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2 authors:

Dedi Nursyamsi
Indonesian Agency for Agricultural Research and Development

Husnain Husnain
Indonesian Agency for Agricultural Research and Development

WFL Publisher
Science and Technology
Meri-Rastilantie 3 B, FI-00980
Helsinki, Finland
e-mail: info@world-food.net

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Accumulation of heavy metals in rice grown in soil irrigated with electroplating industry wastewater treated with coagulants and adsorbents

Dedi Nursyamsi and Husnain Husnain *

Indonesian Agency for Agricultural Research and Development (IAARD), Jl. Tentara Pelajar No. 12, Bogor 16114, Indonesia.
**e-mail: husnain.isri@gmail.com, ddnursyamsi@yahoo.com*

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Abstract

Effectiveness of treating wastewater from electroplating industry with coagulants and adsorbents to remove heavy metals was studied by monitoring heavy metal accumulation in rice grown in soil irrigated with treated wastewater. Chitosan, a nontoxic and degradable biopolymer which can be used in wastewater treatment and activated *Azolla* were the two coagulants. Activated peanut shells and tea waste were used as adsorbents. All possible combinations of treating wastewater with coagulants and adsorbents including no treatment were used before irrigating rice with the treated water. Rice was grown in pots containing 10 kg of 2 mm air dried soil. The soil was collected from Dampyak Subdistrict, Central Java. Fertilizer was applied as much as 300 mg kg^{-1} nitrogen, 200 mg kg^{-1} phosphorus and 100 mg kg^{-1} potassium. The results showed that grain and straw yield of rice increased with all combinations of treating or not treating the wastewater with coagulants and adsorbents. Treating the electroplating wastewater with the two adsorbents and two coagulants reduced the accumulation of heavy metals in both the soil and the rice plant tissue. Treatment with either coagulant, alone or in combination with either adsorbent, reduced the soil Ni and Cu concentrations. Treatment with adsorbent alone reduced the soil Zn concentration. In case of rice, treating the wastewater with any adsorbent or coagulant, alone or in combination, significantly reduced the Cu concentration, whereas treatment only with tea waste was able to reduce the Cr concentration as compared to use of untreated waste water for irrigation.

Key words: Adsorbent, coagulant, electroplating wastewater, heavy metals, rice, soil, wastewater treatment.

Introduction

Electroplating is a major industry in Central Java where electroplating industries contributed about 26.79% to the total Indonesian GDP in 2008 [1]. Wastewater from electroplating industry, however, contain substantial amounts of heavy metals. When these wastewaters are used as irrigation of crops in nearby agricultural lands, soil, water and vegetation can suffer from heavy metal accumulation. Wastewaters from electroplating industry contain substantial amounts of heavy metals. Heavy metal contamination of agricultural lands due to industrial activities is a well known pollution hazard. Metals of concern include cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), iron (Fe), zinc (Zn) and manganese (Mn). Liu *et al.* [2] stated that in particular, plants can easily take up and translocate Cd throughout the plant body, including to parts consumed by humans. Concentrations of heavy metals in plant tissue depend on the contaminant source, duration of environmental release and transport mechanisms after release. Kumar *et al.* [3] reported that soils in Tirupati, India, contained 19.5–23.6 mg kg^{-1} Zn, 0.032–0.036 mg kg^{-1} Cd, 15.8–18.9 mg kg^{-1} Pb and 19.0–23.4 mg kg^{-1} Cu. Concentrations for all of these metals were above the tolerance levels in India. Soil collected in Northern Addis Ababa, Ethiopia, was reported to contain 269 mg kg^{-1} Cr by Alemayehu [4]. Similarly, Cd and Cu pollution due to industrial activity has been reported at locations in the state of Ohio as mentioned by Kuzovkina *et al.* [5]. Dong *et al.* [6] pointed out that in China, Cr pollution was reported as a result of industrial activity, chemical fertilizer use and waste disposal, resulting in significant adverse impacts to farmland. In Canada, heavy metal pollution was reported to be primarily caused by metal and textile factories and wood coatings as described by Bluskov *et al.* [7]. Levels of Zn and Pb could be as high as 310 and 490 mg kg^{-1}, respectively, well above Canadian national standards as concluded by Saint-Laurent *et al.* [8]. Several previous studies have focused on heavy metal contamination as a result of industrial waste in Central Java, particularly in areas where the electroplating industry has been expanding. It was reported that pollution in Tegal Regency, with Cr concentrations as high as 2.55 mg kg^{-1} (quality standard of 0.5 mg kg^{-1}) in irrigation water and 140 mg kg^{-1} (quality standard of 75–100 mg kg^{-1}) in soil as mentioned by Artanti *et al.* [9a]. Artanti *et al.* [9b] showed that in Purbalingga, Central Java Province, Cr was found at 116 mg kg^{-1} in the soil. In Pati area, heavy metal contamination in rice fields was identified, with unacceptable levels of Co found in 2,100 ha (76%), Cr in 595 ha (21%), Mn in 297 ha (10%) and Ni in 131 ha (4%) as reported by Mulyadi *et al.* [10]. Number in percentage in parenthesis refer to total rice fields at Pati area. Although high levels of metals were found in irrigation water and soil, field observations of rice plant tissue concentrations showed substantial variability.

Industrial waste containing heavy metals must be treated to reduce the metal concentrations before recycling. Alternatively, or in parallel with wastewater treatment, certain remediation methods can be used to reduce environmental concentrations and to mitigate the levels of risk. Chemical processes have been widely applied for the treatment of surface wastewaters. Chemical treatment to remove heavy metals includes several steps such as coagulation, coprecipitation and entrapment [11-14]. Sweep coprecipitation by coagulants is a major mechanism that is utilized in current remediation processes. This process results in the formation of metal hydroxides and carbonate [15-18]. By using coagulants such as salts of Fe, Al and Ca, the heavy metal ions in groundwater can be immobilized as insoluble precipitates or captured and removed as floc particles [19-23].

Small-scale electroplating industries in Central Java do not have economic resources, space or engineering capabilities to implement strategies that can reduce heavy metal load of the effluents. We have therefore attempted to study an inexpensive and easily implementable strategy for treating electroplating wastewater. Chitosan and *Azolla* can be used as natural coagulants while tea waste and peanut shells can act as adsorbent materials. Those materials were applied to reduce heavy metals toxicity in snd electroplating industrial waste.These materials are inexpensive and easily available to farmers but there are very limited information of their efficiency to knock out heavy metals.

Therefore, the objective of the present study was to evaluate the efficiency chitosan and *Azolla* as coagulant and tea waste and peanut shells as adsorbent materials for treating electroplating wastewater to remove heavy metals and to study reduction in heavy metal enrichment of soil and rice when treated waters are used for irrigation purposes. The natural adsorbents, coagulants and treatment procedures that were utilized in this study were selected on the basis of the results of a previous study carried out by Nursyamsi *et al.* [24].

Materials and Methods

Preparing coagulant and adsorbent materials: Coagulant and adsorbent materials were prepared in the laboratory at Indonesian Agricultural Environmental Research Institute (IAERI). Two types of coagulants, chitosan and *Azolla* were prepared. Chitosan was made from shrimp skeleton material obtained from a traditional market in Pati Regency. The procedures in preparing chitosan were as described in previous reports [25-28]. *Azolla pinnata* (family Salviniaceae) was collected from an experimental farm at IAERI. Two types of adsorbents, tea waste and peanut shells were prepared. Tea waste was collected from a tea bottle factory in Klaten, Central Java Province, whereas peanut shells were obtained from a traditional market in Jakenan, Central Java Province. Chitosan and *Azolla* were chemically activated by drying at 50°C and keep in the HNO_3 0.1 M solutions for 8 hours [29]. Tea waste and peanut shells were activated by mixing with 0.6 M citric acid at 90°C for 90 min as decribed by Marshall *et al.* [30]. Before application, activated coagulant and adsorbant were air dried, ground and passed through 2 mm sieve.

Collection and treatment of electroplating industry waste water: Waste water was obtained directly from an outlet of the wastewater treatment plant and collected at 7:00 AM and 5:00 PM. The water, which had a clear, light, hazy blue appearance, was placed in a sedimentation tank for approximately 1 week, for preliminary sedimentation of suspended solids. Waste water was treated by coagulant and adsorbent materials before it was used to irrigate plants. 0.5 g/L of adsorbent and coagulant were applied into 1000 ml beaker contained waste water. The beakers were placed in jar test and centrifuged at 200 rpm for 2 min and continued for 20 rpm for 10 min. The solution was kept for 30 min before filtration. The samples were was analysed for heavy metal contents.

Pot experiment and observation: A greenhouse experiment was conducted at IAERI. The pots were filled with an Inceptisol soil collected in bulk from 0 to 20 cm depth of a rice field in Dampyak, Central Java Province. The soil samples were obtained using a clean, uncontaminated soil auger. Soil samples were placed in plastic bags for transport to the laboratory. Samples were air dried, ground and passed through a 2-mm sieve. Each pot was filled with 10 kg soil.

A completely randomized design with three replications was used to conduct the pot experiment. The two experimental treatment factors were waste water treated with (A) Coagulant and (B) Adsorbent. Each factor was tested at three levels. Factor A included the control (untreated waste water; K0), chitosan (K1) and *Azolla* (K2) and Factor B included the control (A0), activated peanut shell (A1) and tea waste (A2). The rice variety used in this experiment was Ciherang.

Soils in the pots (except the control pots) were inundated with water containing both coagulant and adsorbent materials. The pots were incubated for 1 week before the rice was transplanted. During incubation, the water level was maintained at a depth of 2 to 3 cm by adding waste water every 2 days. To facilitate plant growth, approximately 300 mg kg^{-1} N, 200 mg kg^{-1} P and 100 mg kg^{-1} K, in the forms of urea, SP-36 (super phosphate contained 36% P_2O_5) and KCl, respectively, were applied to each pot after incubation. Before planting, the soil was mixed thoroughly to distribute the fertilizer in the pots, which were left undisturbed for 1 day. Rice seedlings were prepared in a batch. Three 20-day-old seedlings were transplanted into each pot. After 1 week, one plant was removed from each pot, leaving two plants to grow for the remainder of the study. The water level was maintained at a depth of 2 to 3 cm during rice growth. Two weeks before harvest, the soil was allowed to dry. Mature seeds were harvested by cutting the rice straw about 2 cm above the soil surface.

Agronomic measurements for this study were plant height (measured from ground level to the tip of the highest leaf), number of productive tillers (determined immediately before harvest) and the dry weights of rice straw and rice grain. The dry weight of the filled grain was obtained by drying the plant material in a 70°C oven until a constant weight was reached.

Laboratory analyses: Before and after treatment, soil samples were air dried, crushed and passed through a 2-mm sieve. Soil pH was measured by the glass electrode method with a soil: water ratio of 1:2.5 [31, 32]. The organic C concentration was determined by the Kurmies procedure [33]. Concentrations of Cr, Ni, Cu and Zn in soil were determined by atomic absorption spectrometry (AAS; AA240FS Varian Type). Soil particle analyses were carried out using pipette method. Exchangeable cations, K, Na, Ca and Mg, were extracted with 1 M NH_4OAc at pH 7. Rice grain samples were grinded to a powder with a tungsten carbide vibrating mixer mill and digested with triple acid mixture of H_2SO_4, HNO_3 and $HClO_4$ [34]. Heavy metal concentrations in rice grain were determined by AAS (AA240FS Varian Type).

Statistical analysis: Statistical analyses were performed using SPSS 16 (SPSS Inc, USA; www.spss.com). Statistically significant differences among treatments were analyzed using ANOVA and least significant difference (LSD) calculation at a 5% significance level (P = 0.05).

Results and Discussion

Soil characteristics: The soil used in the experiment was a slightly alkaline sandy clay loam with a high organic matter content and cation exchange capacity (Table 1). Concentrations of Cr, Ni, Cu and Zn in the soil were relatively low.

Table 1. Initial analysis of rice field surface soil (0–20 cm) taken from Dampyak Subdistrict, Tegal District, Central Java Province.

Soil characteristics (unit)	Value	Note
Texture (%)		
Sand	50	Sandy clay loam
Silt	26	
Clay	24	
pH (water extract)	7.4	Slightly alkaline*
Organic matter (Kurmies)		
Org.-C (%)	3.42	High*
CEC (cmol(+)kg^{-1})	25.99	High*
Heavy metals (mg kg^{-1})		
Cr	10.16	Normal**
Ni	17.94	Normal
Cu	24.49	Normal
Zn	42.61	Normal

*Criteria given in IAARD (2012) [35] and **Alloway (1995) [36].

Pot experiment

Plant growth: Table 2 presents the plant height and number of tillers for rice which was irrigated with electroplating waste water treated with chitosan and *Azolla* as coagulant materials and with peanut shells and tea waste as adsorbent materials. Plant height and tiller number were not significantly altered by irrigation with waste water that had been treated with any coagulant or adsorbent materials. Nursyamsi *et al.* [24] proposed that the concentration of heavy metals in the electroplating waste water that showed no significant effects on plant growth were 2.01 mg kg^{-1} Cr, 1.61 mg kg^{-1} Ni, 1.05 mg kg^{-1} Cu and 3.65 mg kg^{-1} Zn.

Table 2. Rice plant height and number of tillers (before harvest) after irrigation with untreated (K0A0) and treated electroplating wastewater.

Code	Treatment		Plant height (cm)*	Number of tillers
	Coagulant	Adsorbent		
K0A0	-	-	106 a	17 ns**
K1A0	Chitosan	-	100 b	16 ns
K2A0	*Azolla*	-	103 ab	16 ns
K0A1	-	Peanut shells	103 ab	16 ns
K0A2	-	Tea waste	102 ab	17 ns
K1A1	Chitosan	Peanut shells	103 ab	15 ns
K1A2	Chitosan	Tea waste	105 ab	15 ns
K2A1	*Azolla*	Peanut shells	102 ab	16 ns
K2A2	*Azolla*	Tea waste	103 ab	16 ns
CV (%)			2.81	14.66

* Plant heights with the same letter are not significantly different. **ns = not significantly different.

Mahmood *et al.* [37] found that very high concentrations of heavy metals can lead to phytotoxicity which negatively affects plant growth, inhibits seed germination and adversely impacts crop yield. Liu *et al.* [2] believed that cadmium toxicity can inhibit root growth in rice, resulting in decreased biomass and yield. However, the presence of some heavy metals such as Cu and Zn at very low concentrations in the soil may prove beneficial to plants. Copper is an integral component of active enzymes in lignification and Zn is a non-redox micronutrient [40]. Presence of some nonessential elements may even suppress microbial pathogens. For example, the presence of Si and Al in the roots of upland rice might increase resistance to blast disease as concluded by Bakhtiar *et al.* [38]. Although in the present study plant growth was not significantly influenced by heavy metals in the treated or untreated electroplating waste water used as irrigation water, this assessment does not include a food chain analysis of the potential impacts to consumers through food ingestion. Rice straw, for example, is often eaten by livestock and rice grain is a key foodstuff for humans and other animals [39]. Moreover, because heavy metals are adsorbed by soil colloids, they will remain persistent, albeit mostly immobile, in the soil matrix [36]. Once a contaminant (heavy metal) is associated with soil organic matter or inorganic material through complexation, or even trapped between the internal layers of some silicate clays or humus, they pose minimal environmental risk because their bioavailability is substantially reduced [40].

Grain and straw yield of rice: Treating the electroplating industry waste before using as irrigation water with different combinations of coagulants and adsorbents resulted in significant increases in the dry weights of rice straw (i.e., *Azolla*, chitosan + peanut shells, or *Azolla* + tea waste). The most efficacious treatments increasing yield were *Azolla* + tea waste and chitosan + tea waste for the total rice grain yields (Table 3).

Although treating the irrigation water with coagulants and adsorbents did not significantly affect the plant height or number of tillers before harvest (Table 2), this treatment significantly increased the dry weights of rice straw and husked rice. Nursyamsi *et al.* [24] indicated that coagulants (chitosan and *Azolla*), adsorbents (peanut shells and tea waste) and combinations of both materials effectively reduced the concentrations of Cr, Ni, Cu and Zn in electroplating waste water (>40% effectiveness). Declining levels of heavy metals in the waste water resulted in higher crop yields.

Table 3. Dry weight of rice straw and husked rice from rice plants after irrigation with untreated (K0A0) and treated electroplating waste water.

Code	Treatment		Straw	Husked rice
	Coagulant	Adsorbent	g pot^{-1*}	
K0A0	-	-	68.40 b	72.60 b
K1A0	Chitosan	-	68.60 b	72.20 b
K2A0	*Azolla*	-	76.70 a	81.19 ab
K0A1	-	Peanut shells	74.57 ab	81.46 ab
K0A2	-	Tea waste	75.00 ab	85.90 a
K1A1	Chitosan	Peanut shells	78.70 a	72.88 b
K1A2	Chitosan	Tea waste	67.67 b	86.74 a
K2A1	*Azolla*	Peanut shells	65.10 b	69.02 b
K2A2	*Azolla*	Tea waste	79.45 a	81.85 ab
CV (%)			12.45	12.62

*Dry weights in the same category with the same letter are not significantly different among treatment groups.

Heavy metal accumulation in the soil: The concentrations of different heavy metals in the soil before irrigating with treated waste water were 10.16 mg kg^{-1} Cr, 17.94 mg kg^{-1} Ni, 24.49 mg kg^{-1} Cu and 42.61 mg kg^{-1} Zn (Table 1). The critical levels of heavy metals in soil are 75–100 mg kg^{-1} Cr, 60–125 mg kg^{-1} Cu and 70–400 mg kg^{-1} Zn [36]. A critical soil level for Ni has not been established. Thus concentrations of heavy metals in the tested soil were lower than the critical levels.

Treatment of the waste water with coagulant and adsorbent before applying as irrigation water to rice resulted in had varying degrees of success in reducing metal concentrations in soil (Table 4). None of the treatments significantly affected the soil Cr concentration. Treatment of irrigation water with either coagulant (chitosan or *Azolla*), alone or in combination with either adsorbent (peanut shells or tea waste), significantly reduced the soil concentrations of Ni and Cu (with the exception of chitosan alone which did not alter the Cu level). Treating waste water with peanut shells, tea waste or *Azolla*+tea waste significantly reduced the soil Zn concentration. The most efficacious of the tested treatments for irrigation water to reduce the soil metal concentrations were chitosan + tea waste for reducing Ni, *Azolla* + tea waste for reducing Cu and peanut shells for reducing Zn. Coagulants (chitosan and *Azolla*) and adsorbents (peanut shells and waste tea) effectively lowered the soil concentrations of Ni, Cu and Zn as concluded by Nursyamsi *et al.* [24]. The concentrations of heavy metals in the soil irrigated with industrial effluent-polluted water were 0.10 mg kg^{-1} Ni, 1.4 mg kg^{-1} Cu and 1.8 mg kg^{-1} Zn as reported by Mehdi *et al.* [41]. The concentration of heavy metals in soils depends on the particular activity occurring on the land as well as the schedule and process of waste disposal. According to Abbas *et al.* [42], the concentrations of Zn, Cu, Fe and Mn in soil receiving metal-contaminated irrigation water were higher after harvest than before transplanting, a result that is related to the disposal cycle of the waste. The correlation between increased heavy metal concentrations in soil and in waste water was reported by Al-Lahham *et al.* [43]. Heavy metals in soil can be taken up by plant roots and transported to food tissues (fruit, seeds, leaves), making the metals available through the ingestion route to humans. Huang *et al.* [44] pointed out that heavy metals in the soil may affect the uptake of heavy metals by rice plants. Rice grown in Cu, Cd and Pb-contaminated soils had higher levels of those metals in plant roots and shoots than rice grown in uncontaminated soil.

Table 4. Soil concentrations of Cr, Ni, Cu and Zn after irrigation with untreated (K0A0) and treated electroplating wastewater.

Code	Treatment		Cr	Ni	Cu	Zn
	Coagulant	Adsorbent				
			.... mg kg^{-1}*			
K0A0	-	-	28.82 ns	26.01 a	19.42 a	121.72 a
K1A0	Chitosan	-	26.97 ns	22.81 bc	19.19 a	106.45 ab
K2A0	*Azolla*	-	25.45 ns	22.54 bc	14.56 b	112.75 ab
K0A1	-	Peanut shells	21.30 ns	24.23 ab	18.04 a	81.91 b
K0A2	-	Tea waste	23.14 ns	23.73 abc	17.81 a	89.80 b
K1A1	Chitosan	Peanut shells	22.89 ns	22.55 bc	15.10 b	109.51 ab
K1A2	Chitosan	Tea waste	28.78 ns	20.99 c	15.52 b	105.79 ab
K2A1	*Azolla*	Peanut shells	27.49 ns	22.91 bc	14.63 b	113.22 ab
K2A2	*Azolla*	Tea waste	24.44 ns	21.87 bc	14.23 b	120.67 a
CV (%)			17.34	6.86	8.00	18.02

*Concentrations with the same letter are not significantly different. ns = not significantly different.

Heavy metals in rice: Concentrations of heavy metals in the husked rice irrigated with untreated waste water (control) were 1.22 mg kg^{-1} Cr, 9.18 mg kg^{-1} Ni, 4.76 mg kg^{-1} Cu and 36.73 mg kg^{-1} Zn (Table 5). The critical threshold levels of heavy metals in husked rice are as follows: 10 mg kg^{-1} Cu, 40 mg kg^{-1} Zn, 1 mg kg^{-1} Pb, 0.4 mg kg^{-1} Cd, 0.5 mg kg^{-1} As dan 0.05 mg kg^{-1} Hg [45,46]. Critical levels for Cr and Ni have not been established. The Cu and Zn concentrations in husked rice found in this study were lower than the critical levels. Although critical levels for Cr and Ni have not been reported, the concentrations of these two elements exceeded the critical levels of Pb and Cd. An important difference between these two groups of metals is that the former are more mobile in soil and plants than the latter, making Cr and Ni more likely to migrate to edible plant parts and posing a potentially greater health risk through ingestion.

The concentrations of 0.98 mg kg^{-1} Cr and 0.74 mg kg^{-1} Ni in husked rice harvested from fields contaminated with heavy metals was reported by Cheng *et al.* [47]. These concentrations are lower than those found in the current investigation. Abbas *et al.* [42] found that heavy metal concentrations range of 1.16–1.19 mg kg^{-1} Ni, 18.00–19.50 mg kg^{-1} Cu and 27.75–30.00 mg kg^{-1} Zn in husked rice from fields irrigated with water that was contaminated by industrial waste water.

None of the treatments caused a significant decrease in the concentrations of Ni and Zn in husked rice (Table 5). Waste water treated with tea waste significantly reduced the concentration of Cr in husked rice. Treatment with coagulants (chitosan and *Azolla*) and adsorbents (peanut shells and tea waste) as well as combinations of each group, significantly decreased the Cu level in husked rice. Treating irrigation water with tea waste or with chitosan + peanut shells was the best alternative for reducing the Cr or Cu concentration, respectively, in husked rice. Similar results were reported by Nursyamsi *et al.* [24], who found that coagulants (chitosan and *Azolla*) and adsorbents (tea waste) effectively reduced the concentrations of Cr and Cu in soil and electroplating wastewater, thereby reducing heavy metal uptake by plants.

Table 5. Husked rice concentrations of Cr, Ni, Cu and Zn after irrigation with untreated (K0A0) and treated electroplating wastewater.

Code	Treatment		Cr	Ni	Cu	Zn
	Coagulant	Adsorbent				
			.... mg kg^{-1}*			
K0A0	-	-	1.22 a	9.18 ns	4.76 a	36.73 ns
K1A0	Chitosan	-	1.17 a	9.24 ns	3.38 b	33.93 ns
K2A0	*Azolla*	-	1.05 a	9.70 ns	3.79 b	33.42 ns
K0A1	-	Peanut shells	1.06 a	9.14 ns	3.78 b	35.52 ns
K0A2	-	Tea waste	0.98 b	9.20 ns	3.73 b	24.42 ns
K1A1	Chitosan	Peanut shells	1.17 a	9.65 ns	2.98 b	35.27 ns
K1A2	Chitosan	Tea waste	1.07 a	9.42 ns	3.26 b	34.55 ns
K2A1	*Azolla*	Peanut shells	1.19 a	9.60 ns	3.51 b	31.63 ns
K2A2	*Azolla*	Tea waste	1.08 a	9.68 ns	4.70 a	35.27 ns
CV (%)			9.87	17.9	12.07	21.96

*Concentrations with the same letter are not significantly different. ns = not significantly different.

Conclusions

Accumulation of heavy metals in soil and plant could harm environment, animal and human dietary. Treating waste water is usually very costly. Utilization of natural coagulant and adsorbent is an alternative method in treating waste water. Natural coagulant and adsorbent such as peanut shells and tea waste has potential effect to reduce heavy metal content in electroplating waste water. Treating waste water with either coagulant (chitosan and *Azolla*) alone or in combination with either adsorbent (tea waste and peanut shell) significantly decreased the concentrations of Cr, Ni, Cu and Zn in the soil.

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