RESEARCH ARTICLE



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Analyzing the Rapid Mixing Time Effect on Coagulation – Flocculation Process using *Moringa Oleifera*

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Rapid mixing time is one of the most important factors on coagulation – flocculation process in water treatment. In this study, Moringa Oleifera (MO) seed was used as a natural coagulant to remove Fe and Mn in well water. The effects of rapid mixing time to remove Fe, Mn, and turbidity floc size were investigated. Here, rapid mixing time variations were used around 30 - 300 s coagulant doses (equal 33 mg/l) with 100 rpm rapid mixing speed while slow mixing speed of 40 rpm for 10 minutes and settling time for 60 minutes. The result showed that Fe and Mn removal ranging from 26-48 % and 13-31% with optimum rapid mixing time to remove Fe was 180 s; Mn was 150 s; and turbidity was 180 s, respectively. Based on correlation analysis using SPSS software with the Rank Spearman method, the residual concentration of Fe had a very strong correlation with residual Mn (r = 0.967) and a strong correlation with turbidity (r = 0.746) while the residual concentration of Mn has a very strong correlation with turbidity (r = 0.809).

Keywords: Rapid mixing time, *Moringa Oleifera* (MO) seed, coagulant, Fe and Mn, and well water.

1. INTRODUCTION

One source of clean water is ground-water or well water. Groundwater is a main source of raw water for most of Indonesia's people [1]. However, groundwater often contains iron (Fe) and Manganese (Mn) in high concentrations. Excess concentration of Fe in the human body can damage the intestinal wall and cause death, while excess Mn concentration can cause chronic poisoning in humans to cause hyper reflex [2, 3]. Coagulation-flocculation is a water treatment with the addition of coagulant to raw water which is the functions to destabilize colloidal particles, so that floc will be formed. The process of coagulation and flocculation can eliminate Fe, Mn, very small organic compounds, and hardness components [4, 5]. In the other hand, this process is not only effective but also economical because it takes place quickly so as to reduce excess power consumption and energy costs [6]. The most commonly used coagulant is metal salt coagulant, such as aluminum sulfate, ferric chloride and others.

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However, the use of chemicals will damage health if used sustainably [7]. An alternative was confirmed by using natural coagulants. MO seed was confirmed as coagulants to remove Fe and Mn in well water. The process of coagulation-flocculation is influenced by several factors including the rapid mixing time. The results of the other study showed that study by to reduce contaminants optimally, the optimum coagulation time is needed. In that study, it takes 2 minutes as the optimum coagulation time using alum coagulant [8].

2. METHODOLOGY

A. Water Sample

The sample was taken in well water, X University. The parameters that were measured Fe and Mn concentrations, turbidity, C-Organic and pH. Water sample taken using Vertical Water Sampler.

B. MO Coagulant

MO coagulant was prepared by selecting old and brown MO seeds. Then the skin was peeled and ground using blender. Furthermore, MO seeds that have become powder were sieved to get a smaller size, making it easier to dissolve in aquadest. The making of MO seed coagulant solution using 1 gr of old MO seeds powder which has been mashed and dried, then put into 100 mL aquadest. The solution was homogeneous with a magnetic mixer and filtered using paper. The filtered water was used as an aqueous coagulant solution. Coagulant solution must be made immediately after each use, due to MO seeds are organic material that is easy to rot. MO seed solution when stored in a 4°C cooler can last for 3 days [9].

C. Optimum Dose of MO Coagulant

Determination of the optimum coagulant dose was done by varying the coagulant dose based on previous research using the Velp Scientifica Jar Test. Rapid mixing time speed of 100 rpm, rapid mixing time of 1 minute [10], flocculation speed of 40 rpm for 10 minutes and settling for 60 minutes (according to Indonesian National Standard (abbreviated SNI) 19-6449-2000 on Coagulation-Flocculation Testing Methods with Jar Test).

D. Optimum Time of Rapid Mixing

The variations of rapid mixing time were 30; 60; 90; 120; 150; 180; 210; 240; 270 and 300 s. It was carried out using a Jar Test in a 500 ml beaker glass. The speed used for rapid mixing was 100 rpm, slow mixing was 40 rpm [11] for 10 minutes [12] and the settling time is 60 minutes [13]. The dosage used was obtained from a previous experiment. The parameters measured in determining the optimum rapid mixing time were Fe and Mn, turbidity, and floc size.

E. Analytical Methods

In this study, Fe samples were measured in accordance with SNI 06-6989.4-2004 on How to Test Iron (Fe) with Atomic Absorption Spectrophotometer (AAS), whereas Mn samples were measured in accordance with SNI 06-6989.5-2004 on How to Test Manganese (Mn) with Uptake Spectrophotometer Atom (SSA) -Nyala) used the SSA brand of Rayleigh WVX-320. Previously, a standard solution of Fe and Mn was made to obtain absorbent values that were useful in determining Fe and Mn concentrations.

Furthermore, the turbidity of the sample was measured in accordance with SNI 06-6989.25-2005 on the Way of Turbidity Test with a Nephelometer which was calculated in Nephelometric Turbidity Unit (NTU) or Nephelometric Turbidity WPA Unit (UKN) using brand Digital Spectrophotometer CO 210 Colorimeter. Previously, a turbidity standard solution was made to obtain absorbent values that were useful in determining the turbidity concentration while Floc measurements were carried out on floc formed after the deposition process, using an optical microscope from the Olympus SZX10 brand [14].

Thus, the data analysis was carried out using the Statistical Product and Service Solutions (SPSS) program with the Spearman Rank method. The correlation between parameters can be seen through the correlation coefficient (r) and the significant value (p).

3. RESULTS AND DISCUSSION

A. Characteristics of Well Water

The characteristics of well water samples consisted of Fe, Mn, turbidity, C-Organic concentration and pH. The results were compared with Indonesian Minister of Health Regulation No. 492 of 2010 concerning Drinking Water Quality Requirements. The results showed that Fe, Mn and turbidity exceeded the established quality standards. (see Table I).

Table I. Water sample quality

No	Parameters	Unit	Value	Quality Standards [*]	
1	Fe	mg/l	3.11	0.3	
2	Mn	mg/l	1.37	0.4	
3	Turbidity	NTU	35.72	5	
4	C-Organic	mg/l	48	-	
5	pH	-	6.8	6.5-8.5	

^{*} Indonesian Minister of Health Regulation PERMENKES/No.492/2010

B. Optimum Dose of MO Coagulant

The correlation of turbidity concentration with MO seed for coagulant doses of 10 to 80 mg/l (see Figure 1).



Figure 1. Fe, Mn and turbidity removal using 10 - 80 mg/l of coagulant dose

The lowest turbidity concentration ranged from 30 mg/l to 40 mg/l. Then the dosage range used was reduced to 30; 31; 32; 33; 34; 35; 36; 37; 38; 39 and 40 mg/l. This experiment aimed to get the right dose in the sample, then the coagulation-flocculation process takes place effectively (see Figure 2).



Figure 2. Fe, Mn and turbidity removal using 30 – 40 mg/l of coagulant dose

Figure 2 showed that the comparison of removal Fe, Mn and turbidity of well water with the dose of coagulant given. Based on Figure II, the optimum dose in this study was 33 mg/l. The MO coagulant was able to remove Fe, Mn and turbidity with a removal value of 41.379% Fe; Mn 34,333% and turbidity 55,847%. Coagulants are easier to bind to colloids and eliminate turbidity if they have higher initial concentrations. The removal of Fe and Mn in this study was also smaller when compared with the studies with a removal percentage of Fe was 99.43% and Mn was 50.54%. The dose of MO seed coagulant is 1.25 gr/l, while the initial Fe concentration of the sample reached 5.13 mg/l and Mn around 2.11 mg/l.

C. Analysis of Rapid Mixing Time Effect

After obtaining the optimum dose of coagulant, the coagulation time variations were then carried out starting from 30 seconds to 300 seconds with a range of 30 seconds at a speed of 100 rpm (see Figure 3).



Figure 3. The effect of rapid mixing time in Fe and Mn concentration

From the coagulation time of 30 seconds to the optimum coagulation time (optimum coagulation time of Fe was 180 s and Mn was 150 s), the remaining concentrations of Fe and Mn in the sample decreased gradually. This was due to an increase in rapid mixing time (from 30 s to the optimum time) resulting in coagulants added to the sample to be more completely dispersed and bind more Fe and Mn ions. MO seed coagulant contained cationic protein and the active substance 4- (α -L-ramnosyloxy) benzyl isothiocyanate. The hydroxyl group of the active substance to remove heavy metals such as Fe and Mn because it is more positive, while the metal ions are more electronegative, so the two ions bind and can reduce the concentration of Fe and Mn in water [15]. In the optimum rapid mixing time to remove Fe (180 s), MO seed protein is most effective to contact Fe ions in the water while Agglomeration or floc is easier to remove Fe. The time of rapid mixing over floc agglomeration speed was greater than the floc settling speed. Flocs were formed in greater numbers and larger sizes, thereby eliminating more Fe ions in the sample. At the optimum Mn rapid mixing time (150 s), the greatest Mn removal occurred with a residual concentration of Mn which was 0.939 mg / L.

When compared to the optimum rapid mixing time used by Srawaili [8] in the Fe and Mn ion removal process which is 5 minutes with a rapid mixing speed of 100 rpm, the time required was longer because of the greater initial Fe and Mn concentrations of 10 mg / L. The optimum coagulation time would be different for each treatment, depending on the intensity of stirring and the dose of coagulant used [16]. In the time of coagulation that exceeds a optimum time, there was a decrease in removal and an increase in the concentration of residual Fe and Mn in processed water (supernatant). This happened because the speed of floc breaking become greater than a speed of agglomeration, thus destroying the bonds that had formed between the Fe and Mn ions with the MO seed protein in the coagulant. As a result, a ruptured floc will increase the concentration of the remaining Fe and Mn in the supernatant. This increase in concentration occurs gradually until the final coagulation time variation of 300 s. Yukselen and Gregory [17] reported that after an optimum coagulation time of 10 seconds and a coagulation speed of 400 rpm, an increase in the intensity of the stirring caused rupture of the formed floc and increased turbidity.

There was an optimum time difference for Fe and Mn removal. In this study, the optimum rapid mixing time to remove Fe was 180 s and Mn around 150 s. The optimum time difference occurs due to differences in molecular weight, where the molecular weight of Fe is 55,847 gr / mol, greater than the molecular weight of Mn was 54,938 gr/mol.

The greater molecular weight of Fe will cause the metal to be more difficult to set aside because it has high solubility in water [18]. Therefore, the time needed for MO seed protein to contact Fe ions was longer than the contact time with Mn ions (see Figure 4).



Figure 4. The effect of rapid mixing time in Fe and Mn removal

At the optimum rapid mixing time, the greatest removal percentage was 47.701% for Fe removal and 30.994% for Mn removal. The removal of Fe was higher than the removal of Mn because the concentration and molecular weight of Fe is higher than that of Mn, so that more Fe ions were excluded than Mn ions. However, the removal of Fe and Mn. In this study, the relatively lower when compared to other studies. This is due to lower initial concentrations of Fe and Mn, and lower coagulant doses. In the other study, Fe removal was 99.53% and Mn was 99.35% at 300 s rapid mixing time. The coagulant used was MO seeds with dose of 1250 mg/l. Initial Fe and Mn concentrations in artificial samples were 9 mg/l and 8 mg/l.

Other studies stated that the removal of Fe and Mn at three sampling points (A, B and C) produced a significant removal percentage, namely Fe ranging from 85.47% -99.71% and Mn ranging from 0.53% - 50.54% at the time coagulation of 180 s. The initial Fe concentration of the sample was 5.13 mg/l and Mn 2.11 mg/l, while the coagulant dose used was 1.00-1.25 gr/l. Initial concentrations of Fe and Mn, as well as the dose of coagulant used affect the removal of Fe and Mn. Here, the effect of rapid mixing time on turbidity removal can be seen at rapid mixing time was 30 s until the optimum rapid mixing time reached 180 s, the longer the rapid mixing time, the smaller the remaining turbidity in the supernatant. The initial turbidity concentration in the sample was 35.722 NTU and decreased after the coagulation time of 30 s which was 20.722 NTU. The lowest turbidity concentration was achieved at the optimum time of 180 s which was 17.389 NTU (see Figure 5).



Figure 5. The effect of rapid mixing time in turbidity concentration

In the optimum rapid mixing time (180 s), the coagulation-flocculation process works effectively because the chance of contact between the MO seed protein and the colloids that cause turbidity in well water was the most effective. Colloid loading is one of the important factors influencing colloidal stability. The addition of coagulants with different charges with particles in water will result in a decrease in the potential zeta value, forming bonds between particles and floc formation [19].

When the rapid mixing time was increased to 210 s, the remaining turbidity concentration increased to 18.500 NTU and the removal percentage had decreased to 48.212%. Likewise, the rapid mixing time of 240 to 300 seconds had gradually increased until it reached a concentration of 20.722 mg/l. This increase in concentration occurs because the rapid mixing time had reached its optimum limit. Here, Floc has formed will break and cause an increase in the final turbidity after the coagulation-flocculation process. The increase in turbidity value was due to the restoration of colloidal particles due to excessive stirring (see Figure 6).



in turbidity removal

The greatest turbidity removal occurred at the optimum rapid mixing time that was 51.322% when compared Srawaili [8], the turbidity removal in this study was relatively lower. Artificial water with turbidity removal of

99.406%. Initial turbidity concentration of 300 NTU. MO seed coagulant dose used was 1150 mg / L with a coagulation time of 300 s. Research using groundwater samples capable of removing turbidity up to 97.475%. The initial turbidity concentration was 3442.5 NTU. The dose of MO seed coagulant used was 80 mg/l at 180 coagulation time. The initial seconds turbidity concentration and the dose of coagulant used affect the removal of turbidity. The removal percentage in this study before was lower. Because it had a lower initial turbidity concentration value, and the use of fewer coagulant doses. The effect of rapid mixing time can be seen from the different removal percentage results in each variation of the rapid mixing time. The more rapid mixing time increases until the optimum time was reached, the turbidity concentration will gradually decrease. If the coagulation process is carried out with a coagulation time that exceeds the optimum time, the turbidity removal will decrease gradually. Excessive stirring time will destroy the floc that has formed into smaller sizes. This situation results in the floc having a lower positive charge, thereby affecting the capacity to neutralize the negative charge of the particle. The effectiveness of coagulant in binding colloids will decrease if the coagulation time has exceeded the optimum time and will not produce perfect floc formation. The final turbidity will be greater than the initial concentration [20].

Furthermore, in the rapid mixing time of 30 s, floc was formed with a size of $3567.52 \ \mu\text{m}$. The addition of coagulation time to the optimum time results in a gradually larger floc size. Floc size had increased to 4157.12 μ m in optimum coagulation time (180 s). In that time, the coagulant was more perfect because it had the right time for stirring (see Figure 7).



Figure 7. The effect of rapid mixing time in floc size

The difference in floc size was due to differences in the speed and time of coagulation used, and the method, type and dose of coagulant used. Floc size used artificial samples with a turbidity concentration of 50 mg/l. The study was conducted at 120 s with a coagulation speed of 200 rpm using 2.7 mg/l Al2SO4, resulting in a floc size distribution of 450 μ m [21]. The other study, used 7 mg / L of AlCl3 coagulant in an artificial sample with a coagulation speed of 200 rpm for 3 minutes and a

flocculation speed of 40 rpm for 10 minutes, a final floc of 410 µm was produced. The initial turbidity concentration and the dose of coagulant used affect the removal of turbidity [22]. Longer rapid mixing time will give more opportunity to the MO seed protein to contact and bind colloid, so that the agglomeration process goes well. In these conditions, the agglomeration speed was greater than the speed of floc destruction, so that floc formed with a larger size. If the rapid missing time was added past the optimum time, it would cause the formation of floc which had formed, resulting in a smaller final floc size. This was in accordance with the results of the study. Can be seen when the rapid mixing time had passed the optimum time (180 s), there was a decrease in floc size to the last variation of coagulation time (300 s) with floc size of 3,655.52 µm.

D. Analysis of Parameter Correlation

Analysis of parameter correlation in this study using SPSS version 16 (see Table II).

Table II. Water sample qua	alıty
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			Fe	Mn	Turbidity	Floc SIze
<i>Spearman</i> 's rho	Fe	Correlation Coefficient	1.000	0.967**	0.746*	-0.298
		Sig. (2-tailed)	-	0.000	0.013	0.403
	Mn	Correlation Coefficient	0.967**	1.000	0.809**	-0.370
		Sig. (2-tailed)	0.000	-	0.005	0.293
	Turbidity	Correlation Coefficient	0.746*	0.809**	1.000	- 0.778 ^{**}
		Sig. (2-tailed)	0.013	0.005	-	0.008
	Floc Size	Correlation Coefficient	-0.298	-0.370	-0.778**	1.000
		Sig. (2-tailed)	0.403	0.293	0.008	-

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Based on Spearman Rank correlation analysis, Fe residual concentrations and residual Mn concentrations had a very strong, positive and significant correlation. The correlation coefficient (r) between these two parameters was 0.967 and the significant value (p) was 0,000. This correlation shows that the smaller the concentration of residual Fe, the smaller the concentration of residual Mn in the supernatant. This was because Fe and Mn are metals which often coexist in well water [1]. The correlation between residual Fe concentration and turbidity showed a strong correlation (r = 0.746), positive and significant (p = 0.013). These two parameters were interconnected and significant. The smaller the concentration of Fe residue in the supernatant, the turbidity value was also smaller. Whereas the remaining Mn and turbidity showed a very strong correlation (r =(0.809), positive and significant (p = 0.005). As with Fe, a decrease in residual Mn will be followed by a decrease in residual turbidity. Remaining Fe and Mn have a significant correlation with turbidity. Ground water or well water in Indonesia generally contains Fe and Mn. Increased concentrations of Fe and Mn are usually accompanied by increased turbidity [23]. The remaining Fe concentration and floc size showed a very weak correlation (r = -0.298), negative and not significant (p =0.403). A negative sign on the value of r means that there was an inverse correlation between the remaining Fe and floc size. The smaller the concentration of the remaining Fe in the supernatant, the larger the size of the flock However. the correlation between formed. concentrations of Fe residue with floc size was very weak. Similar to Fe, the remaining Mn concentration and floc size showed a very weak correlation (r = -0.370), negative and not significant (p = 0.293). This was because the size of the floc formed was not only influenced by Fe and Mn, but also affected by turbidity caused by colloids in well water.

Here, the correlation between turbidity and floc size showed a strong interpretation (r = -0,778), negative and significant (p = 0.008). The negative sign illustrates that there is an inverse correlation between turbidity and floc size. The smaller the turbidity concentration in the supernatant, the greater the size of the floc formed, and vice versa. This is consistent with the theory the greater the size of the floc, the more colloid is deposited, so the more efficient the process of coagulation and flocculation [25]. Furthermore, if it was seen from the significance value, it can be seen that there was a significant correlation between turbidity and the size of the floc formed.

4. CONCLUSION

The effect of rapid mixing time can be seen from the different removal percentage results in each parameter. The more rapid mixing time increases until the optimum time was reached, the Fe, Mn and turbidity concentration will gradually decrease. The effect also confirmed in floc size formed. Longer rapid mixing time will give more opportunity to the MO seed protein to contact and bind colloid, so that the agglomeration process goes well. It made the floc being bigger. If the rapid missing time was added past the optimum time, it would cause the formation of floc which had formed, resulting in a smaller final floc size

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