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EDTA UTILIZATION FOR REDUCTION OF TRANSITION METAL CONTENT ON BOILER ASH FROM PULP AND PAPER MILL WASTE

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ABSTRACT
EDTA has been used as an effective chelating agent and capable to catch transition metal that improves pulp mill process efficiency such as in peroxide bleaching. In this study, we extend the use of EDTA to extract transition metal of boiler ash from pulp and paper mill waste. The extraction system by using EDTA as collectors combined with organic solvent including dichloromethane, ethanol and n-hexane as media is investigated to reduce transition metal from the boiler ash. It is shown that the use of EDTA as collector and dichloromethane, ethanol, and n-hexane as media have a strong effect on the transition metal extraction. The reduction of transition metal using EDTA as a collector ranged from 50 - 85%, 48 - 87%, 54 - 89%, 46 - 84%, 50 - 89%, 98 - 99%, 92 - 97%, for Cd, Co, Cr, Cu, Fe, Ni and Zn respectively. All three solvents compatible with EDTA in reducing transition metal content, however, ethanol has a higher ability to lowering transition metal content among the solvents. There is a clear trend that the reduction of all transition metal content increase as the EDTA dosage used increased.
Keywords: EDTA, Collector, Transition Metal, Boiler Ash, Mill Waste, Extraction.

INTRODUCTION

Globally the world consumption of pulp and paper-based products has climbed steadily each year and expected to grow from 400 million tons to 500 million tons by 2020. As a result, the pulp and paper industries are growing as one of the largest industries in the world.[1] In the case of Indonesian, the pulp and paper production capacity is increasing from about 8 million tons per year to 10.5 million tons and lead this industry plays an important role in the Indonesia economy. Millions of employment both direct and indirect workers created and in 2017 this industry contributed to about 7% of the Indonesian processing industry's gross domestic product.

The pulp and paper industry generates significant wastewater and solid mill waste. The management of pulp and paper mill wastes in an economically and environmentally acceptable manner is very important and challenging as waste disposal requires large open space, must complying with more restrictive and environmentally friendly legislation, and require higher cost as an increase of cost and taxes. Seventy-seven percent of solid mill wastes are in the form of boiler ash, 20 % are in the form of dregs and grits, while the other 3% is in the form of sludge, lime mud and screen reject.[2] Most of these solid wastes are placed in landfills as a final destination. Research has shown that solid waste placed at landfills may present some hazardous elements that lead to some environmental issues such as contamination of soil, groundwater or aquifers as solid waste may have high organic content, pathogens, ash, and transition metal[3]. Research to find better solid mill waste management instead of landfills is one of the critical issues faced by the pulp and paper industries that need to be further and continuously investigated. Some research has been subjected to solid mill wastes such as dregs used in construction[4] and agriculture as soil amendments[5,6] and lime mud beside used in agriculture[5,7], it was also used in environmental technology[8,9],

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mainly in wastewater treatment.[10] Grits and pulp mill sludge are used in construction[11-14] and further pulp mill sludge also used in agriculture,[15,16] and energy processes.[17,18]

In this current research, considering boiler ash is the highest proportion of solid mill waste produced, the disposal of boiler ash through land application becomes our main focus. Some studies on boiler ash application highlighted the ability of boiler ash to increase soil alkalinity by increasing the soil pH[19,20], improving soil quality including nourishing, conditioning, and buffering of the soil that results in improving plant growth and yield.[21-24] As boiler ash may contain some toxic metals such as chromium (Cr), cobalt (Co), cuprum (Cu) and cadmium (Cd), especially those from coal combustion contain more transition metals content compared to boiler ash from wood-fired power boiler[25] and these transition metal will be absorbed by plant and bio-accumulate in plant tissue, soil and the environment when used directly as land application, then it is very important to find methods and technology to reduce transition metal content in boiler ash to allowable level to be used for land application.

Reducing transition metal content in boiler ash using some alternative techniques has been investigated through several studies including absorption through biopolymers[26], with ligands and supercritical carbon dioxide[27], sequential extraction[28], and some studies suggest converting the transition metal into complex compounds with organonitrogen or amine compounds.[29-32] In this study, we explore the use of ethylene diamine tetraacetic acid (EDTA) to extract transition metal from boiler ash of pulp and paper. The amino polycarboxylates such as EDTA is one of the most commonly used chelating agents in pulp and paper industry to improve process efficiency such as in peroxide bleaching to remove metal ions that promote the formation of hydroxyl radical (OH•) which destroys the cellulose fiber and decompose and degrade the peroxide as the bleaching agents[33-35] and as of today EDTA is one of the chelators for modern bleaching technology. EDTA and sodium thiosulfate as a chelant agent has also been used to remove some metal in freshwater and sea water[36]. Among the extraction solvents, dichloromethane (DCM), ethanol (ET), and n-hexane (NH) are used. DCM is an organochloride compound, which is one of the common solvents in organic synthesis that can coordinate with metal ions[37]. DCM can react with amines in the formation of alkylated products[38]. Ethanol is a very polar organic solvent widely used in synthetic chemistry as it has many sources and simple to prepare. Ethanol is used as the alkylating agent to react with various amines.[39] NH is a solvent obtained from petroleum sources and used for oil extraction. NH able to extract oil higher than other solvents such as petroleum ether and ethyl acetate, in this case oil recovery is higher when using NH as the solvent. NH has a boiling point at a temperature of 63–69°C and good solubilizing ability.[40,41]

In this current research, we focus to reduce transition metal content including Cd, Co, Cr, Cu, ferrum (Fe), nickel (Ni) and zinc (Zn) of boiler ash from pulp and paper mill waste by using two-level EDTA concentrations at 5 g and 15 g; and mixed with DCM, ET, and NH as solvents at 4 and 8 hours contact time. These studies determine and evaluate the most efficient and effective treatment in reducing the transition metal content of boiler ash from pulp and paper mill waste.

EXPERIMENTAL

Materials

The fresh samples of boiler ash were obtained from the combustion of pulp and paper mill at PT. Riau Andalan Pulp and Paper (RAPP) Pangkalan Kerinci, Riau, Indonesia. The required chemicals including EDTA as a collector; DM, ET, and NH as the solvent were purchased from E-Merck. The research work was conducted in the Organic Chemical Laboratory of Faculty of Mathematics and Natural Science, Universitas Sumatera Utara (USU) Medan, North Sumatra, Indonesia and further work to analysis transition metal content was conducted using Inductively Coupled Plasma (ICP) machine at the soil laboratory of research and development department of PT. RAPP.

General Procedure

Using 400 mesh sizes sieves, the prepared boiler ash samples were smoothed and then oven-dried at 100°C for 30 minutes. The 13 samples of boiler ash with 5 g each were prepared and separated into 250 ml Erlenmeyer, this consists of 1 sample for control (blank) and 12 samples for EDTA treatments. The 1st of 6 boiler ash samples were mixed with 5 g EDTA each and the 2nd of 6 boiler ash samples were mixed with 15 g EDTA each. Each of 12 Erlenmeyer was added with 30 ml of 3 kinds of solvents including 4 samples for DCM solvent, 4 samples for ET solvent, and 4 samples for NH solvent. Each solvent will be treated into 4 and 8 hours contact time respectively.

These mixtures were stirred using rotary and shaker where the contact time length was set for 4 hours and 8 hours respectively. Following the completed mixing process, two layers were formed consists of the upper and bottom layers. Both layers were separated using a separation funnel. The first layer in the bottom part as slurry was dried using an oven to obtain a dried sample product.

Product Analysis

The determination of transition metal content from each treatment combination was conducted to the final products of each EDTA treatment using the ICP machine. An ICP is an ionization source that works to decompose a sample into its constituent elements and transforms those elements into ions. The sample ions are taken out through several cones and passed into a mass spectrometer, then the ions are further segregated and a detector obtains an ion signal relative to the concentration of various elements. The ICP machine able to detect metals and several non-metals in liquid samples at very low concentrations.

RESULTS AND DISCUSSION

Both concentrations of EDTA with all three kinds of solvents i.e. dichloromethane (DCM), ethanol (ET), and n-hexane (NH) can be utilized to reduce transition metal content from boiler ash. The reduction of transition metal using EDTA as a collector ranged from 50-85%, 48-87%, 54-89%, 46-84%, 50-89%, 98-99%, 92-97%, for Cd, Co, Cr, Cu, Fe, Ni, and Zn respectively (Table-1).

Table-1: Reduction of Transition Metal Content of Boiler Ash after treated with 5 g and 15 g of EDTA using DCM, ET, and NH Solvents

EDTA Dosage	Solvent	Content Reduction (%)													
		Cd		Co		Cr		Cu		Fe		Ni		Zn	
		4 hr	8 hr	4 hr	8 hr	4 hr	8 hr	4 hr	8 hr	4 hr	8 hr	4 hr	8 hr	4 hr	8 hr
5	DCM	57	54	57	53	61	58	54	46	56	53	60	58	54	53
	ET	64	50	63	55	67	59	60	51	64	54	68	58	63	59
	NH	50	50	48	50	54	55	51	52	50	51	53	53	48	48
15	DCM	81	78	80	76	84	80	78	73	85	82	83	80	80	75
	ET	79	85	79	87	84	89	76	84	85	89	81	88	80	86
	NH	81	75	76	75	82	80	78	76	82	82	80	80	76	77

It was observed that all three solvents compatible with EDTA in reducing transition metal content and among the solvents, ET have a higher ability to lowering transition metal content compared to DM and NH at 0-14%, 0-15%, 1-13%, 0-11%, 1-14%, 0-16%, 1-15% for Cd, Co, Cr, Cu, Fe, Ni, and Zn respectively. There is a clear trend that reduction of all transition metal content increase as the EDTA dosage used increased, for example as indicated in Figure 1-3 for Cd element reduction following treatment with 5 g and 15 g of EDTA using DCM, ET and NH solvents. The overall reduction increment ranged from 21-29%, 13-35%, and 24-32% from DCM, ET, and NH solvent respectively.

Compared to the amine collector such as lauryl amine and stearyl amine used in the previous study[30,31,32], EDTA used in this study have a much higher capacity to reduce transition metal content of boiler ash. This is because EDTA is an effective chelating agent and capable to catch and absorb transition metal from boiler ash. This reaction is even more optimal when using ethanol as a solvent because ethanol is a polar protic solvent that has a large dielectric constant so that it is strong enough to dissolve boiler ash and collectors. Following treatment EDTA with DCM, ET and NH solvent for 4 hours, the Cd content reduced from 3.7mg/kg to 1.6 mg/kg, 1.3 mg/kg and 1.9 mg/kg or at 57%, 64% and 50% when treated with 5 gram EDTA and 0.7 mg/kg, 0.8 mg/kg and 0.7 mg/kg or at 81%, 79% and 81% when treated with 15 gram EDTA. The higher the EDTA dosage used, the Cd content reduction also increased (Fig.-4). The processing time of 8 hours does not consistently increase the reduction of Cd content compared to the 4 hours process time then the 8 hours process time is less considered although for ethanol solvent it produced the highest reduction.

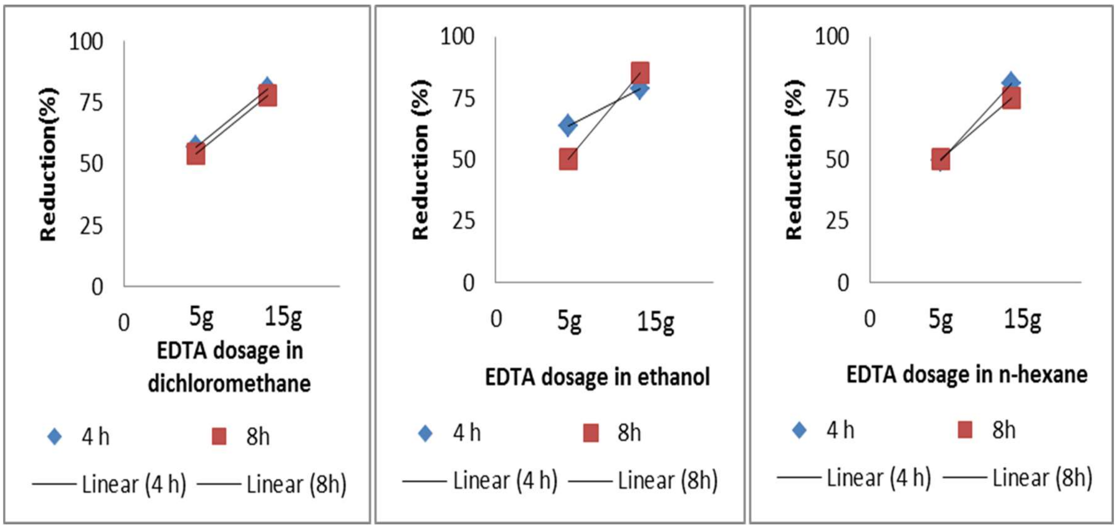


Fig.-1 to 3: Cadmium Reduction Trends of Treatment with 5 g and 15 g of EDTA in DCM, ET and NH Solvents

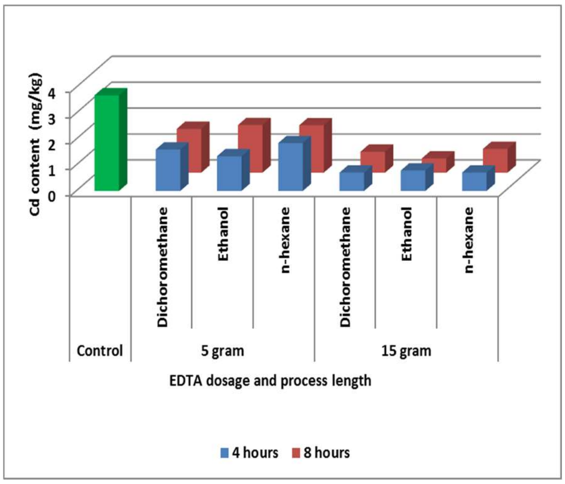
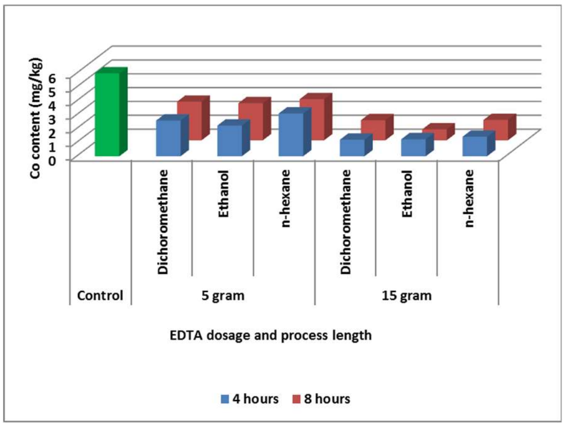
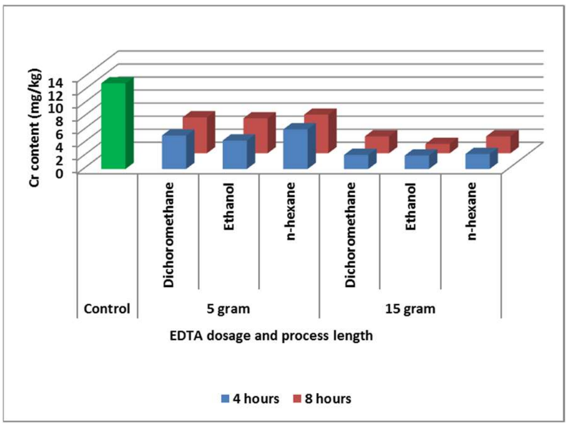


Fig.-4: Reduction of Cd Content From Boiler Ash after treated with 5g and 15g EDTA Treatments





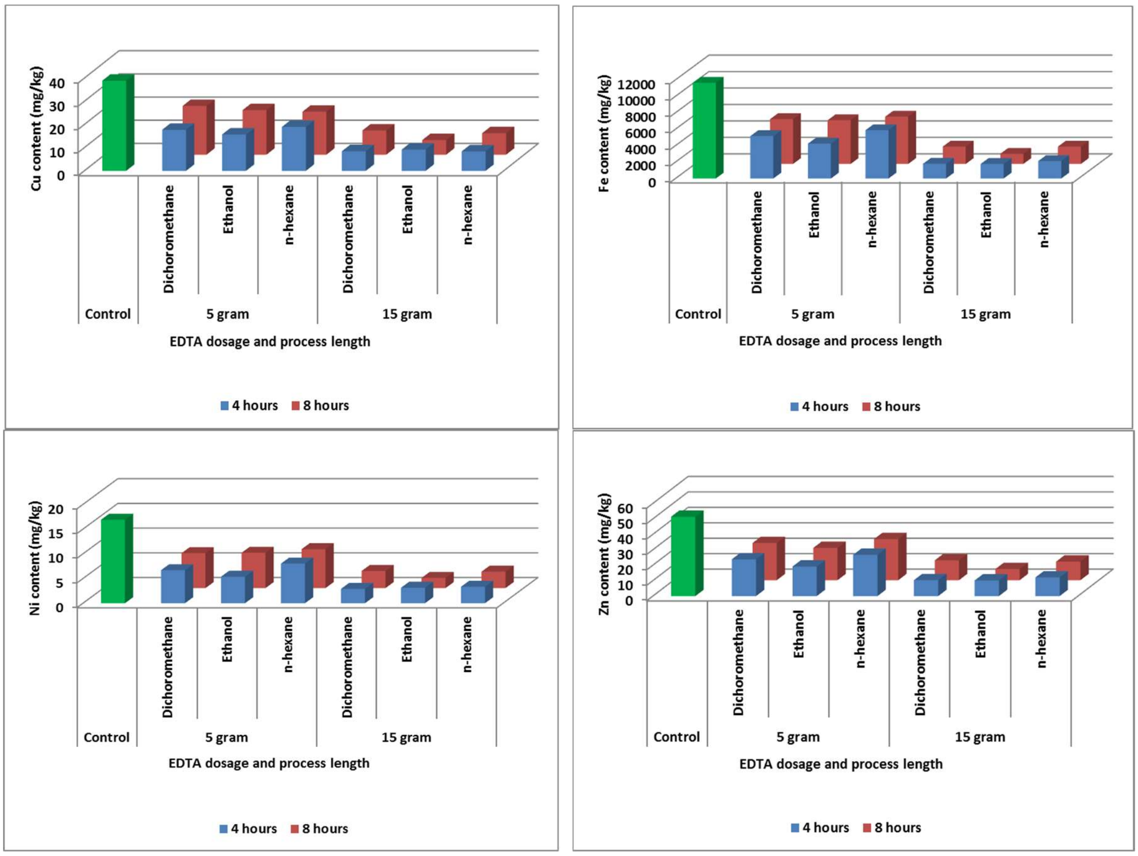


Fig.-5 to 10: Reduction of Co, Cr, Cu, Fe, Ni and Zn Content From Boiler Ash after EDTA Treatments

A similar trend also was shown for Co, Cr, Cu, Fe, Ni, and Zn (Fig.-5 to 10), where the entire element's content was reduced after treated with EDTA and all three solvents. Using 5 g EDTA collector, the reduction of all elements were higher at 4 hours process time compared to 8 hours for both dichloromethane and ethanol solvents but not for n-hexane solvent. This reduction pattern was not followed when using 15 g EDTA collector. Overall the higher dosage of EDTA used, the capacity of EDTA to catch and absorb all elements were increased.

CONCLUSION

The use of EDTA as collector and dichloromethane, ethanol, and n-hexane as a solvent has a strong effect on the transition metal extraction that can be used to reduce the transition metal content of boiler ash from pulp and paper industry. EDTA is an effective chelating agent that compatible with all three solvents in reducing transition metal content. The increase in EDTA dosage used will also increase the reduction capacity. The reduction of transition metal using EDTA as a collector ranged from 50 - 85%, 48 - 87%, 54 - 89%, 46 - 84%, 50 - 89%, 98 - 99%, 92 - 97%, for Cd, Co, Cr, Cu, Fe, Ni and Zn respectively.

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