



THE ABILITY OF A NATURAL FLOCCULANT 'MORINGA OLEIFERA' IN REDUCING THE AMOUNT OF SEAWATER REVERSE OSMOSIS REJECT WATER'S DISSOLVED SOLIDS

Iva Rustanti, Wahyono Hadi and Agus Slamet

Department of Environment Technology, Institut Teknologi Sepuluh, Nopember, Surabaya, Indonesia

E-Mail: wahyono.its@gmail.com

ABSTRACT

Brine water- which derived from *seawater reverse osmosis reject water*(SWRO), has an high amount of dissolved solids (TDS). *Brine water* also contains NaCl concentrates, that in huge quantities has certain economic values, as a raw material in *chlor-alkali* industry, the regeneration of resin-ion exchange and any other substantial benefits. The early stage of NaCl recovery process from reject water starts with separation phase of NaCl from various mineral impurities exist mostly in Calcium and Magnesium. The main purpose of this research was to discover optimum condition of natural flocculant *Moringa oleifera* (MO) on decreasing impurities mineral brine water from SWRO reject water, so that it could produce NaCl solution high concentrate. In this study, response surface methodology (RSM) approach was used to optimize concentration of NaOH as precipitant, flocculant dosage and flocculation velocity gradient (G), and the results will be measured as maximum decreasing of TDS impurities. The final result of this research shows TDS impurities is succeeded to be decreased by the *Moringa oleifera*'s extract in the amount of 84-90%.

Keywords: waste water SWRO, *moringa oleifera*, flocculant, TDS.

1. INTRODUCTION

Desalination method with seawater reverse osmosis (SWRO) has already dominated seawater treatment process by 65% in the entire world (Amri, 2016). This seawater desalination technology is using SWRO to produce *reject water* with mineral salt content that quite high (brine water). Mineral salt content from reject water depends on the membrane efficiency which is used in this research, approximately around 55 - 60%, with extreme concentration 90% (Hastuti & Wardiha, 2012). Reject water also comprehends with leftover desalination process chemicals such as anti-scaling, anti-fouling, biocodes, chemical cleaning and heavy metal from corrosion process (Einav *et al.*, 2003; Höpner and Lattemann, 2003; Lattemann and Höpner, 2008; Morton *et al.*, 1997).

Desalination process reject water with SWRO according to Praneeth *et al.*, (2014) has pH 8.8, conductivity 62.6 mS/cm and TDS around 40.000 - 61.000 mg/L. TDS is being dominated by ions Ca^{2+} , Mg^{2+} , Na^{+} , Cl^{-} , SO_4^{2-} and HCO_3^{-} . If its being directly disposed to the open sea environment without having any process, it probably will damage the receiving environment, for example the existing of anoxic condition at the bottom of the sea and also damage the species that lives especially macrobenthos (Mohamed *et al.*, 2005; Raventos *et al.*, 2006).

Some of the sea species are highly affected by the reject water disposed, such as seaweed *Cymodoceanodosa* and *Caulerppaprolifera* or red algae (*Rissoellaverruculosa*). So that it needs some advanced efforts to minimize the harm effect; like the *recovery* of NaCl from *reject water* (Sadhvani *et al.*, 2005).

The recovery of NaCl from SWRO membrane disposed reject water can produce NaCl solution until concentration 26% (Melián-Martel *et al.*, 2011). NaCl solution with concentration 6 - 12% is required for ion

exchange resin regeneration, while NaCl concentration 20 - 26% mostly required for industry such as the raw material of soda industry (NaOH).

The early stage of NaCl recovery process from reject water is the NaCl segregation stage from various impurities minerals on the reject water. Selective sedimentation process has been proven quite effective to separate NaCl from various impurities minerals especially ions Ca^{2+} and Mg^{2+} . The common precipitous is NaOH and Na_2CO_3 (Melián-Martel *et al.*, 2011). On the other hand, the addition of natural flocculant co-precipitous in the selective sedimentation is very helpful to sedimentation process regarding the neutralization of residual electrons, and interparticle bridging forming (Vigneswaran *et al.*, 2004; Yin, 2010). The adoption of natural flocculant can increase sedimentation process affectivity by 30% (Darwish *et al.*, 2013), and also being expelled from the amount of inorganic solutes enhancement in processed water.

Research regarding natural ingredients as a coagulant has been done a lot. Research done by Aslamiah *et al.*, (2013) regarding coagulation activity of *Moringa* seed extract (*Moringa oleifera* L.), claims that the extract is way more effective compared to alum. *Moringa* seed extract can reduced turbidity amount by 81%, which alum can only reduced by 58%. The addition of *Moringa* seed extract effects waste water pH on the normal range, whereas the alum addition decreases the pH (becomes highly acid). *Moringa oleifera* can be functioned as coagulant because it has protein group that contain cationic coagulating agent. That group has molecular weight 3-6.6 kDa and pH Isoelectric (pI) above 9.6 (Ghebremichael *et al.*, 2005; Okuda *et al.*, 2001).

A lot of research about natural coagulant *Moringa oleifera* (MO) only focused on the turbidity and suspended solids of waste water removal. There is still very few



information regarding the effectively of MO usage as flocculant to decreasing the dissolved solids on alkaline condition (pH > 10).

This research aims to evaluate natural flocculant impact *Moringa oleifera* (MO) on decreasing impurities mineral brine water (ions Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-}) from SWRO reject water, to produce NaCl solution high concentrate.

2. MATERIAL AND METHOD

This research was done on a laboratory scale with batch system method. Research variable involve the dosage of flocculant *Moringa oleifera* (gr/L), NaOH concentration (%) and flocculation gradient velocity (G , sec^{-1}). This research is designed with Surface Response Methodology (RSM), to analyze the impact from various independent variables / design factors that will affect the respond, until it reaches optimal response condition (Harfouchi, Hank and Hellal, 2016).

2.1 Materials

2.1.1. Reject water SWRO

Reject water SWRO as the raw water used in this research originally comes from original waste water of the membran SWRO at power plant installation in East Java, Indonesia, taken with composite random sampling method during May to August 2017.

2.1.2. Chemical reagents

All the chemicals was used in this research were for analysis such as NaOH (CAS No. 1310-73-2, Merck KGaA), n-Hexane (Index No. 601-037-00-0, Merck KGaA), NaCl (CAS No. 7647-14-5, Merck), Sodium Carbonate anhydrous (CAS 497-19-8, Merck).

2.1.3. Extract of *Moringa oleifera* (MO)

Moringa oleifera plant that being used in this research obtained from local collectors in Jombang, East Java, Indonesia. Part of the plant used was the white colored skinless seeds. The dried seeds being processed with coffee grinding mill, then being crushed with mortal and sieved, until the size of Moringa powder 40 - 60 mesh. Moringa seeds contains fat by 0.1 gr/100 gr ingredients (Fahey, 2005). Fat can damage protein solvability in the water, so then it has to be eliminated. The process of fat elimination on Moringa seeds complies work procedure from Susanti *et al.* (2015) and Hidayat, (2009), which gives Hexane solvent to Moringa powder with ratio 1:4 (b/v). Hexane will dissolve fat and floats when centrifuged by 5000 rpm for 10 minutes on room temperature. Supernatant in the form of Hexane was disposed, and the fat-free Moringa sediment poured into beaker glass, and keep being stirred to keep the remaining hexane evaporated. The fat-free Moringa powder then being added with NaCl solution 1 M to extract the protein on

Moringa according to work procedure done by Okuda *et al.* (2001), Sánchez-Martín *et al.* (2012), Fatehah *et al.* (2013), Aslamiah *et al.*, (2013) and (Prihatinningtyas, 2013) which is 5 gr MO powder plus 100ml NaCl solution 1M and keep being stirred with 100 rpm speed for 1 hour. Final extraction filtrate was clear yellowish solution.

2.1.4. Equipments

Jar test equipment used was Jar Test Model JT 203/6 with six 1 L vats, measuring ion in solution using Radiometer ABL 77 Ion analyzer, pH (pHmeter-PG 1800 GEHAKA), chlorides (water kit- Alfakit).

2.1.5. Fourier transform infrared (FT-IR) spectroscopy

A qualitative analysis to reveal the specific surface functional groups on *Moringa oleifera* extract was performed by FT-IR transmission spectra using KBr technique. The analysis was carried out on MAGNA-IR 560, in the wave number of 400-4000 cm^{-1} .

2.2 Methods

2.2.1 Coagulation - Flocculation test

Coagulation - flocculation test was done at various speeds according to variation of conducted treatment research. Flash mixing performed with G factor 390 sec^{-1} for 1 minute, followed by slow mixing for 9 minutes with G factor variation 100 - 75 - 25, 100 - 50 - 25 and 100 - 50 - 10 sec^{-1} . The addition of NaOH solution variable and Na_2CO_3 10% solution are given into reject water sample simultaneously during flash mixing, after that is the addition of *Moringa oleifera* extract variable. Separation of filtrate-sediment performed after 60 minutes jar test process has been done. TDS parameter is measured from the filtration residual

2.2.2 Response surface design

The optimum condition done on research variety involves NaOH solution concentration as precipitate, the dosage of flocculant, and a flocculation gradient rate to remove ion Ca^{2+} , Mg^{2+} , sulfate and carbonate ions. Response surface design for optimum condition quotation was done with two experiment stages; 1st and 2nd experiment structure.

The 1st experiment structure

The 1st experiment structure is the stage of screening experiment with two level fractional factorial design (2^{k-p}). Screening experiment stage was done to identify factors that have huge impact on response. While using two level fractional factorial design, assumed that there was factor k with -1 code for low level and +1 for high level. The codes and scores 1st experiment structure displayed on Table-1, and the combination of 1st structure experiment displayed on Table-2.

**Table-1.** The codes and scores 1st experiment structure.

Factor	Codes	level		
		Low (-1)	0	High (1)
Flocculant Dosage (gr/L)	X ₁	10	20	30
NaOH Concentration (%)	X ₂	20	30	40
G (sec ⁻¹)	X ₃	100-50-10	100-50-25	100-75-25

Table-2. The combination of experiment handling 1st structure.

Std structurer	Run structurer	CenterPt	Blocks	X ₁	X ₂	X ₃	Respons
3	1	1	1	-1	1	-1	y ₁
6	2	1	1	1	-1	-1	y ₂
5	3	1	1	-1	-1	1	y ₃
8	4	1	1	1	1	1	y ₄
2	5	1	1	1	-1	-1	y ₅
1	6	1	1	-1	-1	1	y ₆
7	7	1	1	-1	1	-1	y ₇
4	8	1	1	1	1	1	y ₈

The 2nd experiment structure

This phase was done right after response optimum territory has been discovered from 1st experiment structure. The 2nd experiment structure held to perceive squared curve on the response surface (Harfouchi *et al.*, 2016). Central Composite Design (CCD) is commonly used to estimate 2nd structure response surface model. Input variable pointed into a code as $x = (x_1, \dots, x_k)$. CCD consists of 3 (three) sections which are:

- Corner points n_f with $x_i = -1$, or 1 where $i = 1, \dots, k$, that creates factorial section on the design.
- Centre points n_c with $x_i = 0$, where $i = 1, \dots, k$
- Axial points $x_i = \alpha$, or $-\alpha$ where $i = 1, \dots, k$

Result assumption from 1st experiment structure concludes two or three influential variables, so that the optimization with CCD design will be displayed on Table-3.

Table-3. Central composite design.

	Σ Variabel, k	
	2	3
n_f for 2^{k-p}	2	4
Amount of axial points= 2k	4	6
$\alpha = (n_f)^{1/4}$	1.189	1.414
n_c	2	3
Total	8	13

3. RESULTS AND DISCUSSIONS**3.1. SWRO reject water characteristic**

Chemical characteristic of SWRO reject water was used in this study displayed on Table 4 and Table-5.

**Table-4.** Chemical characteristic of SWRO reject water.

Parameters	Units	Total amount
Calcium	mg/L Ca ²⁺	630.83
Magnesium	mg/L Mg ²⁺	1302.5
Strontium	mg/L Sr ²⁺	3.20
Barium	mg/L Ba ²⁺	<0.0111
Silicate	mg/L SiO ₂	<0.26
Nitrogen	mg/L N	0.0004
Sulfate	mg/L SO ₄ ²⁻	6278
Bicarbonate	mg/L HCO ₃ ²⁻	116.7
Chlorides	mg/L Cl ⁻	21000
Sodium	mg/L Na ⁺	12400
Fluorides	mg/L F ⁻	1.484
Potassium	mg/L K ⁺	2125
Boron	mg/L B	3.79
pH	-	6.7
Conductivity	μS/cm	>1413
Dissolved Solids	mg/L	47790

Table-5. Chemical composition SWRO reject water.

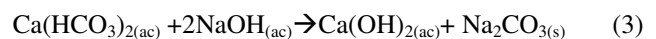
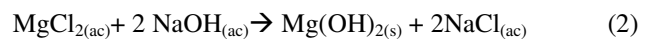
Compounds	meq/L	mg/L	
Ca(HCO ₃) ₂	1.85	153.74	0.32%
CaCl ₂	29.69	1647.79	3.45%
KCl	54.47	4058.02	8.49%
MgCl ₂	107.2	5108.08	10.69%
Na ₂ SO ₄	130.71	9284.33	19.43%
NaCl	408.42	23892.57	50.11%
Other Compounds (SiO ₂ , BaCl ₂ , NaF)			7.51%
Total Amount TDS impurities		20251.96	

The total amount of disposed TDS impurities in SWRO reject water is 20251.96 mg/L.

In chemical precipitation, clarification and filtration stage, the addition of precipitants will remove the dissolved solid impurities. Table-5, shows that most of the calcium appearing as CaCl₂. These impurities respectively removed by chemical precipitation sodium carbonate (Na₂CO₃) solution. The reaction that take place are following:



In order to remove magnesium which appear as MgCl₂ and carbonate ion as sodium bicarbonate (NaHCO₃), a sodium hydroxide (NaOH) solution is used. The following reaction occurs:



Throughout this stage, many different metals impurities, such as strontium, potassium, boron, may also precipitate as hydroxides. All the salts that precipitate together will be removed as sludge. The sludge produced in clarification process was formed by the following precipitates: calcium, magnesium, sulphate. For this process, moringa oleifera extract will be used as flocculant. In this research, the filtration process was done using 450 micrometer filter paper.



3.2 The characteristic of extract *Moringa oleifera* active clusters

Identification of coagulation function cluster has been measured with FTIR method (Fourier Transform Infra Red). That FITR method used to quantitatively identify organic/ inorganic compounds. The final check of spectral cluster from *Moringa oleifera* active extract which displayed on Figure-1, shows that specific peak number of *Moringa oleifera* extract occurs on wavelength region 3495, 26 - 455,13(cm^{-1}). Specific peak number indicates

that MO extract has *Aliphatic Primary Amides* and *Primary Aliphatic Alcohol* function cluster. Amide cluster indicates that flocculant is positive polyelectrolyte solvent (Prihatinningtyas, 2013; De Paula *et al.*, 2014).

3.3. The 1st Experiment structure

Response value of filtrate total dissolved solids (TDS) from 1st experiment structure is shown on Table 6. Data processing on 1st experiment structure develops below result shown on Table-7.

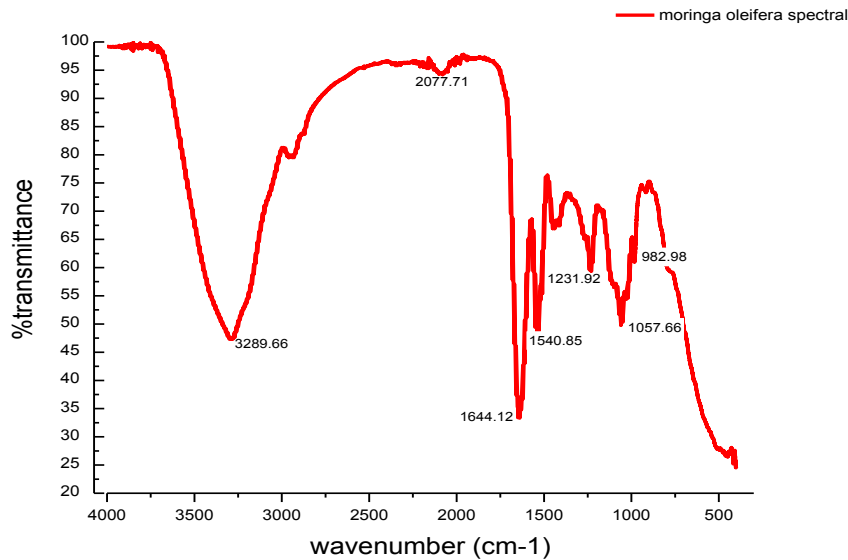


Figure-1. IR Spectral of *Moringa oleifera* extract.

Table-6. Response of combined treatment result.

StdOrder	RunOrder	CenterPt	Blocks	X_1	X_2	X_3	TDS (mg/L)
3	1	1	1	-1	1	-1	24424.69
6	2	1	1	1	-1	-1	16724.02
5	3	1	1	-1	-1	1	13876.15
8	4	1	1	1	1	1	27770.43
2	5	1	1	1	-1	-1	17306.47
1	6	1	1	-1	-1	1	12569.49
7	7	1	1	-1	1	-1	19439.26
4	8	1	1	1	1	1	24254.58

Where:

X_1 : NaOH concentration, %

X_2 : MO flocculant dosage, mg/L

X_3 : G flocculation, sec^{-1}

TDS : TDS filtrate, mg/L



Table-7. The regression coefficient of 1st experiment structure.

Source	Df	Sum of squares	Mean square	F-ratio	P-value
Model	3	187791779	62597260	12.75	0.016
Linier	3	187791779	62597260	12.75	0.016
X ₁	1	30991710	30991710	6.31	0.046
X ₂	1	156758566	156758566	31.94	0.005
X ₃	1	41502	41501	0.01	0.931
Error	4	19631161	4907790		
Total	7	207422939			

Response value of filtrat total dissolved solid from 1st experiment structure was 12569.49 -27770.43 mg/L. The impact of 3 variables on TDS also appropriate with factorial plots graphic which shown on Figure-2. From the regression parameter test done simultaneously in all variables it was concluded that 2 variables which are NaOH concentration and flocculant dosage give a significant effect for model ($P_{value} < 0.05$ or lower than the significance degree $\alpha=5\%$). But one variabel variabel (G flocculation) was not model representative (Figure-2), which can be shown on flat chart.

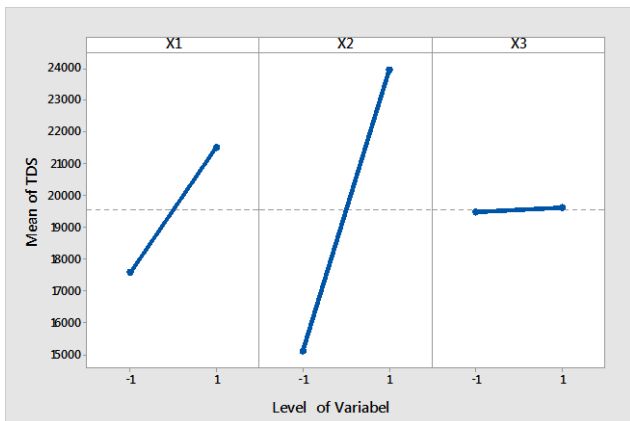


Figure-2. Variables impact on mean of TDS.

Where

- X₁ : Flocculant Dosage (gr/L)
- X₂ : NaOH Concentration (%)
- X₃ : Flocculation gradient velocity (G, sec⁻¹)

It is shown in Figure-2 that flocculant dosage and NaOH concentration have huge impact on filtrate total dissolved solids (TDS). The higher the flocculant dosage level and the NaOH concentration, also resulted higher filtrate TDS. G flocculation delivers less significant impact on filtrate TDS, which can be shown on flat chart. For the 2nd experiment structure, it has been secermined that G flocculation variable is specified on level (-1).

3.4. The 2nd Experiment structure

The 2nd Experiment Structure is used to obtain the quadratic curve on response surface (Montgomery, 2001). Central Composite Design (CCD) is commonly used for model estimating on 2nd experiment structure response surface. Code definition, level score and 2nd experiment structure response variable are shown on Table 8, whereas the CCD design will be shown on Table-9.

The percentage removal of TDS impurities in the filtrate from 2nd experiment structure was 84.38 - 90.59%. This results indicates that concentration of precipitant and dosage flocculant have significant impact toward the removing of TDS impurities (Table-9). The adequacy and significance of the quadratic model was justified by the analysis of variance (ANOVA). The ANOVA summary is given in Table-10.

Table-8. Codes and level scores of 2nd Experiment structure.

Factors	Code	Level				
		-1.414	-1	0	1	1.414
NaOH Concentrations (%)	X ₁	15.86	20	30	40	44.14
Flocculant Dosages (gr/L)	X ₂	5.86	10	20	30	34.14
G flocculation	X ₃	100-50-10				
Response:	y-%TDS					
% filtrate TDS decreased (mg/L)						

**Table-9.** Central Composite Design (CCD) of 2nd Experiment structure.

StdOrder	RunOrder	PtType	Blocks	X ₁	X ₂	y-%TDSi
7	1	-1	1	0	-1.41421	89.00
11	2	0	1	0	0	86.18
4	3	1	1	1	1	90.59
13	4	0	1	0	0	86.04
8	5	-1	1	0	1.41421	84.62
5	6	-1	1	-1.41421	0	89.98
9	7	0	1	0	0	85.77
2	8	1	1	1	-1	84.38
10	9	0	1	0	0	86.06
3	10	1	1	-1	1	85.20
6	11	-1	1	1.41421	0	84.78
1	12	1	1	-1	-1	85.73
12	13	0	1	0	0	85.71

Table-10. ANOVA 2nd Experiment structure test result.

Source	Df	Sum of squares	Mean square	F-ratio	P-value
Model	5	12421818	2484364	3.50	0.048
Limier	2	1318745	659373	0.40	0.035
X1	1	16336	163360	0.10	0.012
X2	1	1155385	1155385	0.70	0.031
Square	2	10510173	5255087	0.70	0.031
X1*X2	1	10375315	10375315	6.28	0.041
X2*X2	1	3141	3141	0.00	0.036
2-way Interaction	1	592900	592900	0.36	0.068
X1*X2	1	592900	592900	0.36	0.068
Error	7	11571105	1653015		
Lack of fit	3	1955105	651702	1.27	0.074
Pure Error	4	9616000	2404000		
Total	12	23992923			

The ANOVA on 2nd experiment structure which is shown on Table 10, indicates that with $\alpha = 5\%$, variables such as dosage flocculant and NaOH concentration created significant impact towards model, because $P_{\text{value}} < 5\%$. Variable quadratic also created significant impact towards model, whether the two-way interactions between NaOH concentration - flocculant dosage has no significant impact towards model, because $P_{\text{value}} < 5\%$. Another test procedures that has been done regarding model feasibility is Lack of Fit test. The statistical hypothesis is suitable regression model (lack of fit is not found) if $P_{\text{value}} > \alpha$. Table-11 shows that lack of fit score has $P_{\text{value}} = 0.074$ or $>$ significance degree $\alpha = 0.05$, so that there is no model gap. Table 11 also indicates that $F_{\text{count}}^{\text{model}} = 3, 50$ and $F_{\text{table}} = F_{(5;12;0.05)} = 3.11$ (Iriawandan

Astuti, 2006). If $F_{\text{count}} > F_{\text{table}}$, means that independent variables have significant impact towards model.

Figure-3 and Figure-4, show surface plots and contour plots of the predicted response function to two variabls, the other variabls was kept in central of interval. The removal efficiency of TDS impurities decreases when concentration of precipitant (NaOH) and Moringa oleifera extract dosage increases up to 34% NaOH concentration and coagulant dose 21 gr / L. The TDS impurities will increase again when given more concentrated NaOH and more coagulant dosage.

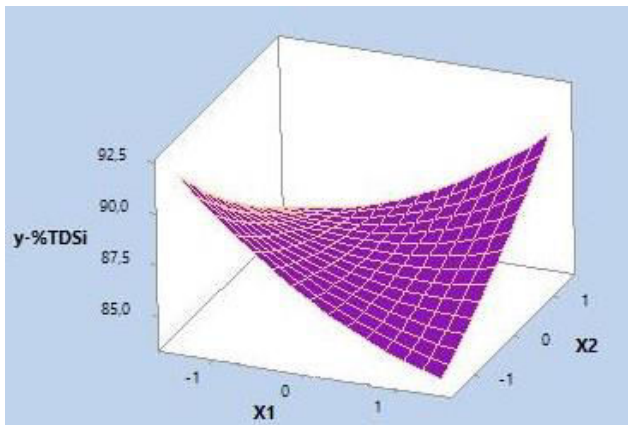


Figure-3. Surface plot of y-%TDS_i vs X₁;X₂.

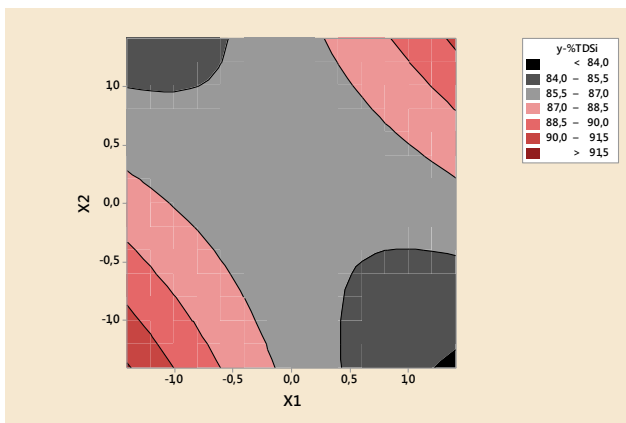


Figure-4. Contour plot of y-%TDS_i vs X₁;X₂.

where y-%TDS:percentage decrease of dissolved solid in filtrat

X₁ : NaOH concentration variable (%)

X₂ : MO extract dosage, mg/L

3.5. The optimum point model

According to Table 10, it also known that P_{value} for linear model, square < α (0, 05), then the perfect model is quadratic model, which is :

$$y\text{-}\%TDS = 103.8 - 0.700 X_1 - 0.655 X_2 + 0.00537 X_1^2 + 0.00342 X_2^2 + 0.0169 X_1 * X_2$$

where

y-%TDS :percentage decrease of dissolved solid in filtrat

X₁ : NaOH concentration variable (%)

X₂ : MO extract dosage, mg/L

3.6. Optimization design by the method of desirability function

Optimum condition for removal TDS impurities process were searched by applying desirability function. As shown in Figure-5, the optimum point of the decreasing TDS impurities quadratic model using Moringa oleifera is at 15.85% NaOH concentration, dosage of flocculant 5.86 gr/ L, gradient of flocculation velocity (G)

100-50-10 sec⁻¹ with the 91.85% decrease of TDS impurities.

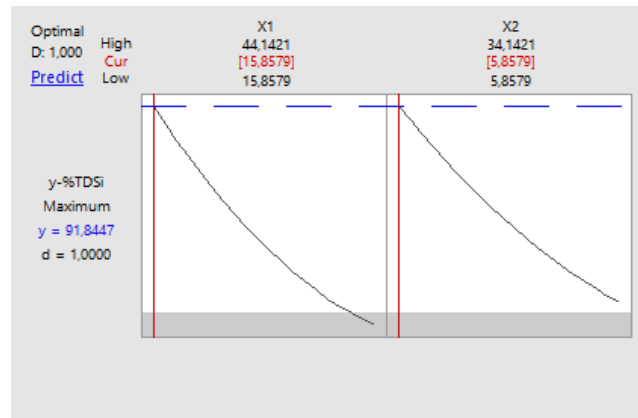


Figure-5. Desirability function of TDS impurities from SWRO reject water.

3.7. Performance of moringa oleifera extract in flocculation process

Figure-1 show that in Moringa oleifera extract many polipeptide such as polyamide, poly(N-methyl acrylamide), phthalamide polymer, pantothenyl compound. these compounds indicate that the moringa oleifera extract is amphoteric because it has two active groups, polyelectrolyte amide cluster which positively charged and polyelectrolyte hydroxyl cluster which negatively charged.

Certain scientific researches identify that Moringa oleifera can be functioned as flocculant because it conceive soluble protein in the water with low molecule (Fahey, 2005). Protein will be positively charged when it dissolved in the water. Protein will be acted as positive synthesis substance. The most possible mechanism that will occur on the moringa coagulation process is adsorption and voltage neutralization or adsorption and unstable particle bonds. It's hard to secermine which mechanism that possibly occur because both of it occurs simultaneously (De Paula *et al.*, 2014). The pH is an important factor that influences coagulation process. Optimum pH for each flocculant is different. MO optimum pH is 6 - 8 (Hendrawati *et al.*, 2016).

The positive charge that being released into solvent caused solvent pH decreased from 11 to 7 - 8. That acid condition is moringaflocculant optimum pH. Metal ion degradation occurs because of the hydroxyl cluster which negatively charged being removed by moringa amphoteric protein, and bonding with metal ion. It also supported by the fact that treatment without flocculant, the formed hydroxide metal due to NaOH addition and Na₂CO₃ is remain stable and can't be settled. Metal sediment will become more stable if the water pH is above 10,5 (Jiang, 2015).

4. CONCLUSIONS

Natural flocculant active cluster from Moringa oleifera extract is Aliphatic Primary Amides and Primary



Aliphatic Alcohol. Amide cluster shows that polyelectrolyte flocculant solvent is positively charged, while polyelectrolyte hydroxyl cluster is negatively charged. The mechanism that occurs on the MO flocculant process is adsorption and voltage neutralization or adsorption and unstable particles bond.

The test results of analysis response surface showed that the variables of flocculant dosage and NaOH concentration grant a huge impact on the amount of soluble degradation impurities which dissolved in the filtrate, compared with the flocculation velocity gradient (G) variable. The model generated from the response analysis is a quadratic model.

The amount of degradation impurities compound from SWRO reject water has optimum point to generate the highest percentage decrease which is NaOH concentration by 15.85% ; Moringa oleifera dosage by 5.86 gr/L. Fit predicted is decreased to 91, 84 ± 1%.

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