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Research Article

Coagulation and adsorption techniques for purification of the amalgamation slurry waste

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Abstract: Amalgamation in the processing of community gold mines may leave slurry waste with the potential for heavy metal contamination of the environment. Technical studies for handling these wastes are very necessary to process the waste using a simple and applicable manner in the community. The purpose of this study was to examine the coagulation-adsorption technique of liquid waste from the amalgamation process. Slurry waste samples from the amalgamation process were collected from amalgamation sites in Boto Village, Wonogiri regency which had the highest Hg and Pb levels in the slurry. The coagulation-adsorption process is carried out by a continuous process with the gravitational flow because the area of the amalgamation process has a steep slope. Coagulation of particles in the slurry used two kinds of natural ingredients, i.e. papaya seed, and moringa seed extracts. The adsorption was conducted using two types of minerals, i.e. Ca-bentonite and zeolite which had been activated. The results of this study showed that the coagulation process was a simple process to purify amalgamation slurry waste and reduce the levels of Fe, Mn, Hg, and Pb metals. Then the following step by using the absorption process to produce clear water from amalgamation liquid waste and reduce the levels of Fe and Mn metals. Coagulation using papaya seeds might purify amalgamation slurry waste and reduce heavy metal content of Fe 99.996%; Mn 99.994%; Pb 100%; Hg 100%. Based on these results, the Hg and Pb metals were metals that were very easy to settle. Adsorption on the liquid result of the coagulation process using unactivated zeolite reduced the metal content of Fe> 99.40% and Mn> 88.69%.

***Keywords**: adsorption, coagulation, heavy metals, slurry*

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Introduction

The business of gold processing done by the mining community in one village in Wonogiri Regency that uses the amalgamation method produces bullion. This business has been going on for decades and spread in some locations in this village. The amalgamation location is located in settlement and agricultural areas and is located in the upstream area where the water is used for the daily needs of local settlement. The amalgamation process produces waste that consists of solid waste and liquid waste as slurry. The nature of the slurry which is easy to flow to nearby lower locations and entering the river, so that liquid waste needs to be handled so as not to spread to further locations. This slurry material from amalgamation is a suspension consisting of liquid and solids. Based on the results of the preliminary study, there are heavy metals including Fe, Mn, Pb, and Hg which exceeds the wastewater quality standard in both liquid and sediment. It is also found in the waste generated by artisanal gold mining, with high mercury and gold contents in several areas in South America (de Andrade Lima et al., 2008). Accordinglu\y, a certain technique must be developed to coagulate the solid particles present in the slurry that quickly settles. After this, a technique is needed to adsorb dissolved heavy metals in the liquid resulting coagulation.

To help the coagulation process, it is needed a material that is able to bind heavy metals; then it would be followed by material that is able to adsorb soluble heavy metals from a liquid. In the present research, it was used the bio-coagulant which available in the location research. There were two kinds of seeds from crops of papaya (*Carica papaya*) and *Moringa oleifera.* While adsorbents used were zeolite and Ca-Bentonite that are easily found from the surrounding Wonogiri Regency. The coagulation process was aimed to accelerate the deposition of suspended solids in the slurry. This is done to prevent the clogging of the adsorbent pore by solid particles mixed with slurry. The basis for choosing Moringa and papaya seeds is because this type of plant is easily found at the research site. Moringa and papaya seeds have high protein content, that is a long polymer compound from amino acids that join through peptide bonds. While amino acids are organic compounds that have a functional group carboxyl (-COOH) and amine (-NH_2). The carboxyl group provides acidic properties and the amine group provides basic properties so that amino acids are capable of having positive and negative charges termed zwitter ions (Choy et al., 2014). With the positive charge on papaya seeds and Moringa seeds, Moringa seeds and papaya seeds can coagulate solids in amalgamation liquid wastes in the form of negatively charged colloidal soil (Shamshuddin and Anda, 2008).

The choice of zeolite and Ca-bentonite is because both types of adsorbent are relatively inexpensive and effective for adsorbing heavy metals. Zeolite is an aluminium silicate mineral that has three components of structure namely aluminosilicate frame, interconnected empty space that contains metal cations and water molecules (Dainyak et al., 2006). The structure of zeolite consists of a three-dimensional skeleton of tetrahedral SiO_4^{-4} and AlO_4^{-5}. A small amount of aluminium ion closes the middle position of the tetrahedron from 4 oxygen atoms, and the isomorphic change of Si^{-4} and Al^{-3} produces a negative charge on the lattice. With this structure, zeolite can bind heavy metals with ion exchange processes (Khachatryan, 2014). Bentonite has the main content of montmorillonite, consisting of three sheets, namely one sheet of octahedral alumina (Al_2O_3) which is flanked by two sheets of silica (SiO_4) in the form of tetrahedral. Between the silicate layers, there is a space between layers containing cations. Such structures make Ca-Bentonite the ability to absorb heavy metals (Fernández-Nava et al., 2011; Ghadiri et al., 2015). The smectite mineral includes type 2:1 clay minerals, consisting of two octahedral layers which flank one tetrahedral layer. The presence of isomorphic substitution that occurs in sheet structures, both octahedral and tetrahedral layers, causes the space between the mineral unit layers to be occupied by elements, such as Al, Si, etc. (Nurcholis and Buntoro, 2012). The behaviour of smectite minerals can be easily identified by X-ray diffraction (XRD) analysis. Smectite minerals have a specific behaviour with saturation with Mg or K, and solvation of glycerol or glycol in Mg saturated clay or saturated clay K with heating. The behaviour of this mineral can be seen by changes in peak from d-spacing to X-ray diffraction treatment. Mg produces a peak of 1.45-1.55 nm. However, Nurcholis and Tokashiki (1998) found the peak of saturated smectite Mg which reached 1.60 nm. Solvation with glycerol in saturated smectite Mg can develop to 1.80 nm. The objectives of this study were: (1) To compare the ability of papaya seed extract and Moringa seed extract to coagulate solids in amalgamated liquid waste. (2) Comparing the ability of zeolite and Ca-Bentonite to absorb Fe, Co, Mn, Pb, and Hg metals in amalgamation liquid waste after the coagulation process. It is hoped that the result of the research on the use of coagulant and adsorbent materials can be applied and accepted in the community of gold amalgamation industry because of its relatively low cost but significant benefits to reduce heavy metal content.

Materials and Methods

Materials

Waste amalgamation, from the processing of the people's gold mine in Wonogiri, Central Java Province, is slurry from the gold separation process using mercury (Hg) resulting in the Au-Hg amalgam. The mashed rock is put into the ball-mill and then mixed with mercury and water. Inside the ball-mill is two iron rods used to smooth rocks and react with Hg (Annicaert, 2013). In this process, refining rock particles and binding of gold metal particles by mercury metal. This mixture of gold metal and mercury is called amalgam. The waste of this is in the form of a slurry. The Ca-Bentonite used in this study was collected from Kulon Progo, Yogyakarta Special Region, while the zeolite used was from Gunung Kidul Yogyakarta Special Region. Mineral identification was carried out using XRD (X-Ray Diffraction) analysis and interpretation of peak XRD using the Handbook of Mineralogy database (Anthony et al., 2010). Coagulant uses Moringa seeds and papaya seeds which had been mature and then they were dried. Both types of seed were crushed using mortar until smooth with a size that passed the sieve size of 20 mesh. In this study, moringa and papaya seeds were 200 mg each for a volume of 500 mL amalgamated waste slurry. The preparation and activation stages of adsorbents include size reduction, heating, activation using HCl, washing and drying. For Ca-Bentonite the heating process is not carried out.

Adsorbent materials used were natural Ca-bentonite and zeolite minerals, and there were collected from mining area with a size of more than 25.6 cm. These chunks of minerals were then broken down using a hammer to get a size that matches the feed size of the jaw crusher, i.e. 4 inches. Then it was inserted into the jaw crusher to get a grain size of 28 to 35 mesh. For the purpose of the present study, it was needed Ca-Bentonite and zeolite was 0.5 kg respectively.

After size reduction, zeolite was heated using an oven at a temperature of 300°C for 2 hours to remove water (H_2O) and OH^- in zeolite pores and crystal structures so that it was able to increase the number of active pores in zeolite (Aidha, 2013). Activation of adsorbents was carried out using a solution of 1.5 M hydrochloric acid (HCl) to remove cations that were adsorbed on the surface of mineral crystals. It was done a dilution of concentrated 12.28 M HCl 100 mL was put into a glass beaker then added 700 mL of distilled water so that the final HCl concentration of 1.5 M of 800 mL was obtained. The activation dose used was 40 mL HCl for each gram of adsorbent (40 mL/g). Then each adsorbent is mixed with HCl and stirred using a glass stirrer for 15 minutes, and then let stand for 10 minutes. After activation, each adsorbent was washed using distilled water. The adsorbent was first filtered from HCl and then mixed with distilled water at a dose of 40 mL/g. Then the mixture was stirred for 5 minutes then filtered from distilled water. After filtering the adsorbent was then dried in the oven for 1 hour with a temperature of 100°C.

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Methods

Six litres slurry was poured in a tube then added coagulant, there were two kinds of coagulants, namely papaya seed and Moringa seed extracts. To speed up mixing, it was shaken for 20 times in 1 minute. The control was done by using slurry without the addition of coagulants. Observations were done for the speed of settling suspended particles for 5 hours. EC and pH of the suspension were measured in the deposition process. The results of the deposition process were then analyzed for heavy metals: Hg, Pb, Fe, Co, and Mn using AAS (atomic absorption spectrophotometer).

The adsorption experiment was done by using a pipe column with a diameter of 2 inches and a length of 12 cm. The column is mounted upright on the funnel that is connected to a reservoir bottle as for the result of the process. At the base of the column, gauze with a size of 200 mesh was installed as a cover which was capable of flowing liquid but not for solid particles including adsorbents enter into the funnel. The adsorbents used were 140 grams for every 1,500 mL of wastewater, or one column filled with 140 grams of adsorbent and used to treat liquid waste up to totally 1,500 mL. The liquid produced by coagulation was flowed into the column until the column was full. Then the water was allowed to flow until it was exhausted, then it was refilled until all the water had run out so that the water that had been treated was produced, and then the pH, EC, and heavy metal content would be measured. The adsorbents used were zeolite and Ca-bentonite, both of which were without and with activation (Aidha, 2013).

Results and Discussion

Slurry of amalgamation waste

The people's mining business in the Wonogiri area is done manually by processing using amalgamation techniques (Figure 1). Rocks and weathered materials containing gold ore which has been collected from the mine area are comminuted first to a small size. Then this material is inserted into the drum with a hummer-mill for the amalgamation process, with the addition of water and Hg (mercury). The amalgamation process is performed by turning the drum for two hours. The results of the process are termed as amalgam, and the remnant as slurry is a suspension containing solid particles and heavy metals (Figure 1). Slurry spills from amalgamation waste on the ground can cause potential contamination of heavy metals. Handling of suspensions is needed to separate the contents of solid particles with heavy metals and proper liquids to be flowed on the surface.

Wastewater quality standards are stated in the Regulation of the Minister of Environment No. 5 of 2014. In this regulation, the business on gold using amalgamation technique is not specifically formulated so that the waste quality standards are categorized as businesses that do not yet have wastewater quality standards. In article 14 of the regulation, it is stated that businesses and or activities do not have the specified wastewater quality standard, the wastewater quality standard is applied as stated in Appendix XLVII which is an integral part of this Ministerial Regulation paragraph 1.

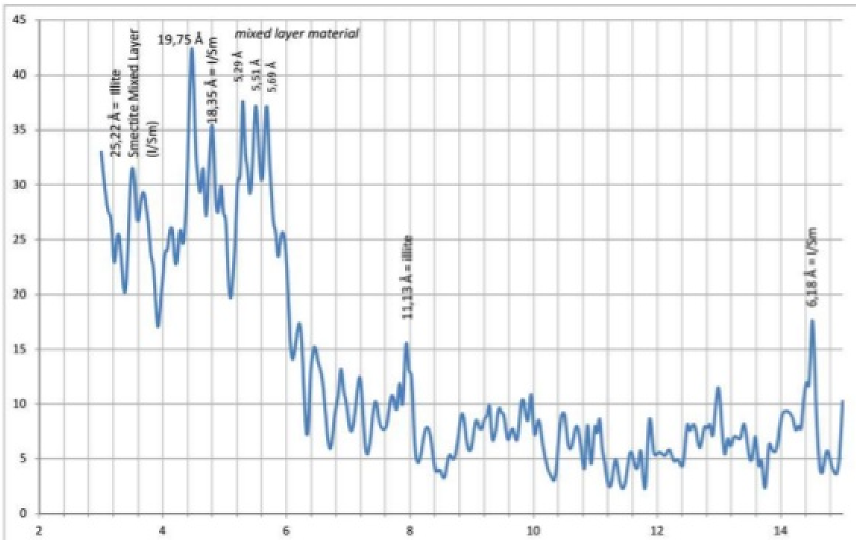
(a) **(b)**

Figure 1. Slurry of amalgamation waste (a) and slurry spill on the soil surface (b).

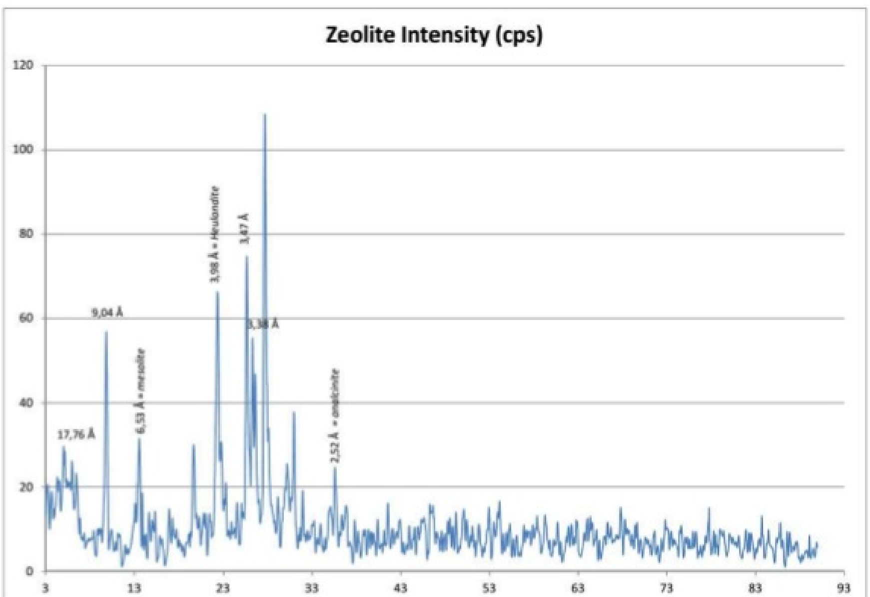
XRD of zeolite and Ca-bentonite

The results of X-ray diffraction analysis on powder samples showed numbers of peaks of 15.52A, 16.03A, 16.69A, 18.35A, 19.75A (Figure 2a). Based on these peaks, it can be stated that the bentonite used in this study was dominated by smectite clay minerals (peaks of 15.52A, 16.03A, 16.69 A, 18.35A, 19.75A), and also illite-smectite mixed layers and illite minerals (peak of 11.13A). Minerals in bentonite are formed in nature, so clay minerals formed are not pure only mineral smectite, but have a clay mineral gangue. The results of previous studies showed that bentonite used had high Ca^{2+} content. The presence of Ca^{2+} is in an exchange complex on the surface and in the space between the lattices of the crystalline smectite mineral crystals. By activating using HCl, it is expected that Ca^{2+} cations that occupy the negative charge of clay minerals as an exchangeable cation can be cleaned. Negative charges that are not occupied by cations can be occupied by heavy metals in the solution and colloidal phase resulting from coagulation and sedimentation of slurry.

Zeolite used in this study contains minerals of Stilbite (9.03A), mesolite (6.58A), mordenite (3.47A), analcime (3.46A), phillipsite (3.22A), heulandite (3.98A), and analcinite (Figure 2b). In addition, there are minerals with d-spacing 17.76A, it is possible mineral smectite. Zeolite is a mineral formed in a water-rich environment with low pressure, low density zeolite (density 2.12 - 2.45 kg m^{-3}), the variation of zeolite species is determined by the temperature at the time of formation of zeolite minerals. In high pressure, zeolite mineral structure can be damaged. Mesolite is a zeolite with a framework structure similar to natrolite, with relatively medium silica content (Teschernich, 1992). Mordenite is the main zeolite species that develops from silica-rich tuffs, but the silica content of this mineral is lower than mesolite. Modernite formed in natural zeolite has great potential in decontamination of radioactive Cs (Johan et al., 2015).



(a)



(b)

Figure 2. XRD patterns of powder (a) bentonite dan (b) zeolite.

Zeolites crystallize in a water-rich environment under a wide range of temperatures. Most zeolites crystallize in a low-pressure environment. Increasing pressure seems to have little effect on which zeolite species crystallizes. Zeolites are low density, open framework structures that high pressure collapses. At high pressure, heulandite or laumontite is replaced by lawsonite, and analcime by albite or jadeite. The zeolite species present in altered volcanic tuff is controlled by the composition of the ash. In silica-rich tuffs, derived from rhyolite or andesite, silica-rich heulandite (= clinoptilolite) and mordenite are of major importance, with minor phillipsite, analcime, and potassium feldspar at deeper levels. The resulting fluid is now rich in aluminium, silicon, sodium, calcium, and potassium that can crystallize zeolites as the temperature decreases in a general sequence controlled by a decrease in silica content. For example, clay> phillipsite> chabazite or clay> levyne-offretite > mesolite-scolecite-thomsonite > chabazite or clay> heulandite-mordenite > stilbite > scolecite-mesolite > chabazite.

Properties of slurry

The pH and electrical conductivity (EC) values of amalgamation slurry are presented in Table 1. The pH value of amalgamation waste slurry is 7.18, and this value is in the range of safe pH values. The EC of slurry value is 0.1 mS/dm, and is also included in the low category. The problems that arise are the levels of heavy metals Fe, Mn, Hg, and Pb; whose value exceeds the allowable threshold. While the content of Co element in the slurry is very low.

Coagulation

The results of the coagulation using Moringa seed and papaya seed extracts are presented in Table 2. Solid particles in slurry bind abundant heavy metals of Fe, Mn, Pb and Hg (Table 1). The solid particles in the slurry are relatively stable suspensions, which naturally require a long time to settle. With the deposition process of the suspension may separate water from its solid containing heavy metals. The role of Moringa and papaya seed extracts is to accelerate the particles deposition in the slurry, it is because of the protein bonds in the seed extract react with minerals in solids. Both moringa and papaya seed extracts which have protein content are able to react with particles in the slurry. Based on the results of the coagulation process, all heavy metals in the water have been coagulated together with solid particles in the slurry, and then sedimented.

Table 1. PH, EC, and heavy metal levels in amalgamation slurry before coagulation.

Parameter	Value			Standard	Judgment
	Suspended Solids*	Solute*	Total		
pH	-	-	7.18	6.0 – 9.0	allowed
EC (mS/dm)	-	-	0.10	-	-
Heavy metal content					
1. Co (ppm)	< 0.1	< 0.1	< 0.1	< 0.4	allowed
2. Fe (ppm)	77,268.0	12.3	77,281.3	< 5	not allowed
3. Mn (ppm)	3,606.0	0.5	3,606.7	< 2	not allowed
4. Pb (ppm)	346.0	0.2	346.2	< 0.1	not allowed
5. Hg (ppm)	2.1	$<0.3 \times 10^{-4}$	2.1	< 0.002	not allowed

* Metal content analysis is carried out by separation of suspended solids and liquids.

Table 2. PH, EC, and heavy metal levels in amalgamation slurry after coagulation.

Parameter	Standard	Treatments			
		Moringa seed extract	Judgment	Papaya seed extract	Judgment
pH	6.0 – 9.0	6.65	Allowed	6.77	allowed
DHL (mS/dm)	-	0.2	-	0.3	-
Heavy metal content					
1. Co (ppm)	< 0.4	< 0.1	Allowed	< 0.1	allowed
2. Fe (ppm)	< 5	4.29	Allowed	3.335	allowed
3. Mn (ppm)	< 2	0.146	Allowed	0.221	allowed
4. Pb (ppm)	< 0.1	< 0.01	Allowed	< 0.01	allowed
5. Hg (ppm)	< 0.002	<0.000025	Allowed	<0.000025	allowed

Adsorption

The adsorption process using zeolite and Ca-bentonite gives varying results on the liquids resulting in the coagulation (Table 2 and 3). In both tables, it shows that adsorbent may increase the EC value of the liquid resulting from slurry coagulation, then the addition of liquid decreases the EC value. The metal Fe and Mn in the liquid decrease sharply over the adsorption by unactivated zeolite. The results of adsorption by activated zeolite showed a decrease in pH and an increase in EC. This is due to the presence of residual HCl in the process of zeolite activation, even though it has been leached using water as flushing. Fe and Mn in the liquid from adsorption by activated zeolite decreased, but the results were still better in the unactivated zeolite. The use of Ca-bentonite as adsorbent also shows results similar to zeolite applications. Unactivated Ca-Bentonite as an adsorbent also shows better results than those that have been activated. Activation of Ca-bentonite also leaves HCl residue which causes a decrease in liquid pH results and increased EC.

Table 3. Values of pH, EC, heavy metals of purification results on the slurry after treatment with coagulants and adsorbents.

Volume of slurry waste	**pH**	**EC (mS/dm)**	**Heavy metals content (ppm)**				
			Co	**Fe**	**Mn**	**Pb**	**Hg**
Treatment with coagulant of moringa seed extract and adsorbent of unactivated zeolite							
0.5 L	6.55	0.50	< 0.1	< 0.02	0.024	< 0.01	<0.000025
1.0 L	6.68	0.30	< 0.1	0.242	0.005	< 0.01	<0.000025
1.5 L	6.60	0.20	< 0.1	0.261	0.061	< 0.01	<0.000025
Treatment with coagulant of moringa seed extract and adsorbent of activated zeolite							
0.5 L	3.51*	0.70	< 0.1	1.410	0.512	< 0.01	<0.000025
1.0 L	3.61*	0.60	< 0.1	0.153	0.045	< 0.01	<0.000025
1.5 L	3.62*	0.60	< 0.1	0.496	0.070	< 0.01	<0.000025
Treatment with coagulant of moringa seed extract and adsorbent of unactivated Ca-bentonite							
0.5 L	6.77	0.30	< 0.1	0.163	< 0.025	< 0.01	<0.000025
1.0 L	6.74	0.30	< 0.1	0.065	0.005	< 0.01	<0.000025
1.5 L	6.75	0.30	< 0.1	0.095	< 0.025	< 0.01	<0.000025
Treatment with coagulant of moringa seed extract and adsorbent of activated Ca-bentonite							
0.5 L	4.31*	0.10	< 0.1	0.848	0.078	< 0.01	<0.000025
1.0 L	3.92*	1.10	< 0.1	2.913	1.032	< 0.01	<0.000025
1.5 L	3.18*	2.70	< 0.1	4.459	2.574*	< 0.01	<0.000025
Treatment with coagulant of papaya seed extract and adsorbent of unactivated zeolite							
0.5 L	6.88	0.20	< 0.1	< 0.02	< 0.025	< 0.01	<0.000025
1.0 L	6.94	0.20	< 0.1	0.208	< 0.025	< 0.01	<0.000025
1.5 L	7.29	0.20	< 0.1	0.208	0.025	< 0.01	<0.000025
Treatment with coagulant of papaya seed extract and adsorbent of activated zeolite							
0.5 L	3.41*	2.60	< 0.1	2.397	1.618	< 0.01	<0.000025
1.0 L	4.61*	0.20	< 0.1	0.060	0.098	< 0.01	<0.000025
1.5 L	5.75*	0.14	< 0.1	< 0.02	< 0.025	0.054	<0.000025
Treatment with coagulant of papaya seed extract and adsorbent of unactivated Ca-bentonit							
0.5 L	7.15	0.20	< 0.1	< 0.02	< 0.025	0.156*	<0.000025
1.0 L	7.19	0.20	< 0.1	< 0.02	< 0.025	< 0.01	<0.000025
1.5 L	6.86	0.20	< 0.1	< 0.02	< 0.025	0.054	<0.000025
Treatment with coagulant of papaya seed extract and adsorbent of activated Ca-bentonite							
0.5 L	3.68*	2.00	< 0.1	4.751	1.659	< 0.01	<0.000025
1.0 L	4.63*	0.10	< 0.1	0.455	0.032	0.122*	<0.000025
1.5 L	5.15*	0.10	< 0.1	0.093	< 0.025	< 0.01	<0.000025

* = not allowed to the wastewater standard.

The role of coagulation and adsorption

All heavy metals in slurry decreased significantly after purification process except for Co. Based on Tables 1 and 2, Co levels were already low, and it did not change either before or after the coagulant was added which is equal to less than 0.1 ppm. Based on these data, it can be stated that amalgamation liquid waste contains only very small amounts of Co metal. While For Pb and Hg metals, after adding the two types of coagulants expressed a very significant decrease to below of the detection limit the AAS (atomic absorption spectrophotometry) tool that was used, which was 0.01 ppm for Pb metal and 0.000025 ppm for Hg metals. So it can be stated that almost 100% of Pb and Hg metals have been deposited in the solid particles during the coagulation process. Whereas for Fe and Mn metals still have relatively low levels but allowed to wastewater quality standards. So it can be stated that not all Fe and Mn metals are deposited after the coagulation process. The best coagulant in this study was using papaya seed extract. After the coagulation process using liquid waste papaya seed extract has a pH of 6.77; EC 0.30 mS/dm; and decreased Co 0% metal content; Fe 99.996%; Mn 99.994%; Pb 100%; Hg 100%.

Moringa seeds contain bioactive components, such as abundant content of low molecular proteins, which is 31% (Anwar and Rashid, 2007), and the presence of this protein has cations that react with negative charges from stable colloids resulting in neutralization (Saini et al., 2016) This condition causes reduction on their repulsions among particles in the colloid, thus forming microflocs, which then becomes larger size. The larger the particle size in the suspension results in an increase in particles mass, and also consequently increases a weight force, and then it causes the acceleration of the sedimentation of the slurry suspension.

The results of the coagulation process showed that the levels of all metals decreased significantly (Table 1 and 2). After deposition of particles in the slurry, the metal content in liquid waste has also decreased significantly, especially Pb and Hg metals. Only Fe and Mn are relatively high compared to Pb and Hg even though Fe and Mn levels meet the quality standards of wastewater. Based on Table 2 and 3 it can be seen that the coagulation process has a greater role in decreasing heavy metal content. Figure 3 shows that all types of adsorbents used in this study produce fluids with clarity that looks the same. Based on this figure, it is seen that liquid waste is clearer than before adsorption. This is because there are still many remnants of coagulants left in liquid waste, causing liquid waste to become a little cloudy. After the liquid waste is passed into the adsorbent column, it appears that the remnants of the coagulant have been greatly reduced and the liquid waste looks very clear. Based on this study it can be said that the adsorption process able to clean up liquid waste from the remnants of the coagulant so that the adsorption process is needed to make the liquid clearer. The best adsorbent in this study is to use unactivated zeolite which can reduce Co 0% metal content; Fe> 99.40%; Mn> 88.69%; Pb 0%; and Hg 0%. The application of zeolite and bentonite to adsorb heavy metals for groundwater from an urban area in Yogyakarta, namely Cd, Cr, Cu, Fe, Zn showed that zeolite was faster than bentonite in the water purification process (Pich et al., 2010).

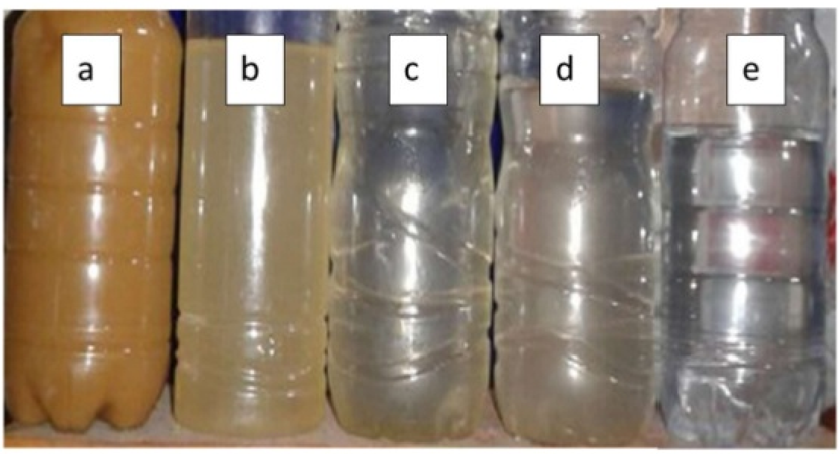


Figure 3. (a) slurry of amalgamation waste, (b) after 5 hours settling without treatment, (c) after 5 hours settling with moringa seed treatment, (d) after 5 hours settling with papaya seed treatment, (e) after 5 hours settling with seed treatment and adsorbent.

Purification process

The process of purification of this amalgamation liquid waste is divided into two parts, namely coagulation and adsorption. The coagulation process can use Moringa seed extract or papaya seeds. Stirring the wastewater that has been added to the coagulant is needed to seal the coagulant and particles in the slurry. After stirring, then wait until it is deposited. The results of the coagulation and precipitation process were continued by adsorption using adsorbent zeolite and Ca-Bentonite in a pipe column to adsorb heavy metals Hg, Pb, Mn, and Fe. After all stages using the coagulation and adsorption techniques, the results of clear water and metal content that meets the standard standards are obtained.

Based on the present result of the study, there is no problem regarding pH of the slurry of the amalgamation waste (Table 1). However, the result of the adsorption process using activated adsorbents showed that the pH decreased to values in the range from 3.0 to 5.0. This can be due to the lack of water volume used to flush residual HCl as activator from the adsorbent so that there is still enough HCl which ultimately causes the pH of liquid to drop.

Most of the treatment results have a low metal content below the wastewater quality standard and have a very high decrease compared to original waste (Table 1 and 2). Although there are still results that have metal levels above the quality standard, namely coagulation of papaya seeds and activated bentonite adsorption with a volume of 1 L, namely Pb content of 0.122 ppm, as for bentonite without activation with volume of 0.5 L produce P15 0.156 ppm, moringa seeds and activated bentonite, volume 1.5 L produces liquids with Fe content of 4.459 ppm and Mn 2.574. Of all treatments that have met the quality standards of wastewater, there are two treatments that produce the lowest levels of heavy metals, namely the papaya seeds and zeolite without activation, also papaya seeds and bentonite without activation.

The treatment of papaya seeds and zeolite without activation is able to adsorb all heavy metals perfectly, that is until the metal content is below the detection limit of AAS equipment, until the flow of 1,500 mL of wastewater. Except for the adsorption of Fe and Mn metals, the treatment of papaya seeds and zeolite without activation is only able to adsorb perfectly on the first 500 mL the running wastewater. The following 500 mL wastewater showed a decrease in the adsorption ability of Fe and Mn metal (Table 3). However, the levels of Fe and Mn in purified liquids are still within the limits of quality standards for wastewater. As for the treatment of papaya seed and bentonite without activation, it is also able to adsorb all metals completely until the total flow of 1,500 mL of wastewater. Except when adsorbing Pb metal, the treatment using papaya seeds and bentonite without activation was only capable of perfectly adsorbing until total 1,000 mL wastewater. At the time of flowing 500 mL or totally 1,500 mL showed a decrease in Pb adsorption. Even when the first 500 mL wastewater, the treatment of papaya seeds and bentonite without activation was only able to adsorb low Pb from wastewater so that the Pb content is still very high, that was at 0.156 ppm, and it is above the wastewater quality standard. Even though in terms of adsorption of Co, Fe, Mn, and Hg metals have a better ability than papaya and zeolite seeds without activation, the Pb adsorption ability of papaya and bentonite seeds without activation is very low even the resulting Pb levels are still above the value wastewater quality standards (Table 3).

Conclusion

Addition of coagulant is the first process required to purify liquid waste of amalgamation and reduce the levels of heavy metals, where the best coagulant is papaya seeds. After adding the papaya seeds to the liquid waste resulted in liquid with pH of 6.77; EC 0.30 mS; and decreased Co 0% metal content; Fe 99.996%; Mn 99.994%; Pb 100%; Hg 100%. Hg and Pb are metals that are very easy to settle. The adsorption process is a continuation of the coagulation process that is needed to reduce the levels of Fe and Mn metals and resulted in the liquid waste amalgamation clearer. The unactivated zeolite adsorbent is the best adsorbent which can reduce Co 0% metal content; Fe> 99.40%; Mn> 88.69%; Pb 0%; and Hg 0%.

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