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Effectiveness of Moringa Seeds Powder and Tamarind seeds Powder Asnatural Coagulant for Increasing Tofu Industrial Waste Water Quality

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Abstract : This research investigated the effectiveness of moringa seed and tamarind seed as a natural coagulant. Both of natural coagulant was used to increase tofu industrial waste water, that contains very high organic material. Based on the results of this experiment, the tofuwaste water contains BOD (510mg/L), COD (800 mg/L) and TSS (2800 mg/L). So, it must be treated before discharged into the environment to reduce the contaminants. Moringa seeds powder (4,81% v/v in water) and tamarind seed powder as organiccoagulant (particle size 70 mesh), variations of stirring time of 1, 1.5, 1, 2.5 and 3 minutes were used in this experiments. The jar test methods was used to know the optimum dosage from the both of the natural coagulant. This results showed that moringa seed powder was more effective to reduce BOD, COD and TSS content than tamarind was. The best result of moringa seeds powder treatment could be reduce the BOD content to 76 mg/L, COD content to 96 mg/L and TSS content to 400 mg/L.
Keywords : organiccoagulant,moringa seeds, tamarind seeds, tofu, wastewater.

1. Introduction

Coagulants are chemicals that water needs to help the process of precipitation of small particles that can't settle by themselves. Commonly, industrial treatment used inorganic coagulants such as alum, PAC, ferric chloride, ferric sulfate and cation polymer in their waste water treatment. Inorganic coagulants are more effective than organic coagulants, but in high doses, they may cause precipitates that are difficult to treat. This reason make organic coagulant as an alternative to replace inorganc one. Plant seeds are commonly used as organic coagulants raw material (Coniwanti, 2013).

Moringa seeds can be used as one of the alternative organic coagulants available locally. The mature moringa seeds with less than 10% water content were used as materials (Putra et al, 2013). The effectiveness of moringa coagulation is determined by the cationic protein content. The active substance contained in the moringa seed is 4-α-L-rhamnosyloxy-benzyl-isothiocyanate (Coniwanti, 2013). The active substance has capability for adsorbing waste water particles. Reducing seeds to smaller size will increase surface area and active sites. High moisture content wil decrease its adsorb ability because the active sites were blocked by water (Bangun et al, 2013).

Tamarind seeds can be used as coagulant because The seeds protein content that acts as a polyelectrolyte (Hendrawati et al, 2013). According to Dobrynin & Michael (2005), polyelectrolytes are polymers that carry positive or negative charges of ionized groups. In a polar solvent such as water, the group may dissociate, leaving the charge on its polymer chain and releasing the opposing ion in solution. The addition of a polyelectrolyte concentration will result in reduced colloidal stability and will reduce the rejecting force between particles to support the precipitation process.

Coagulation-flocculation is a necessary process to remove waste material in the form of suspense or colloid. Colloid is a particle that can not settle within a certain time and can't be removed by the usual physics treatment process (Coniwanti, 2013). Coagulation is a process of destabilizing particles of colloid compounds in wastewater. It can also be said that a settling process by adding the coagulant ingredients into the liquid waste so that there is sediment on the bottom of the sedimentation tank (Suharto, 2011). The basic principle of the coagulation process is the pulling force between negative ions and positive ions. Those acting as negative ions are particles composed of organic substances (colloidal particles), microorganisms and bacteria. Flocculation is a next process of the coagulation process, where the coagulated microfloc begin to agglomerate colloidal particles into larger deposited flocs and this process is aided by slow stirring. The coagulation-flocculation process can't be separated in industrial wastewater treatment. Macroflocs formation in the flocculation process takes place from collisions between colloidal particles (Bangun, 2013).

In the coagulation process, colloidal particles attract positive ions from chemicals added as coagulants. Concentrated coagulants form layers on colloidal particles surface. The layer is surrounded by negative ions and slowly mixes with positive ions. Positive ion coatings are known as sturdy coatings, while layers that surround negative ions are known as diffuse layers. This diffusive layer then contracts and removes the sturdy layer, causing the attraction between the colloidal particles. This process requires quick and slow stirring. Homogeneous stirring should be done to ensure coagulants can react with the particles or ions in the suspension. The use of too much coagulant dose will cause the coagulant to become saturated, thus decreasing the ability of coagulant to clear the liquid waste.

The solid waste of the tofu industry can be used as animal feed, so they did not categorized as pollutant. The wastewater of industrial tofu is the largest and potentially pollute the environment. The liquid waste of tofu industry contains very high organic ingredients. Organic compounds in waste water can be proteins, carbohydrates, fats and oils. Protein and fat are the biggest components in tofu liquid waste.

Characteristics of tofu industrial waste water consist of physical and chemical characteristics.Physical characteristic include total solids, suspended solids, temperature, color and odor. Chemical characteristics include organic materials, inorganic materials and gases. Waste water temperature ranges from 37-45°C, turbidity 535-585 FTU, ammonia 23,3-23,5 mg/L, BOD5 6,000-8,000 mg/L and COD 7,500-14.000 mg/L (Kaswinarni, 2007). These compounds contain 40-60% protein, 25-50% carbohydrate and 10% fat. The tofu industrial waste water quality depends on the process used. The good process water treatment will loweing organic matter content in the waste water. The largest component is protein with N_{total} of 226,06-434,78 mg/L (Coniwanti, 2013). The threshold of soybean processing waste is BOD 150 mg/L, COD 300 mg/L, TSS 200 mg/L and pH 6-9 (Regulation of State Minister of Environment of Republic of Indonesia No. 5,year 2014 concerning Wastewater Quality Standard)

2. Experimental

This study aims to determine the effectiveness of Moringa and Tamarind seed powder as organic coagulant for decreasing COD, BOD and TSS (Total Suspended Solid) in the tofu industry wastewater. The preliminary research will be done to determine optimum dosage of organic coagulant by using floculator tool with jar test method. The optimum coagulant dose was used for flocculation process with flocculator. The results were analyzed for COD, BOD, and TSS at the time before and after organic coagulant is put into waste sample industrial tofu as well as flocculation-coagulation process done. Samples of tofu industrial liquid waste used are taken in Malang city, then analyzed in Chemical Engineering Laboratory, Institut Teknologi Nasional Malang.

The moringa seeds are dried, peeled and milled to obtain 70 mesh size. The dried seeds were dried in hot air oven at 105°C for 2 hours or until less than 10% water content. Tamarind seedswere dried with roasted, peeled and milled to obtain 70 mesh. The dried Tamarind seeds were dried in hot air oven at 105°C for 30 minutes.

The optimum dose determination procedure of organic coagulant of Moringa seeds and Tamarind seeds, rapid agitation time and their effect to BOD, COD, TSS for tofu industry liquid waste. AnalysizingBOD, COD, TSS to determine the quality of tofu industry liquid waste. Furthermore, 1000mL of liquid waste was added with Moringa and Tamarind seeds coagulants in beaker glass with optimum dose and fast stirring at 100rpm, stirring time (1, 1.5, 2, 2.5 and 3 minutes),reducedstirring speed to 40 rpm for 25 min and sedimentated for 35 min for the final analysis (BOD, COD and TSS analyzes).

3. Results and Discussion

All test results are analyzed and compared to Regulation of the State Minister of Environment of the Republic of Indonesia No. 5 Year 2014 concerning Water Quality Standards of Wastewater. The tests include BOD (standard quality = 150 mg/L), COD (standard quality = 300 mg/L) and TSS (standard quality = 200 mg/L).

BOD(*Biochemichal Oxygen Demand*) Testing

The result of BOD testing of liquid waste of tofu industry that has been processed using moringa seeds and tamarind seedscoagulant can be seen in Table 1. Liquid waste from coagulant treatment of moringa seeds and tamarind seeds coagulant has decreased BOD valuefor increasing faster stirring time (Figure 1). It takes 3 minutes stirring time to reach the BOD value below the standard threshold of the tofu industry liquid waste quality of 76 mg/L for moringa seed coagulant and 107 mg/L for tamarind seeds. This coagulation-flocculation process can reduce the BOD content of 85.09% for moringa seeds coagulant and 79.02% for tamarind seedscoagulant.This is due to the stirring process which has the ability to spread the seeds of moringa seeds and powder of tamarind seeds to evenly, and increase the opportunity between the particles to react. As well as having the ability to bind organic ingredients in the tofu industry liquid waste in combining the particles of moringa seeds powder as well as tamarind seeds powder with organic matter in the waste water. This is in line with the theories of Sawyer and Mc. Carty (1967) in Elykurniati (2010) that the stirring speed is one of the factors affecting the coagulation-flocculation process.

Table1. BOD testing result

Time (min)	Initial BOD of waste water (mg/L)	BOD Water Quality Standards (mg/L)	Moringa Coagulant Treatment		Tamarind Coagulant Treatment	
			BOD value mg/L	% reduction	BOD value mg/L	% reduction
1	510	150	377	26,08	475	6,86
1,5	510	150	298	41,57	394	22,74
2	510	150	201	60,59	283	44,51
2,5	510	150	172	66,27	206	59,61
3	510	150	76	85,09	107	79,02

Moringa seeds powder coagulant was more effective than tamarind seeds, because of more BOD reduction. The effectiveness of moringa seeds because of cationic protein content in the form 4α-L-rhamnosyloxy-benzyl-isothiocyanate (Coniwanti, 2013).

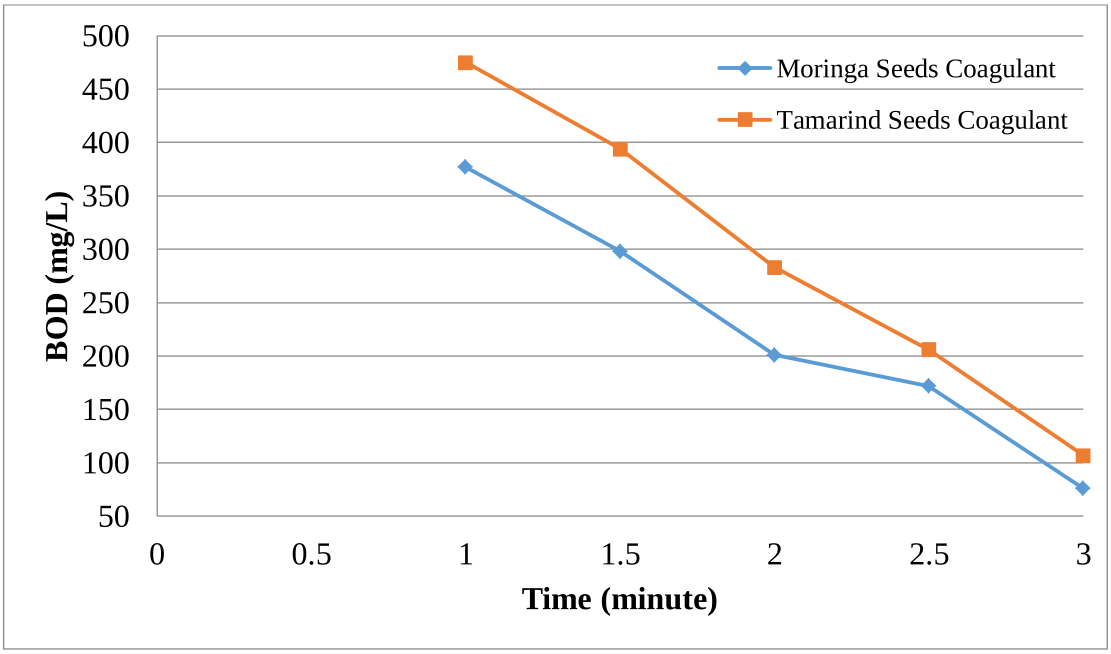

Figure 1.The effect of stirring time to BOD value

COD (*Chemcial Oxygen Demand*)testing result

The result of COD test of liquid waste of tofu industry that has been processed using coagulant of moringa seeds and tamarind seeds can be seen in Table 2. Liquid waste from coagulant treatment of moringa and tamarind seeds decreased COD value for increasing faster stirring time (Figure 2). However, there was deviation on organic coagulant of moringa seeds powder at 1 and 1.5 minute stirring time, obtained COD value of 480 mg/L and 352 mg/L. The deviation also occurred at tamarind seeds treatment result at the time of 1, 1.5 and 2 minutes rapid stirring, obtained COD value of 512, 416 and 320mg/L. Not all coagulant particles react to form floc because stirring time was too fast and the duration was too short. The amount of organic and inorganic content in the tofu industry liquid waste, causing the decline in the value of COD can not reach a predetermined quality standard.

Table2. COD testing result

Time (min)	Initial COD of waste water (mg/L)	COD Water Quality Standards (mg/L)	Moringa Coagulant Treatment		Tamarind Coagulant Treatment	
			COD value mg/L	% reduction	COD value mg/L	% reduction
1	800	300	480	40	512	36
1,5	800	300	352	56	416	48
2	800	300	288	64	320	60
2,5	800	300	224	72	224	72
3	800	300	96	88	128	84

Figure 2 shows that the longer the stirring time, the lower the COD value. Moringa seeds coagulant resulted in a faster COD decrease (starting 2 min) compared to the tamarind seeds coagulant.

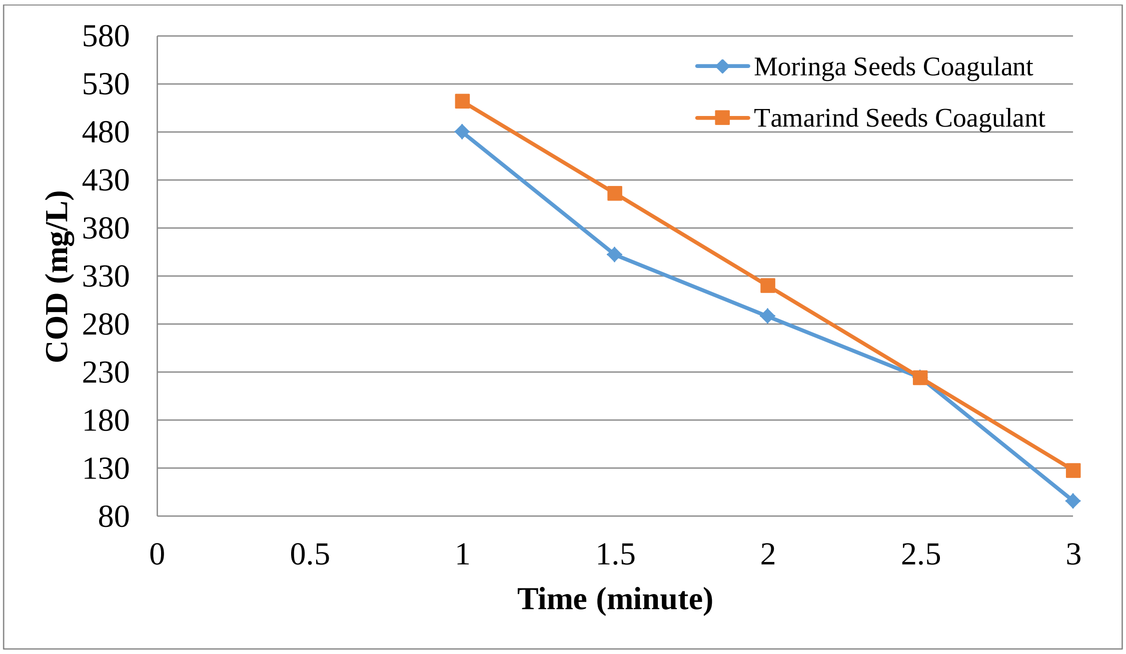

Figure 2.The effect of stirring time to COD value

According to Sawyer and Mc. Carty (1967) in Elykusnati (2010), stirring time will affect the formation of flocs. Organic coagulant of moringa seeds powder is more effective because it can decrease COD faster than tamarind seeds powder to meet the threshold set by the government. The effectiveness of the use of moringa coagulant is due to the presence of cationic protein content of 4-α-L-rhamnosyloxy-benzyl-isothiocyanate (Coniwanti, 2013).

TSS(*Total Suspended Solid*) testing result

Total suspended solids (TSS) are suspended materials (diameter> 1 μm) retained on a Millipore filter with a pore diameter of 0.45 μm. The TSS testing result of tofu industry liquid waste has been processed using moringa and tamarind seeds powder coagulant can be seen in Table 3. Liquid waste from the both treatment decreased TSS content along with the longer stirring time (Figure 3).

Moringa and tamarind seeds coagulant can't reduce the TSS content below waste water threshold. The resulting TSS content is still above the government-set threshold. This indicates that the use of moringa and tamarind seeds powder of 2000 mg/L with various variations of speed stirring agitation time has not been able to precipitate suspended material particles in tofu industry waste water.

Tabel 3. TSS testing result

Time (min)	Initial TSS of waste water (mg/L)	TSS Water Quality Standards (mg/L)	Moringa Coagulant Treatment		Tamarind Coagulant Treatment	
			TSS value mg/L	% reduction	TSS value mg/L	% reduction
1	2800	200	1200	57,14	1600	42,86
1,5	2800	200	800	71,43	1200	57,14
2	2800	200	800	71,43	1200	57,14
2,5	2800	200	800	71,43	800	57,14
3	2800	200	400	85,72	800	71,43

Based on TSS content obtained, organic coagulant of moringa seed powder is more effective than tamarind seed. This was caused by the use of moringa seed powder with a 3 minutes rapid stirring time can reduce the TSS content upto400 mg/L although the value is still above of the government quality standard.

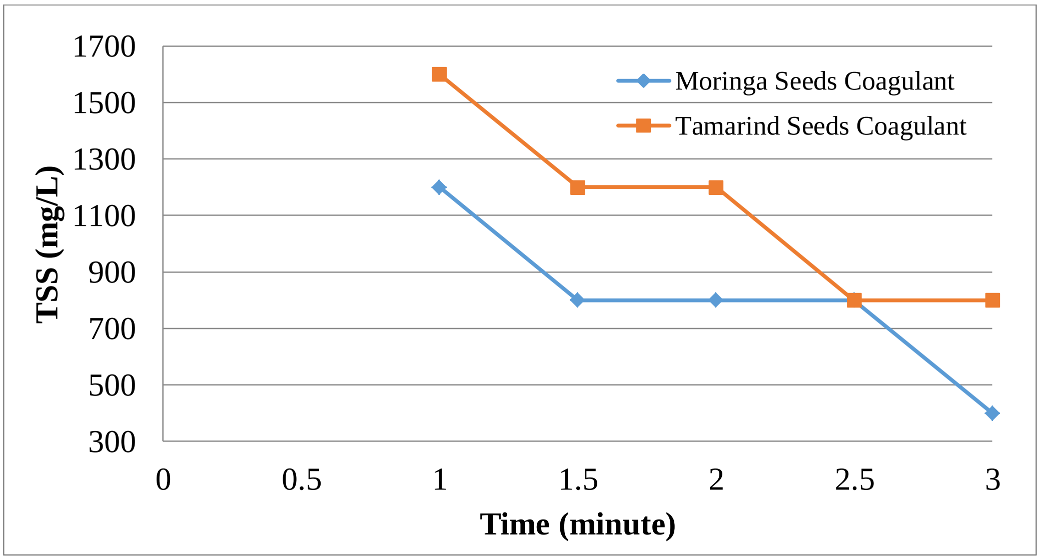

Figure 3.The effect of stirring time to TSS content

Reaction Mechanisms between tofu industrial liquid wastewith organic coagulants

The liquid waste of the tofu industry contains high organic ingredients such as protein, carbohydrates and fats. Protein contained in the tofu industry liquid waste amounted to 40-60%. Proteins are natural polymers composed by numbers of amino acid that are bonded to one another over amide (or peptide) bonds (Hart et al., 2012). One of the amino acids contained in the tofu industry liquid waste is glutamic acid, which has an isoelectric point of 3.2. The chemical structure of glutamic acid can be seen in Figure 4a.

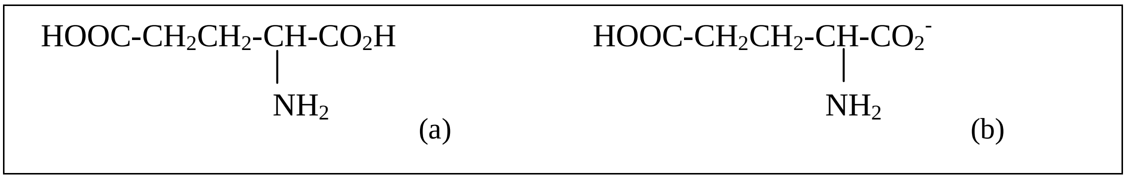

Figure 4. Chemical structure of glutamic acid in neutral (a) and bases (b) conditions

According to Hart et al (2012), if the pH solution is smaller than the isoelectric point, there is a proton, but if the pH solution is greater than the isoelectric point there is no proton. Glutamic acid loses its proton because the pH of the coagulation-flocculation process (pH = 4) is greater than its isoelectric point (3,2), the chemical structure of glutamic acid changes as Figure 4b. Coagulants of Moringa seed powder and tamarind seed powders contain protein. One of the amino acids that make up the moringa seed powder is methionine (5.7isoelectric point). One of the amino acids contained in tamarind seed is glycine (6.0 isoelectric point)

Reaction mechanism of tofuindustrial liquid waste with moringa seed coagulant

The industrial liquid waste of tofu contains glutamic acid (3.2 isoelectric point. This glutamic acid has a negative charge because the isoelectric point is below the pH of the coagulation-flocculation process (pH 4). Methionine contained in the moringa seeds has an isoelectric point of 5.7, this point is above the pH of the coagulation-flocculation process, the methionine has a positive charge. Methionine has a chemical structure such as Figure 5a.

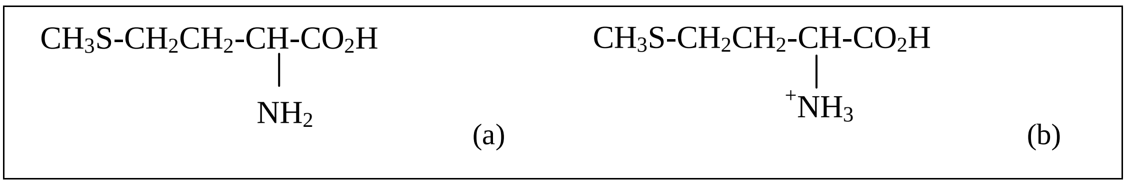

Figure 5. The chemical structure of methionine in a neutral (a) and acid (b) condition

If the pH of the solution is smaller than its isoelectric point then the proton is present, if the pH of the solution is greater than its isoelectric point then the proton is absent (Hart et al, 2012). the proton in methionine increases because the pH of the coagulation-flocculation process is smaller than the isoelectric point of methionine (5,7). The chemical structure of methionine in this condition can be seen in Figure 5b. Both amino acids have different charges so that these two proteins repulse and bind to form flocsin the process of coagulation-flocculation. The reaction of glutamic acid and methionine can be seen in Figure 6.

$HOOC\text{-}CH_2CH_2\text{-}CH\text{-}CO_2^- + CH_3S\text{-}CH_2CH_2\text{-}CH\text{-}CO_2H \rightarrow (^+NH_3 + CO_2^-)$ (flok) +

(CH of glutamic acid bears NH_2; CH of methionine bears $^+NH_3$)

$COO^-\text{-}CH_2CH_2\text{-}CH\text{-}H + CH_3^-\text{-}CH_2CH_2\text{-}CH\text{-}CO_2H$

(CH of the first bears NH_2; CH of the second bears S)

Figure 6.The reaction between glutamic acid and methionine.

Reaction mechanism of tofu industrial liquid waste with tamarind seed coagulant

The tofu industrial liquid waste contains glutamic acid (isoelectric point 3,2). Glutamic acid is negatively charged because its isoelectric point is below the pH of the coagulation-flocculation process (pH 4). While the tamarind seed contains glycine (6.0 isoelectric point) which is above the process pH so it is positively charged. The chemical structure of glycine can be seen in figure 7a.

$H\text{-}CH\text{-}CO_2H$ (CH bears NH_2) (a)	$H\text{-}CH\text{-}CO_2H$ (CH bears $^+NH_3$) (b)

Figure7. The chemical structure of glysine in a neutral (a) and acid (b) condition

If the pH solution is smaller than its isoelectric point then the proton is present, if the pH solution is greater than the isoelectric point then the proton is absent (Hart et al., 2012). the proton in glycine increases because the coagulation-flocculation process (pH = 4) is smaller than the glycine isoelectric point (6.0), the chemical structure of the glycine under this conditions changes to the model as shown in figure 7b.

Both of these amino acids can be reacted because they are both proteins and have different charges.In the coagulation-flocculation process, these two amino acids bind to form flocs. The reaction of glutamic acid and glycine can be seen in Figure 8.

$HOOC\text{-}CH_2CH_2\text{-}CH\text{-}CO_2^- + H\text{-}CH\text{-}CO_2H \rightarrow (^+NH_3 + CO_2^-)$ (flok) +

(CH of glutamic acid bears NH_2; CH of glycine bears $^+NH_3$)

$COO^-\text{-}CH_2CH_2\text{-}CH\text{-}H + H\text{-}CH\text{-}CO_2^-$

(CH of the first bears NH_2; CH of the second bears H)

Figure 8. Reaction between glutamic acid and glycine

Thus, the proteins present in the tofu industrial wastewater as impurities can bind to amino acids present in the organic coagulants of moringa seed powder as well as the powder of the tamarind seeds. Because of difference between these two charges, the amino acid in tofu liquid waste negatively charged while amino acid in the positive organic coagulant. Then the proteins are pulling each other and bind to form flocs and settled. So that moringa and tamarind seeds can be used as organic coagulant to reduce levels of BOD, COD and TSS in tofu industry liquid waste.

4. Conclusions

Moringa seed powder coagulant is more effective than the tamarind seed powder when used for the coagulation-flocculation process of tofu industrial waste water treatment.This can be seen from the decrease in BOD, COD and TSS is greater.

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