

REMOVAL OF Mg^{2+} , K^+ , SO_4^{2-} IONS FROM SEAWATER BY PRECIPITATION METHOD

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ABSTRACT

Removal of Mg^{2+} , K^+ and SO_4^{2-} ions in seawater has been successfully done by precipitation in a mixing tank method. This study aims to remove the content of magnesium ions (Mg^{2+}), potassium (K^+) and sulfate (SO_4^{2-}) in sea water with the addition of chemicals disodium phosphate (1.2 % volume), calcium chloride (2 % volume) and sodium hydroxide (2% volume). Stirring is performed at 100 rpm and the pH solution is adjusted to 9. Disodium phosphate serves to bind magnesium ions and potassium, $CaCl_2$ serves to bind the sulfate ion, while sodium hydroxide is used to adjust the pH of the solution mixture and also reacted with magnesium ions. In total, the removal efficiencies of Mg^{2+} , K^+ and SO_4^{2-} ions in seawater were 97%, 96%, and 92%, respectively. The precipitated solids contains component of PO_4^- (14.5%), Mg^{2+} (13.8%), SO_4^{2-} (28.2%), Ca^{2+} (24.1%) and K^+ (1.9%) ions.

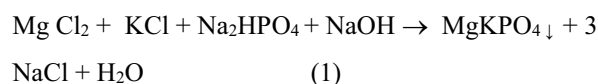
Keywords: sea water, disodium phosphate, calcium chloride, precipitation, removal ions

INTRODUCTION

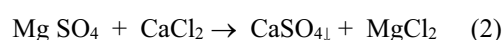
The average waters of the world's oceans contain 3.5% dissolved salts, 96.5% water and average salinity is about 35 g/kg. When salts dissolve in water they usually react with water and dissociate (break apart) into ions, positively and negatively charged atoms or groups of atoms. These ions are either negatively charged anions, or positively charged cations. Six major ions make up > 99% of the salts dissolved in seawater: four cations sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+); and two anions: chloride (Cl^-) and sulphate (SO_4^{2-}). These six ions and the five next most common ones make up the major constituents of seawater and comprise 99.99% of dissolved materials. Sodium chloride ($NaCl$), makes up 86% of dissolved ions in seawater. Many other elements (trace elements) are dissolved in seawater in concentrations less than one part per million (ppm).

The molar concentration of magnesium in sea water is about five times higher than calcium. In fact, both magnesium and calcium are in a delicate equilibrium where slight change in alkalinity and carbon dioxide tension may cause precipitation (Irving, 1926). Jijun et al, (2012) developed the precipitation of calcium and magnesium from seawater using CO_2 . Mg ion can rarely incorporate into the solid precipitates, compared, for example, to calcium salts. The rate of Mg phosphates nucleation is several orders of magnitude lower than that of Ca phosphates, at the same values of pH and total phosphate concentration (Golubeva, 2001). The removal rate of Ca is higher than the removal rate of Mg in pH value between 8.0 and 9.0. In the Mg -free seawater system, the removal rate is high enough in pH value between 8.0 and 9.0. Meanwhile, in the Ca -free seawater system, there is no precipitation between pH 8.0 and 8.3 (Jijun et al, 2012). Precipitation of phosphate is high enough in pH range from 8 to 10. However, it decreased as pH is increased from 10 to 12, probably because of competition between phosphate and hydroxyl OH^- ions (Liu and Warmadhewanti, 2009). Fernando and Lerida (2005) developed a method of

binding magnesium and potassium ions in bittern by disodium phosphate to produce a phosphate-based fertilizer following the reaction:



Magnesium chloride ($MgCl_2$) was more effective than magnesium oxide (MgO) in inducing precipitation reactions between magnesium and phosphate. The magnesium- potassium- phosphate ($MgKPO_4$) precipitation is an efficient method for the simultaneous removal of P and K to yield multi-nutrient products (Xu et al, 2011). In addition, the removal of SO_4 ions from bittern using $CaCl_2$ is using the following precipitation reaction: (6,776,972. AS)



$CaCl_2$ solid is not ionized, but in aqueous solution only $Ca(aq)^{2+}$ and $Cl(aq)^-$ exist. The salvation and ionization of the cations are chemical processes responsible for the heat evolved. Magnesium hydroxide will precipitate from the alkalinity part and calcium sulfate will precipitate from the calcium part. Basically, any solutions of a soluble calcium salt and a soluble sulfate salt can be used to prepare calcium sulfate (Yun-Wei et al, 2011) Most sulfates (SO_4^{2-}) are soluble. $CaSO_4$ is slightly soluble so the yield is may be a little lower than the theoretical.

In the previous study, to improve the quality of the salt is done by purification with the addition of binder impurities. In the process of recrystallization the salt that has been formed then dissolved by water to form the solution of salt. The removal of impurities in salt solution performed by the addition of certain chemicals such as $NaOH$, $BaCO_3$, and $Ca(OH)_2$. This process becomes less efficient due to the salt production process requires two stages of crystallization (Sumada et al, 2012)

Some separation process was carried out for the recovery of salt from sea water which is a chemical treatment (Fernandez, 1993), nanofiltration (Telzhenky et al, 2011), and ion exchange.

This study developed a purification of salt through the removal of ions in sea water by precipitation method. The precipitation is also influenced by the pH of the mixture due to quite diverse the components in sea water. It is important to adjust pH in the precipitation process.

METHODOLOGY

The sea water used in this study is obtained from Segoro Tambak, Sedati, Sidoarjo, East Java Indonesia. Seawater sampling was conducted during different times to obtain the average number of components in sea water. Table 1 shows the concentration of some components of sea water using AAS and Spectrophotometer. In the present study, ions removal from seawater process is done in a stirred tank at 100 rpm, and at room temperature. The concentration of Na₂HPO₄ is 15% w, CaCl₂ is 15% w and residence time is 10, 20, 30 minutes. The first stage of the preliminary process is carried out using each Na₂HPO₄-free seawater system and CaCl₂-free seawater system while the second stage is done using these two chemicals. The first stage: 1) sea water 1000 ml was entered in a stirred tank and then added with Na₂HPO₄ solution in the range of 8-16 ml, stirred for 10 minutes and then added with NaOH 2N solution until the mixture solution reaches pH about 9, then stirred until a specified time. 2) In the same way as point (1) but using the CaCl₂ solution in the range of 10-30 ml. For the second stage: 1000 ml sea water was entered in stirred tank then added with Na₂HPO₄ solution in the range of 8-16 ml, stirred for 10 minutes then added CaCl₂ solution in the range of 10-30 ml; stirred for 10 minutes then added with NaOH solution until the mixture reaches a pH 9 then stirred until a specified time. Figure 1 showed the flow diagram of experimental procedures.

Table-1. The Concentration of some components of sea water (Segoro Tambak, East Java).

No	Parameters	Concentration (mg/L)			Average
		I	II	III	
1	NaCl (%)	1.97	1.99	2.03	1.997
2	MgCl ₂	842.75	872.16	869.42	861.44
3	MgSO ₄	2526.23	1978.56	2164.4	2223.06
4	KCl	308.5	288.06	301.56	299.37
	Total averages				3657.68

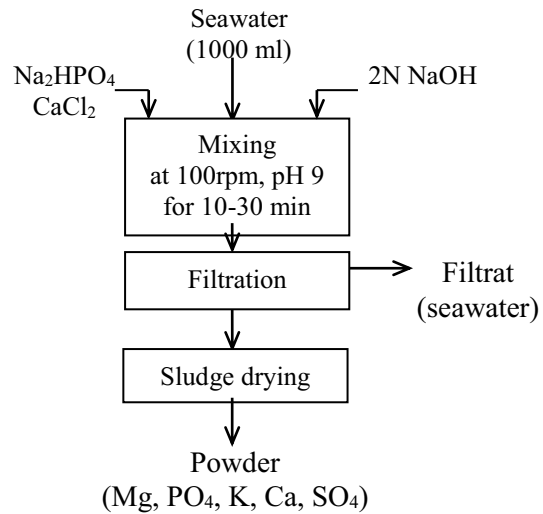


Figure-1. Schematic of experimental procedure for ions removal from seawater

The analysis of components of Na, K, Ca and Mg ions used Absorption Atomic Spectrophotometry (AAS), while for components Cl, SO₄ and PO₄ ions, a spectrophotometer. EDAX and X-ray fluorescence (XRF) were used for component analysis in the precipitated solid product.

RESULT AND DISCUSSION

Figure 2 shows the effect of the volume of Na₂HPO₄ solution on the removal of magnesium ions. The results showed that the larger volume of the solution of disodium phosphate the bigger of magnesium ions are removed until it reaches a constant. The effect of reaction time on the percentage removal rates of the constituent ions of Mg²⁺ dosed at Na₂HPO₄ 12 ml with only 20min when pH value was about 9. This suggests that Mg²⁺ is formed homogeneously under certain conditions and that nucleation is rapid. Due to the abundance of foreign solid phases in a seawater treatment, the principal precipitation mechanism is likely to be heterogeneous, however, precipitation is still expected to be rapid.

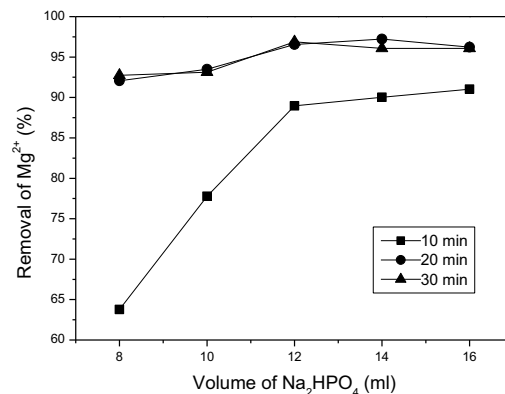


Figure-2. Effect of disodium phosphate (Na₂HPO₄) solution on the removal of magnesium ions.

The reaction time of 30 min is no longer effective because the same ions removal results are obtained with a reaction time at 20min. It indicates the maximum condition in which the Mg²⁺ ions could be separated in addition

solution of 12 ml and a stirring of 20min while the removal percentage of Mg^{2+} ions reached 97.15%.

Figure 3 shows the effect of the Na_2HPO_4 solution on the removal of K^+ ions. The same trend as the removal of Mg^{2+} ions occurs in the removal of K^+ ions. K^+ ions concentration in sea water almost unchanged on the addition of 12 ml to 16 ml Na_2HPO_4 and in residence time from 20 minutes to 30 minutes. The removal rate of K^+ ions reached 96.26 % in 20min and pH 9.

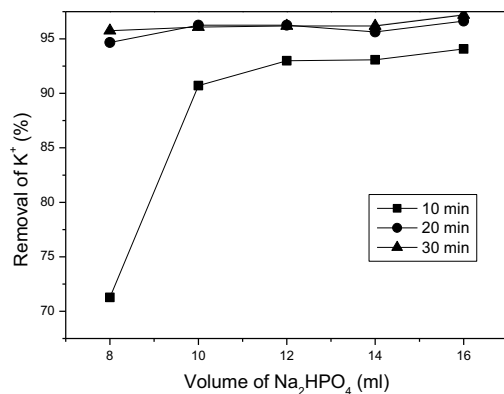


Figure-3. Effect of disodium phosphate (Na_2HPO_4) solution on the removal of potassium ions.

Figure-4 shows the effect of $CaCl_2$ solution on the removal of SO_4^{2-} ions. The results showed that the larger the volume of the solution of calcium chloride, the greater the removal of SO_4^{2-} ions, until it is relatively unchanged on the addition of 15 ml to 30 ml calcium chloride and in a residence time from 20 minutes to 30 minutes. The percentage of SO_4^{2-} ions removal reached 92.29 %.

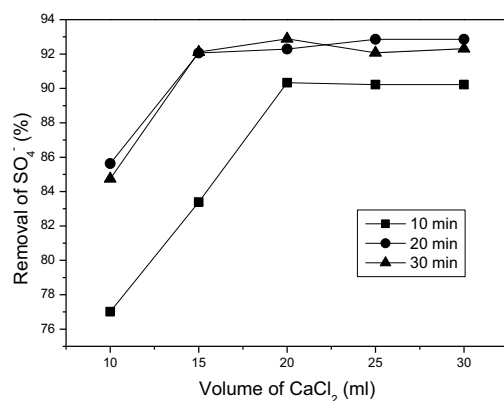


Figure-4. Effect of calcium chloride ($CaCl_2$) solution on the removal of sulfate ions.

Figure 5 shows the XRD pattern for precipitated solid produced from seawater and $CaCl_2$. Whereas Figure 6 shows the XRD pattern for precipitated solid produced from seawater and Na_2HPO_4 . This indicated that the precipitated solid product prepared by Na_2HPO_4 is amorphous with a little trace crystalline. The precipitate solid prepared by $CaCl_2$ shows more peaks, it proves that there are several types of ions contained in the precipitate.

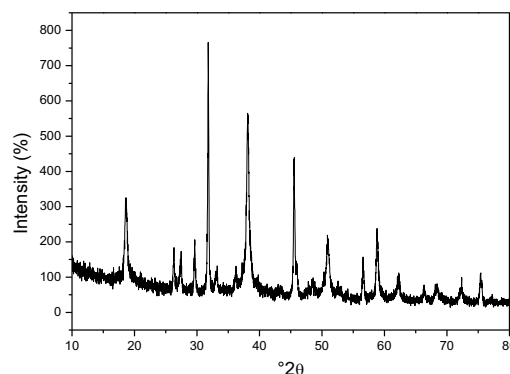


Figure-5. X-ray diffraction (XRD) patterns of precipitated solid produced from seawater and $CaCl_2$.

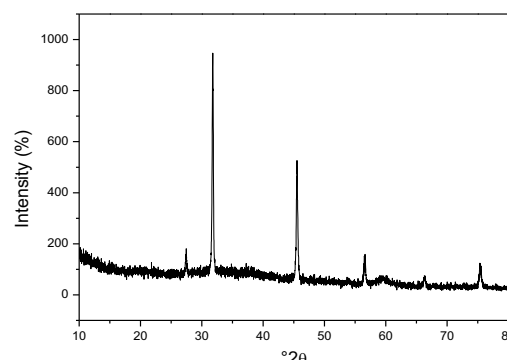


Figure-6. X-ray diffraction (XRD) patterns of precipitated solid produced from seawater and Na_2HPO_4 .

Figure 7 shows ions distribution in the precipitated solid by EDAX analysis. The results show that the precipitated solids consist of PO_4^- (14.5%), Mg^{2+} (13.8%), SO_4^{2-} (28.2%), Ca (24.1%) and K (1.9%) ions. The removal rate of Mg^{2+} ions reached 95% and the removal rate of SO_4^{2-} ions reached 93% when the pH value is about 9.0. The precipitated solid in the $CaCl_2$ -free seawater system mainly consisted of PO_4^- (41.4%), Mg^{2+} (37.3%), SO_4^{2-} and K (7.2%) ions. Meanwhile, the precipitated solid in the Na_2HPO_4 -free seawater system mainly consists of Mg^{2+} (9.3%), SO_4^{2-} (38.8%), and Ca (37.9%) ions.

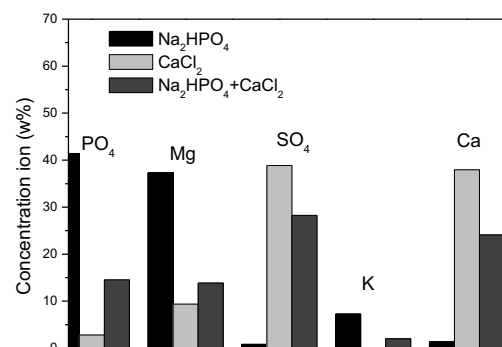


Figure-7. Distribution of ions in the precipitated product as reaction proceeds of ions removal.

CONCLUSION

The results showed that it is possible to remove Mg^{2+} , K^+ and SO_4^{2-} ions in seawater by precipitation method using Na_2HPO_4 and $CaCl_2$. The removal efficiencies of Mg^{2+} , K^+ and SO_4^{2-} ions in seawater were 97%, 96%, and 92%, respectively.

The solid precipitated can be used as some fertilizer components (Mg, P, K).

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