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Implementation of Freundlich Equation Absorption of Calcium and Magnesium Ions on Saturated Salt Solution

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Abstract

Traditional salt contains NaCl between 80-92% and the other is impurity such as magnesium (Mg), calcium (Ca), potassium (K) and sulfate (SO_4) ions., The NaCl content of salt is under government regulations, namely NaCl 94.7% for consumption salt and NaCl above 98% for industrial salt. Improved salt quality is done through increasing NaCl concentration or decreasing concentration of impurities. In this research, salt quality improvement was carried out by reducing the concentration of impurities through ion exchange methods. The ion exchange method is carried out by using 2 (two) types of resin namely cationic resin and anion. Cationic resin serves to exchange positively charged ions such as Mg^{2+}, Ca^{2+} and K^+ ion and anionic resin for negatively charged ions such as SO_4^{2-}. The purpose of this study is to obtain Freundlich mathematical equations which can be used to calculate resin requirements. The study was conducted using a stirred tank with a variable amount of cationic resin from 25-150 grams per 1 liter of saturated salt solution and stirring time of 5 - 30 minutes. The saturated salt solution used contains 28.4% NaCl, 0.4% calcium and 0.09% magnesium. The results obtained were 36.99% NaCl, 0.025% Calcium and 0.044% Magnesium, 25 minutes contact time, 100 grams cation resin Freundlich equation obtained Calcium ion: ln (x / m) = 1.087 ln C - 4.2282, R^2 = 0. 9544, Magnesium Ion: ln (x / m) = 5.6278

Keywords: Salt impurity, saturated salt solution, chemical adsorption, and resin.

INTRODUCTION

94.7 % (SNI 3556-2016) and for industry more than 98% and pharmaceuticals are above 99.5% (SNI 0303-2012). The salt traditional produced in salt industry in Indonesia contains NaCl ranging from 80-93% and the other is known as impurities as calcium (Ca), magnesium (Mg), and sulfate (SO4) ions. Base on the quality of the salt produced and the requirements for consumption and industry salt a study is needed to increase NaCl contain or decrease of its impurities. Some method that can be used to decrease of salt impurities are chemical processes for example by adding sodium phosphate sodium carbonate (Pujiastuti et al, 2016) and Ion Exchange Method. Ion exchange method is a method that using ion exchange media is called Resin. Cationic resin can exchanging positive ion (Ca^{2+}, Mg^{2+} and K^+) and anionic resin for negative (SO_4^{2-}).

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Ion Exchange Mechanism

Ion exchange mechanism can be illustrated as follow :

Cationic Resin Mechanism :

$$B_1^+ + R^- B_2^+ \rightleftharpoons B_2^+ + R^- B_1^+$$

Anionic Resin Mechanism :

$$A_1^- + R^+ A_2^- \rightleftharpoons A_2^- + R^+ A_1^+$$

Which :

B_1^+, B_2^+ = Cations of 2 different species (types).

A_1^-, A_2^- = Anions of 2 different species.

R-, R + = Exchange media of anionic and cationic materials (Pujiastuti, 2008)

B_1^+ is positive ion in solution, B_2^+ is positive ion in cationic resin (H^+)

A_1^- is negative ion in solution, A_2^- is negative ion in anionic resin (OH^-)

There is a mechanism on ion exchange method that known as ion selectivity where ions with the largest valence ion will exchange first, if ions have the same valence, ions that having the greatest atomic weight will exchange firs.

Thus it can be described as follows ((Montgomery, 1985):

Ion Cation: $Ca^{2+} > Mg^{2+} > K^+ > Na^+$

Anion Ion: $SO_4^{2-} > Cl^-$

There are several factors that can affect the performance of ion exchange, including:

1. The type of resin used

The type of resin in the ion exchange process determines the mechanism. Each type of resin has a different physical resin structure. (Toteja, 1997).

2. Contact time.

The effect of contact time on ion exchange shows that the percentage of absorbed metal ions increases with increasing equilibration time but at a certain time it will stabilize and the reaction will go back and forth, where the absorbed metal ions will be released again. (Pehlivan & Turkan, 2006).

3. Amount (weight)of resin

Increasing the amount of resin has an effect on increasing sorption density, and the number of metal ions per unit of mass adsorbed increases. (Pehlivan & Turkan, 2006)

4. pH

Effect In general, experimental conditions, such as pH concentration, have a strong effect on the distribution coefficient, Kd and can be used as a comparative measure of the efficiency of various pH exchangers. pH value is very significant for exchange performance. (Irwin, 1987)

5. Temperature

The value of the equilibrium constant (Kd) for metal ions and reaction products is affected by temperature. Ion exchange reactions are endothermic (requires heat) in divalent cations. The equilibrium constant for the reaction increases with higher temperatures, also the reaction product increases at high temperatures. (Pehlivan &Turkan, 2006).

The ion transfer mechanism from solution to ion exchange media can be illustrated by ion adsorption method. The adsorption is a surface phenomenon, the place where accumulation of interfaces (interphase) of two phases interact. In other words, adsorption is a molecular binding event of substances from a fluid in both liquid and gas forms to the surface of solid substances (Maron S.H., Maron 1990). This mechanism depends on the affinity between adsorbent (ion exchange media) and adsorbate (ion ion solution).

There are two types of adsorption, namely physical adsorption and chemical adsorption (Treybal, 1981).

1. Physical Adsorption

The physical adsorption mechanism is almost the same as the condensation process Physics adsorption Van der Waals is an attractive force between molecules of solid objects with substances absorbed. This adsorption can occur on all solid-liquid surfaces, also if the fluid does not approach or below the dew point or the solid is not very porous filled with fine capillaries (Smith, 1981).

2. Chemical Adsorption

The chemical adsorption is one form of chemical adsorption (Treyball, 1981). Where ion exchange occurs between electrolytes in solids and electrolytes in the fluid. This adsorption involves forces that are far greater than physical adsorption. According to Langmuir, molecules = adsorbed molecules are attracted to the surface by valence forces as they often do between atoms in a molecule. This adsorption forms new molecules. There are two kinds of chemical adsorption, namely: chemical adsorption activation, which is energy adsorption near zero so that it occurs very quickly and chemical adsorption by activation, the reaction rate depends on activation energy with a certain temperature.

Isothermal Adsorption

Isothermal Adsorption is adsorption with phase concentration absorbed in bulk liquid. Adsorption studies can be more easily observed in conditions that are isotherm (constant temperature). In the adsorption process, the study is how much absorbent material is needed, the amount of waste water to be processed. The equation often used to describe isotherm adsorption is Langmuir isotherm, Freundlich isotherm and BET isotherm (Brunaur, Emmet, Teller). The Freundlich and Langmuir equation models are most often used for wastewater treatment.

a. Isotherm Langmuir

This model was first developed for the process of absorption of gases on solid surfaces. Langmuir considers the surface of a solid substance consisting of elementary spaces, each of which can adsorb one gas molecule and the presence of gas molecules in one space will not affect the nature of the space nearby. This model is based on several assumptions :

- Maximum adsorption that occurs during a comprehensive monolayer.
- The amount of energy is constant and does not depend on the nature of the surface.
- Adsorption occurs without the interaction between the adsorbate molecules.

The Langmuir equation in a solid-liquid system is formulated :

$$\frac{x}{m} = \frac{a.b.Ce}{1+b.Ce} \qquad (2.1)$$

The equation (2.1) can be written to be

:

$$\frac{(x/m)}{Ce} = \frac{a.b}{1+b.Ce} \qquad (2.2)$$

$$\frac{Ce}{(x/m)} = \frac{1}{a.b} + \frac{1}{a}Ce \qquad (2.3)$$

b. Isotherm Freundlich

This equation is generally accepted and very satisfying if applied to a dilute solution. In solid-liquid systems it can be formulated (Metcalf & Eddy, 1991):

Equations:

$$\frac{x}{m} = k\ Ce^{1/n} \quad (2.5)$$

The equation (2.5) can be written to be

$$\log \frac{x}{m} = \log k + \log Ce^{1/n} \quad (2.6)$$

$$\ln \frac{x}{m} = \ln k + 1/n \ln Ce \quad (2.7)$$

Which :

x/m = the amount of ion absorbed by the absorbent media

Co = initial concentration

Ce = component equilibrium concentration after adsorption

a, b, = the empirical constant of Langmuir isotherm

k, n = Freundlich's empirical constant

METHODS

The material used in this study is traditional salt from Sampang Madura with a NaCl content of 92.03%, Ca^{2+} : 0.5%, Mg^{2+} : 0.56%, and SO_4^{2-} : 2.03%., Aquadest and Cationic and Anionic resin obtained from CV Van Jaya Medica Surabaya. The saturated salt solution is made by dissolving as much as 360 grams of salt in 1000 ml of water. The variables in this study were stirring time (5,10,15,20,25 minutes), weight of cation resin (25,50, 75, 100, 125, 150 gr) while the volume of saturated salt solution (1000 ml) and speed stirring of 200 rpm. A 1000 ml saturated salt solution is added cationic resin according to the variable carried out. The solution is stirred at a speed of 200 rpm during the specified time variation. after that filtration is carried out to separate the resin and the solution. The filtration solution was evaporated and the salt produced was analyzed for the content of NaCl and Ca^{2+} ions, Mg^{2+} ions, SO_4^{2-} ions.

RESULT AND DISCUSSION

The quality of the saturated salt solution used in this study is acontain 28.40 % of NaCl, Ca^{2+} : 0. 252 gr /liter, Mg^{2+} ion 0.324 gr/liter, K^+ : 0.144 gr/liter and SO_4^{2-} : 1.44 gr /liter.

Table 1. Effect of weight of cation resin on final concentration of solution

Weight of Cationic Resin (gr)	Time of stirring (minutes)	Ion Concentration (gr/ liter)		
		Ca^{+2}	Mg^{+2}	K^+
25	5	0.2088	0.2484	0.1368
	10	0.2016	0.2412	0.1368
	15	0.1980	0.2340	0.1332
	20	0.1944	0.2160	0.1260
	25	0.1908	0.1980	0.1296
	30	0.1908	0.2016	0.1224
50	5	0.1872	0.2160	0.1332
	10	0.1800	0.2124	0.1332
	15	0.1764	0.1980	0.1296
	20	0.1584	0.1980	0.1188
	25	0.1548	0.1800	0.1224
	30	0.1548	0.1800	0.1152
75	5	0,1620	0.2016	0.1296
	10	0.1512	0.1980	0.1296
	15	0.1476	0.1728	0.1260

	20	0.1404	0.1836	0.1152
	25	0.1368	0.1728	0.1116
	30	0.1404	0.1692	0.1044
100	5	0.1440	0.1800	0.1260
	10	0.1368	0.1728	0.1260
	15	0.1296	0.1584	0.1224
	20	0.1152	0.1692	0.1116
	25	0.1080	0.1620	0.1080
	30	0.1116	0.1620	0.1044
125	5	0.1260	0.1692	0.1224
	10	0.1260	0.1584	0.1260
	15	0.1188	0.1512	0.1188
	20	0.1080	0.1656	0.1080
	25	0.1008	0.1548	0.1044
	30	0.1044	0.1512	0.1044
150	5	0.1188	0.1584	0.1224
	10	0.1080	0.1512	0.1224
	15	0.1116	0.1512	0.1188
	20	0.0972	0.1620	0.1080
	25	0.0936	0.1548	0.1044
	30	0.0963	0.1512	0.1044

Effect of cation resin weight and contact time on final consentrations such Ca^{2+}, Mg^{2+} , K^{+} as shown in table-1. The more cation resins are added, the lower the consentration of Ca^{2+}, Mg^{2+} and K^{+} ions is smaller. The more resin is added the ability of the resin to absorb more and more ions. The longer the contact time, the more absorbed Ca^{2+} ions exceed the magnesium (Mg^{2+}) and Kalium (K^{+}) ions. This is in accordance with the ion selectivity concept, namely in ion having the same valence ion, the greater the ion atomic weight, the more absorbed high into resin.

In the range of 25-30 minutes ion concentration is almost constant. So that it can be concluded that when stirring 25 minutes equilibrium occurs. While the more addition of cation resin, the more impuritis is absorbed (swapped). The Freundlich chemical adsorption equation that can be obtained from the data above is as below.

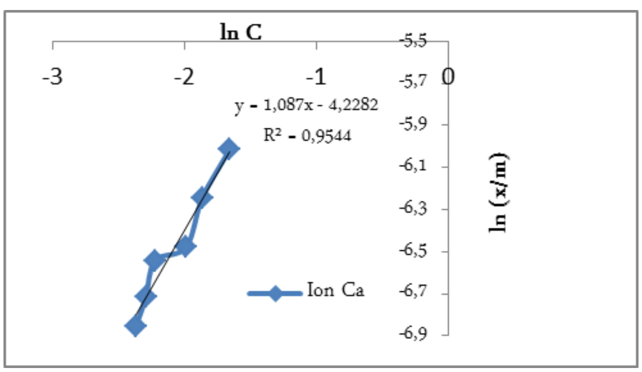

Figure 1 . The Freundlich Equation of Calcium Ion.

The Freundlich Equation for Calcium Ion (Ca^{+2}): $\ln (x / m) = 1.087 \ln C - 4.2282$, $R^2 = 0. 9544$.

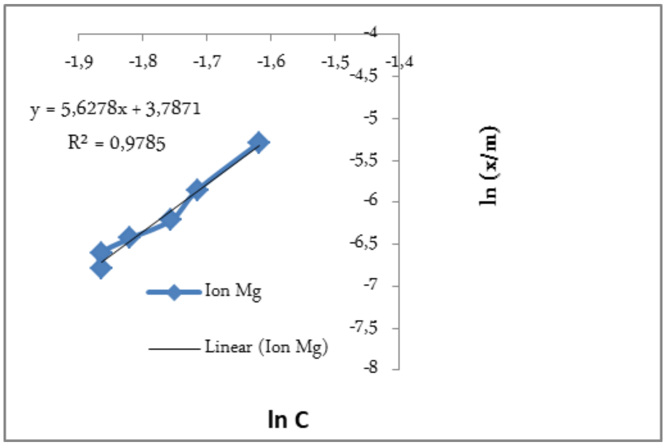

Figure 2 . The Freundlich Equation of Magnesium Ion

The Freundlich Equation for Magnesium Ion (Mg^{+2}): ln (x / m) = 5.6278 ln C +3.7871, R^2 = 0. 9785

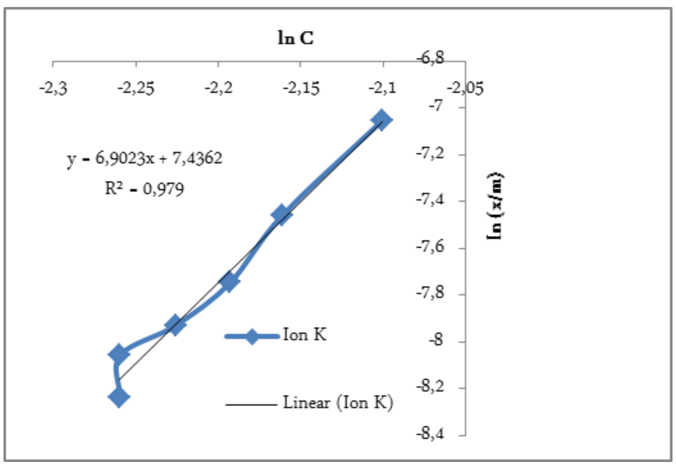

Figure 3 . The Freundlich Equation of Potassium Ion

The Freundlich Equation for Potassium Ion (K^+): ln (x / m) = 6.9023 ln C +7.4362, R^2 = 0. 979

CONCLUSION

The best results were obtained by adding 100 gr of cationic resin for stirring time of 25 minutes. The salt product contains NaCl : 99.41%, Ca : 0.032%, Mg : 0.118%, K : 0.081% and SO_4 : 0.295%.

The Freundlich Equation Form are :

Calcium Ion (Ca^{+2}): ln (x / m) = 1.087 ln C - 4.2282, R^2 = 0. 9544

Magnesium Ion (Mg^{+2}): ln (x / m) = 5.6278 ln C +3.7871, R^2 = 0. 9785

Potassium Ion (K^+): ln (x / m) = 6.9023 ln C +7.4362, R^2 = 0. 979.

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