND DISCUSSION

Wood Extraction Recycling

The concentration of Cr, Cu, and As in each cycle of extraction solution was analyzed by ICP, and the results are shown in Figure 1. In cycle 1 solution, the concentration of Cr, Cu, and As were 120 mg L⁻¹, 121 mg L⁻¹ and 176 mg L⁻¹, respectively. Each extraction cycle resulted in the removal of the metals with different amounts. In cycle 2 extraction solution, the concentration of Cr, Cu, and As was 167 mg L⁻¹, 202 mg L⁻¹, and 292 mg L⁻¹, respectively. The increment concentration of Cr, Cu, and As between these two cycles was 47 mg L⁻¹, 81 mg L⁻¹, and 116 mg L⁻¹, respectively. The absolute concentration value of each metal component showed an incremental trend while the extraction cycles continue. After extraction cycle 12 was finished, the accumulated concentration of arsenic reached 930.78 mg L⁻¹. The pH of each extraction cycle solution was similar, the average pH value was 1.63 with a standard deviation of 0.05. This low pH of extraction solution showed the potential to continue removing metals from the wood particles. If the process were to continue after 12 cycles, the metal concentration in the extract cycle may still increase and it may have the potential to reach the same concentration with commercially used CCA solution (the diluted CCA which is ready for treatment).

Figure 2 shows the CCA recovery rate of each cycle. This recovery rate was calculated based on the CCA concentration in the wood particle residues after extraction. Of the CCA components, arsenic was most easily extracted with mixed acids in microwave treatment followed by copper, and chromium was the most resistant against extraction. In cycle 1 where fresh acids were applied, the As, Cr, and Cu extraction efficiencies were 95%, 51%, and 96%, respectively. These results revealed that acid extraction microwave treatment is a fast and effective method for CCA-removal.

Clausen (2004) investigated the effect of oxalic acid in multiple extractions and found that each extraction resulted in the removal of Cu, Cr, and As with equal efficiency. The extraction efficiency was different in reused extraction liquid. When the extraction liquid was reused in cycle 2, about 91% of As and 92% of Cu were removed, but the Cr extraction efficiency dropped to 31%. The recycling liquids showed a strong ability for As removal. Even in cycle 12, 81% of As was extracted from wood particles. The Cu recovery rate was above or around 90% in the first 4 cycles, but it dropped dramatically after cycle 8. The recovery rate of Cr decreased at the first 4 cycles, and fluctuated throughout the remaining cycles.

Antifungal Activities Against White-rot and Brown-rot Fungi

In order to check the possibility to reuse the extracted liquids as preservatives, the effectiveness of the extraction liquid was examined. Therefore, the antifungal activity of the extraction liquid from cycle 1 against white-rot and brown-rot fungi was investigated. Table 1 shows the daily growth rate of white rot and brown rot fungi on control and treated Petri dishes. (Note: the diameter of the inoculated fungi plug was 0.6 cm, so the diameter of fungal mycelia started at 0.6 cm). It took the white rot fungi 9 days to reach the edges of the control dishes. On the contrary, it took the brown rot fungi 19 days to reach the edges of the control dishes, which means the white rot fungi grew twice as fast than brown rot fungi in the control media.

Cycle 1 extraction liquid was used as treatment at different dilutions. Since copper is a known effective fungicide, the concentration of copper in the medium was applied to express the medium concentration here. A large clearance area in the Petri dish showed a strong inhibition ability to the extraction liquid. While the copper concentration increased, both white rot and brown rot fungal inhibition effects increased, but the efficiency was different (Figure 3).

At lower copper concentration, the daily growth rate of white rot fungi was faster than brown rot fungi. When the copper concentration reached 4.06 mg L⁻¹, the growth rate of the white rot fungi was similar with the brown rot fungi, both grew about 0.2 cm per day. For example, at day five, the diameter of both fungi was 1.2 cm. When copper concentration was even higher, the brown rot fungi grew faster than white rot fungi, which were contrary to the control results. This showed the extraction liquid has a stronger inhibition ability to white rot fungi than brown rot fungi. Lower pH was found to contribute more to copper tolerance (Green and Clausen, 2003). Although GT is a copper-sensitive brown rot fungus (Hastrup et al. 2005), the low pH of the extraction liquid may also introduce the lower inhibition of brown rot fungi as compared to white rot fungi at certain copper concentration.

There was a clear concentration dependency for AI (Figure 4). For white rot fungi, the AI became 100% when copper concentration reached 5.55 mg L⁻¹. At this concentration; the AI for brown rot fungi was 77%. The AI for brown rot fungi became 100% until the copper concentration was 7.3 mg L⁻¹. This concentration is markedly low for 100% AI, which means the recycled extraction is an effective fungicide based on the Petri dish test.

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CONCLUSIONS

CCA-treated wood can be decontaminated to a high degree by mixed acids at a temperature of 145°C and in a relatively short time of 20 min. A smaller amount of process liquid with a relatively high concentration of Cu, Cr, and As was obtained when the extraction acid was continually reused. The extraction efficiency was different when the extraction acid was reused. The recycling acid showed a strong ability for As removal. The Cu recovery rate showed a clear decrease after cycle 8. The recovery rate of Cr was relatively low compared with As and Cu. The AI was 100% when copper concentration was 5.55mg L⁻¹ for white rot fungi and 7.3 mg L⁻¹ for brown rot fungi. Both of these concentrations are substantially low, which means the recycled extraction is an effective fungicide based on the Petri dish test. In some previous acid extraction studies, the wood particles become damaged and transform into sludge after treatment. In this study, the wood particles still maintain their original configuration after the microwave treatment. This enhances the potential of this material to be re-used as raw material for other applications, such as medium-density particle board.

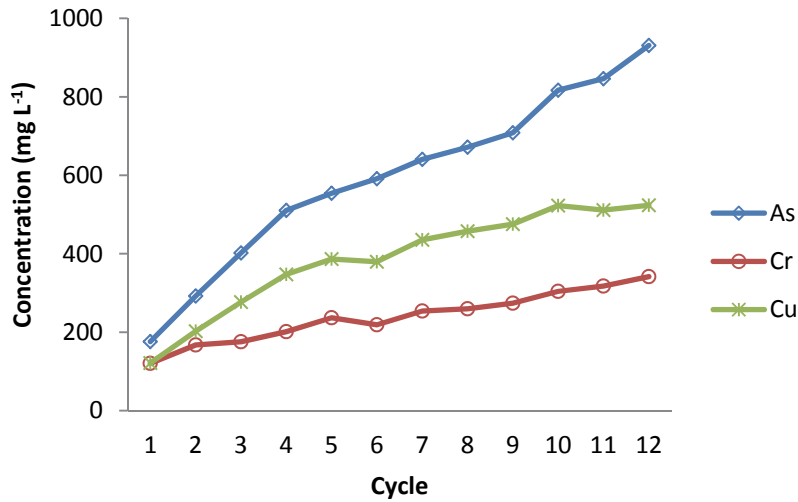


Figure 1: The cumulative concentration of Arsenic (As), Chromium (Cr), and Copper (Cu) in the extraction liquid of each cycle (unit: mg L⁻¹)

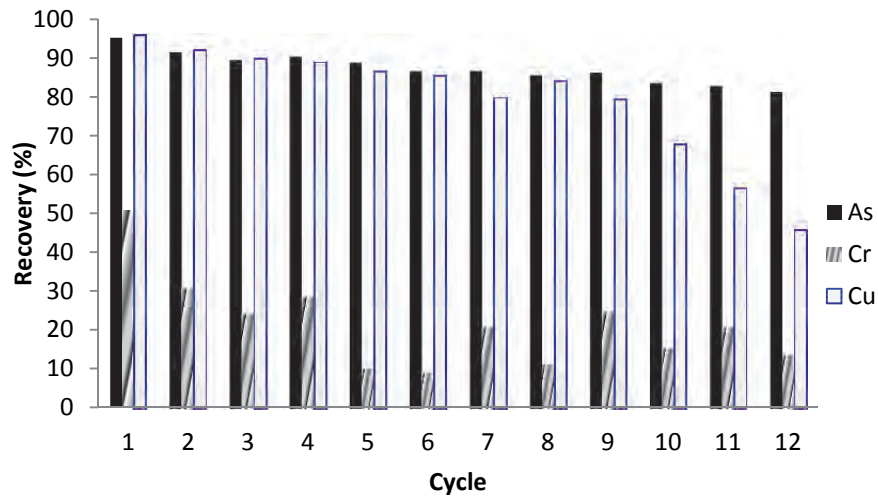


Figure 2: Percentage As, Cr, and Cu removed from spent CCA-treated wood particles through microwave treatment in each extraction cycle

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Table 1: The daily growth rate of fungi (a) white-rot fungi (*Trametes versicolor*), (b) brown-rot fungi (*Gloeophyllum trabeum*)

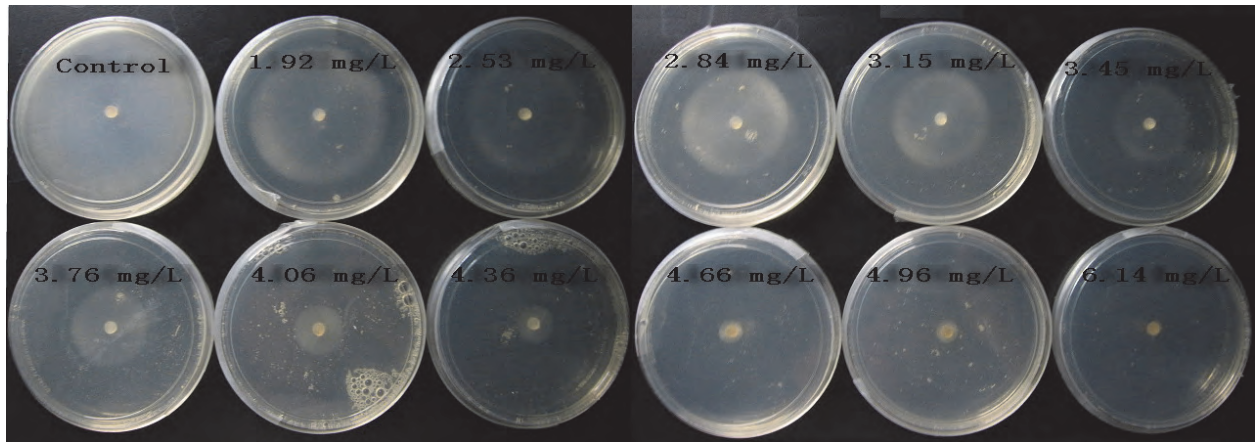
(a)

concentration (mg L ⁻¹)	day						
	2	3	4	5	7	8	9
control	1.65	2.45	3.50	4.50	6.60	7.55	8.70
1.92	1.10	1.80	2.50	3.20	4.70	5.65	6.30
2.53	1.00	1.70	2.20	2.80	4.10	4.80	5.40
2.84	0.95	1.50	1.90	2.50	3.70	4.40	5.00
3.15	0.95	1.40	1.80	2.40	3.45	4.00	4.50
3.45	0.80	1.20	1.55	2.00	2.95	3.45	3.80
3.76	0.65	1.05	1.45	1.90	2.65	3.20	3.60
4.06	-	0.81	1.00	1.20	1.70	2.00	2.20
4.36	-	0.50	0.70	0.90	1.30	1.50	1.65
4.66	-	-	-	0.65	0.85	1.00	1.10
4.96	-	-	-	-	0.80	0.90	0.98
5.55	-	-	-	-	-	-	0.00

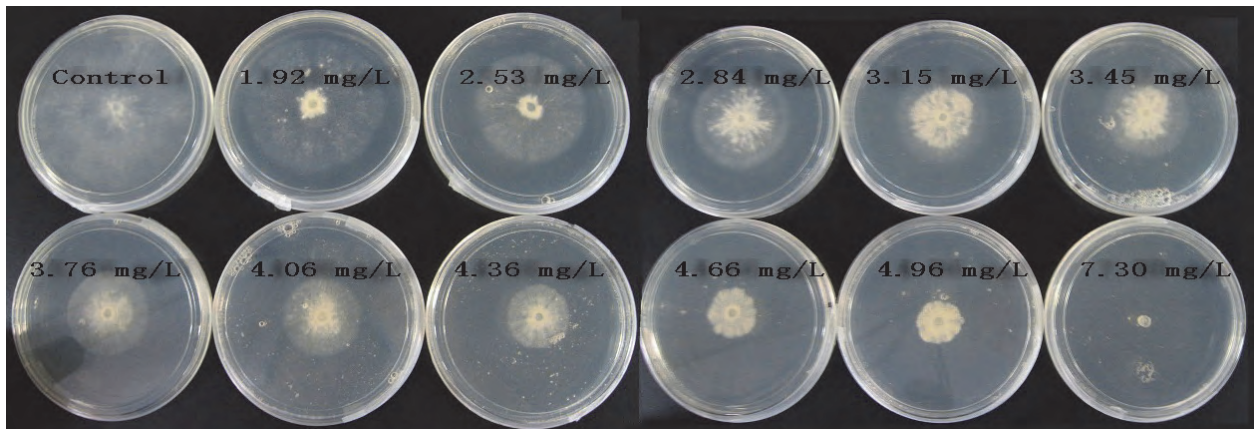
(b)

concentration (mg L ⁻¹)	day												
	2	3	4	5	7	8	9	10	12	14	16	18	19
control	1.25	1.90	2.60	3.35	3.85	4.35	4.90	5.30	6.15	6.90	7.55	8.35	8.70
1.92	0.88	1.25	1.70	2.05	2.85	3.25	3.60	3.95	4.65	5.10	5.65	6.00	6.25
2.53	0.75	1.05	1.30	1.68	2.20	2.50	2.80	3.10	3.65	4.00	4.55	4.80	5.05
2.84	0.73	1.00	1.30	1.60	2.10	2.45	2.70	3.00	3.45	3.90	4.40	4.70	4.85
3.15	0.65	0.90	1.10	1.40	1.90	2.20	2.40	2.70	3.10	3.60	4.00	4.25	4.55
3.45	0.70	0.90	1.10	1.40	1.80	2.10	2.30	2.60	2.95	3.30	3.70	3.95	4.15
3.76	0.55	0.70	0.90	1.00	1.55	1.75	1.95	2.10	2.45	2.85	3.30	3.50	3.75
4.06	-	0.80	1.00	1.20	1.60	1.75	1.95	2.10	2.45	2.75	3.10	3.30	3.45
4.36	-	0.60	0.80	0.95	1.20	1.40	1.50	1.75	2.00	2.25	2.50	2.70	2.80
4.66	-	-	0.70	0.80	1.00	1.20	1.30	1.40	1.70	1.90	2.05	2.20	2.35
4.96	-	-	0.60	0.80	1.00	1.15	1.30	1.40	1.60	1.80	2.00	2.10	2.30
5.55	-	-	-	0.65	0.80	0.90	1.00	1.10	1.30	1.50	1.75	1.90	2.00
6.14	-	-	-	-	0.65	0.75	0.85	0.95	1.15	1.40	1.60	1.80	1.90
7.3	-	-	-	-	-	-	-	-	-	-	-	-	0.00

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(a)



(b)

Figure 3: Antifungal effects of cycle 1 extraction liquid from different copper concentrations (a) white-rot fungi (*Trametes versicolor*), (b) brown-rot fungi (*Gloeophyllum trabeum*)

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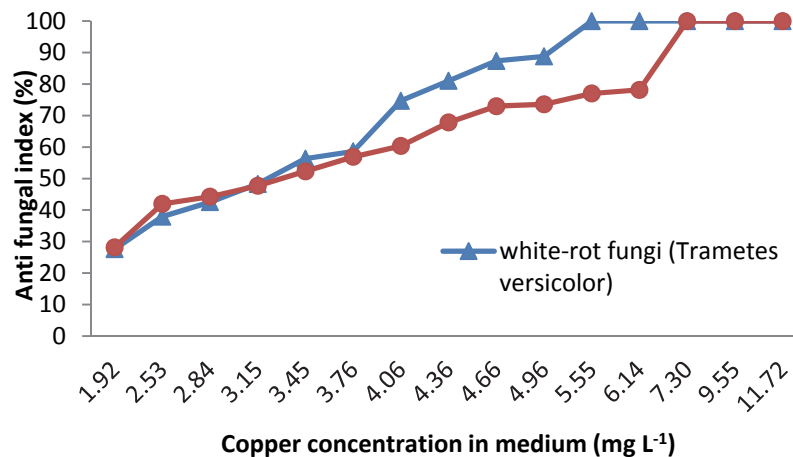


Figure 4: Plot of antifungal index (AI) versus copper concentration

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