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Physicochemical Properties of Sea Water and Bittern in Indonesia: Quality Improvement and Potential Resources Utilization for Marine Environmental Sustainability

Mirna Apriani[1,2*], Wahyono Hadi[1], Ali Masduqi[1]

[1] Department of Environmental Engineering, Faculty of Civil, Environment and Geo Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

[2] Study program of Safety Engineering, Politeknik Perkapalan Negeri Surabaya, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

* Corresponding author's e-mail: mirnaapriani@gmail.com

ABSTRACT

The traditional salt production in Indonesia was investigated to report the preparation and processing of salt, determine the characteristics of sea water and bittern as well as explore the potential of bittern management with appropriate technology. Field study and comprehensive analysis were performed so as to better understand the salt making, providing valuable information for the proposal of targeted management strategies in salt quality improvement and wastewater recovery. The results show that Na^+, Cl^- and Ca^{2+} in East Java Province seawater were found greater than the majority of values found in the literature. The highest concentrations of Na^+, Cl^- and Ca^{2+} were measured in Camplong-Sampang District. The highest concentrations of Mg^{2+} and trace metals were recorded in Panceng-Gresik District. The trace metals found in sea water and bittern need particular concern to be removed without disposing of sea water minerals. The potential number of bittern in Indonesia promoted the development of the bittern management for magnesium recovery and achieving marine environment sustainability. High purified material recovery can be achieved by using crystallization technology.

Keywords: magnesium, management, recovery, sustainability

INTRODUCTION

Traditional salt production plants are man-made systems exploiting sea water for salt production by wind and solar evaporation. Sea water bitterns are encountered in the sea salt production and desalination process in which large quantities of bittern and brine are produced as by-product and waste-product. Bittern (supernatant liquid) remains after evaporation and crystallization of sodium chloride salt, rich in compounds of magnesium, potassium, chloride and sulfates (Rodrigues et al. 2011; Hussein et al. 2017). Indonesia, a maritime country with the second longest coastline in the world, has to develop good management in order to achieve high marine productivity and environmental marine sustainability (Ministry of Maritime Affairs and Fisheries, 2017).

East Java Province is second largest Indonesia salt buffer zone of after East Nusa Tenggara. East Java is located between Longitude 111°0'E – 114°4'E and Latitude 7°12'S – 8°48'S has 229 islands with a total land area of 47,995 km^2. It is divided by two areas; Java Island and Madura Island, which constitute about 90% and 10% area of this province, respectively. East Java coastal area is the largest, compared to other coastal area in Java Island. It is grouped into the north coast, the east coast and the south coast. Generally, the north and east coastal areas are used for marine transportation, environmental protection, tourism and fishing settlement. On the other hand, the southern coast, is generally a rugged coastline washed by large waves of the Indian Ocean. Therefore, only certain parts can be used as a fishing settlement and tourism area. The coast of

East Java has almost twice the land area, reaching 75,700 km^2. It was calculated from 12-mile border province, while the coastline has ± 2,128 km along the active and potential coast. East Java is not only characterized by wide area; it also has rich natural resources, such as carrying capacity for province development (Ministry of Maritime Affairs and Fisheries, 2013). Indonesian salt was produced in more than 70% in Java Island by traditional processes (Susanto et al., 2015).

Tewari et al., (2003) reported that bittern, as effluent from salt production, could be a pollutant for marine when discharged directly to the sea. The experiment investigated the effect of bittern discharged to the coastal water. The experiment was conducted using mangrove *Avicennia marina*. The bittern could be growth inhibitory with 50% concentration for mangrove. The 100% concentration of bittern was lethal after 8 hour-exposure during 10 days for mangrove *Avicennia marina*.

Sea water, as a part of marine environment, has to be protected due to its sustainability. Sea water has a role of supporting good conditions for the development of marine life. As marine environment, sea water addresses the aquatic ecosystem and supports mankind's life in coastal areas. Sea water is used as raw material for traditional salt production and constitutes environment for marine life to support fisheries. Salt production and fisheries can support economy for communities who live in coast.

The main purpose of the experiment is to promote utilization bittern to add economic value and to protect marine environment. The first objective of this work is reporting the preparation stages and processing to produce salt. To our knowledge, there are no studies on the traditional salt ponds preparation and processing of sea water. However, understanding how these preparation stages and processes interact to product sea salt traditionally remains a major challenge in marine productivity. The second objective is to observe the characteristics of sea water as raw material for traditional salt production in Indonesia as well as a waste by-product. More information is needed to closely define the possible range in the major mineral and trace element composition of raw material and bittern. Reporting the preparation stages, processing and characterizing sea water and bittern would provide valuable information for the improvement of Indonesian salt quality, develop environment sustainability and add value for itself. The third objective is to investigate the potential of waste by-product utilization from traditional salt maker in Indonesia and promote the technology of magnesium recovery from bittern. Several studies have been conducted on bittern utilization; however, there are no data showing the real number of bittern resulting in Indonesia per year. This data contributes to the stimulation of the on national program to manage bittern, i.e. readily-available and promising raw material for magnesium recovery. Comprehensive bittern management has the possibility of giving an economic value for bittern and to protect the marine environment. Safe marine environment can support its sustainability resulting high marine productivity. Appropriate technology for magnesium recovery is needed for the production of new, highly-purified materials.

METHODS

Study area

East Java Province is located in eastern Java; it includes the island of Madura, which is connected to Java by the longest bridge in Indonesia, the Suramadu Bridge. In order to represent the characteristic raw water for salt in East Java, twenty sampling locations, code named 1 to 20, were selected. The assumed sampling location is shown in Figures 1 and 2.

Sampling, on site analysis and interviews

Field studies were conducted to investigate the traditional salt preparation and production process through on site visits of salt ponds, interview with the salt farmer and sample collection to characterize the raw material. Raw water sample were collected in plastics bottles and stored at room temperature prior to the laboratory analysis.

Physical and chemical analysis

The conducted analyses were based on the standard methods given by American Water Works Association. Atomic Absorption Spectrometry method used to measure Na^+, K^+, Br^-, B^-, Sr^{2+} and trace metals (Pb^{2+}, Cu^{2+}, As^{2+}, Hg^{2+}). Complexometry method was used to measure Ca^{2+} and Mg^{2+}. Argentometry method used to conduct the measurement of Cl^-. Iodometry method was used to analyze I^-. Spectrophotometry method was employed to measure F^-, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, SO_4^{2-}. Furthermore, salinity of the sample

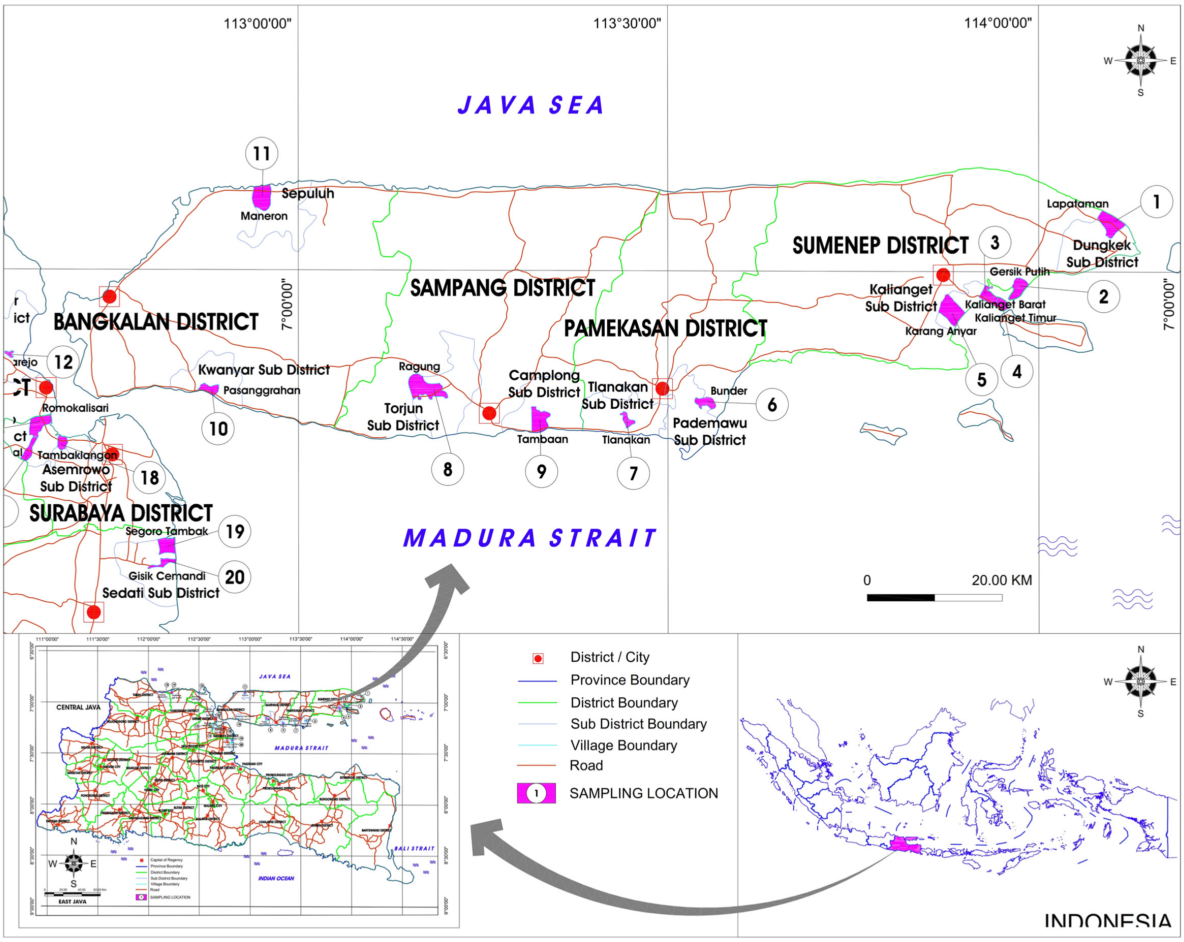

Figure 1. Sampling location in the present study (code name 1–12 and 18–20)

was measured by salinometer. Baume degree of sea water was determined by means of a hydrometer, whereas pH was measured by using a pH meter (CyberScan pH 510-Eutech).

RESULTS AND DISCUSSION

The preparation stages and processing of traditional salt production

The results of the field study showed that traditional salt production used some ponds to evaporate the sea water. In general, the ponds involve (i) stabilization, reservoir of feed sea water as raw material and settling to remove large particle from sea water (ii) evaporation (iii) concentration, and (iv) crystallization (Susanto et al., 2015). Traditional salt production ponds can be illustrated in Figure 3. The pond preparation stages were reported in the following reviews. At the rainy season, some of salt ponds are utilized for fish pond or are allowed to be filled by rain water. Sea water flowed to the ponds through sea water channel called *caren* (A). Water was distributed in several ponds using a windmill that utilized wind as an energy source (B). In some cases, when wind is not available or insufficient to move windmill, the water distribution in salt ponds is performed using a long bamboo scoop (C). The preparation phase for salt production processing is started by draining water and cleaning up the plants grown during the rainy season from the pond (D). If there are holes in the pond, they will be closed manually (E). The land surface of a pond is flattened using a wooden tool called serkot, i.e. short serkot (F); long serkot (G). After flattening the pond surface, pond is dried by sun evaporation (H). Surface dried pond is then smoothed by a traditional cylinder called *guluk* (I). After being smoothed (J), the pond is filled with sea water and allowed stagnant for approximately two days. If the pond surface become cracked (K) or a footprint is left when tread on (L), the farmer has to repeat stages F to I until the surface pond is flat, as well as no cracking and or footprints are visible when tread on (J). The preparation stages can be illustrated in Figure 4.

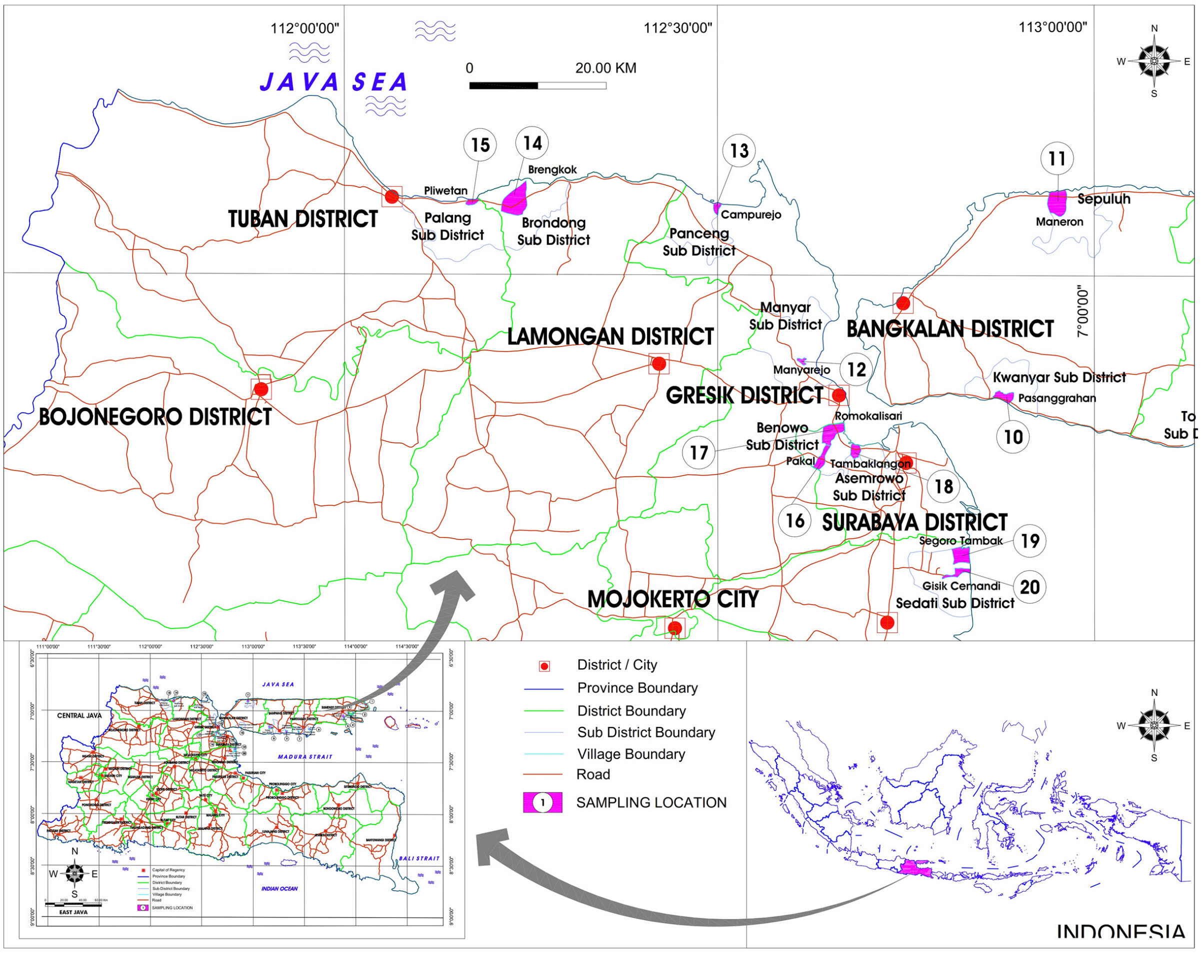

Figure 2. Sampling location in the present study (code name 10–20)

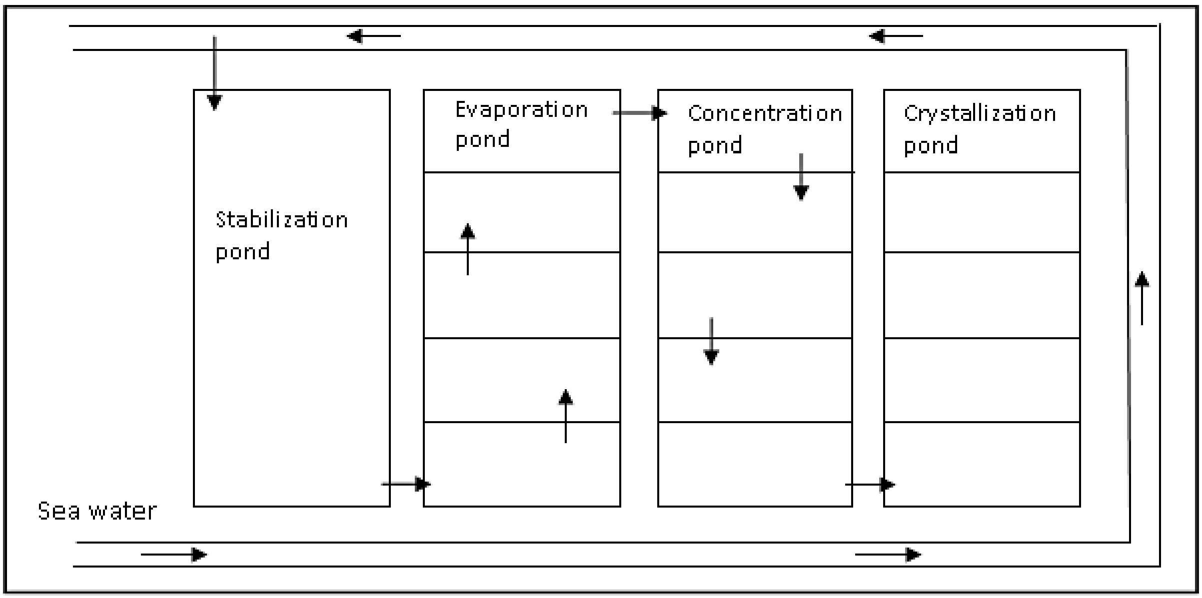

Figure 3. Illustration of traditional salt production (Susanto et al., 2015)

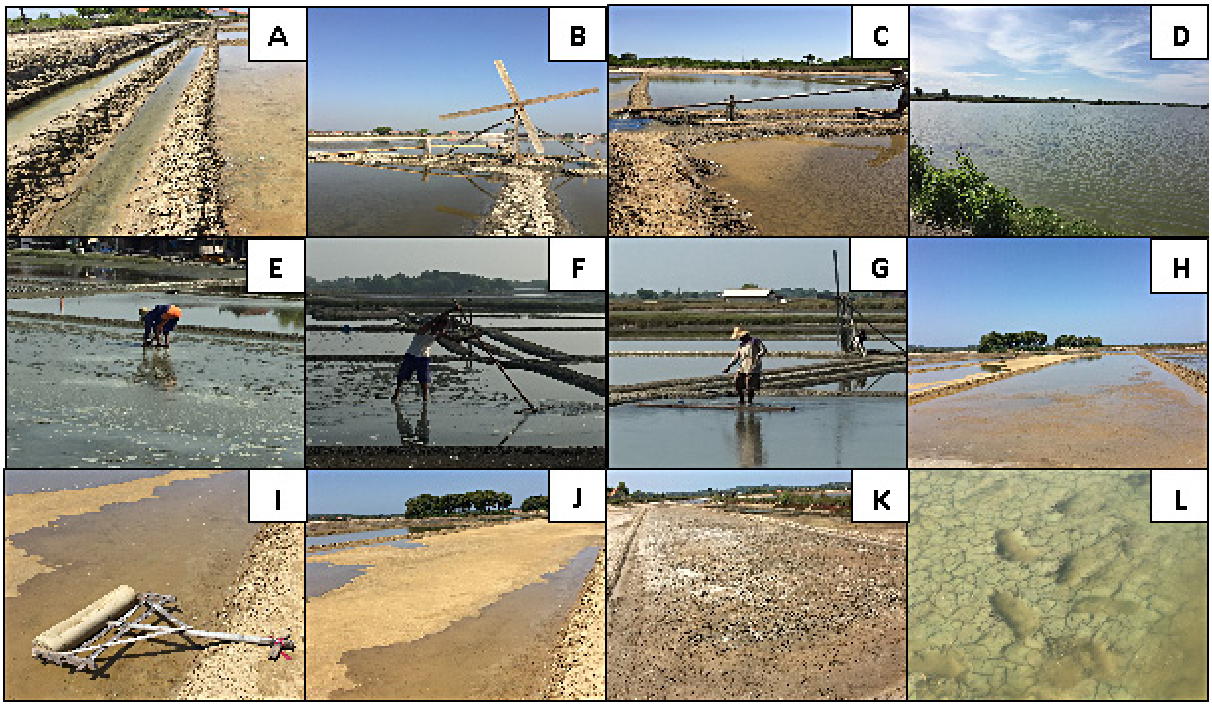

Figure 4. The stages of preparation traditional salt production

After all of the ponds have been prepared for use, the next step involves processing sea water to produce the salt. Sea water constituted the raw material distributed by gravity in the ponds and exposed to sunlight. The density of sea water in every pond has to be monitored regularly during the salt production process using the Baume (°BE) degree hydrometer. Densities of seawater every pond in the salt production process will be regularly monitored during the process flow of water in a salt pond. The success of salt production process depends on the density. Initially, the stabilization pond was filled with sea water (0°BE), after rising up to 5°BE, it flowed to the evaporation pond. In the evaporation pond, evaporated sea water became 11°BE and flowed to the concentration pond. After sea water reached 22°BE, it was poured to the crystallization pond until 29°BE was achieved. The sea water in the crystallization pond became sodium chloride crystal salt and was ready to harvest. The sea water is poured into the pond in the sequence starting from stabilization-evaporation-concentration-crystallization. Salt harvesting was conducted in crystallization ponds. The salt deposit on the crystallization pond floor is piled up next to pond and left to dry. Some salt farmers discharge concentrated liquid remains of salt harvesting back to the sea. Others recycled the bittern in salt plot for mixing with sea water as raw material.

Physical and chemical characteristics of raw water

The results of the physical parameters and chemical characteristics of the raw water samples are reported in Tables 1 and 2. Table 1 represents the physical characteristics, including pH, °BE and salinity in the sampling location villages in some districts of East Java. Table 2 shows the chemical characteristics of the raw water samples. The pH parameter was around 6–8 for all samples. The °BE varied from 0 to 29, while salinity varied from 4 to 92 ppt. The correlation of °BE and salinity showed the linear relations, the higher the °BE, the higher the salinity. The chemical characteristics represented by various parameter of major ions are dominated by Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, F^-, Br^-. The highest concentration of Mg^{2+} is 28,714 mg/L, found in Campurejo Village, Panceng Sub District, Gresik District with °BE of 28 and concentration of Ca^{2+}, Na^+, K^+ and Cl^- of 0 mg/L, 181,640 mg/L, 23.23 mg/L and 280,000 mg/L, respectively. In Sumenep District, the highest concentration of Mg^{2+} is 14,914 mg/L was found in Kalianget Timur Village, Kalianget Sub District. This sample has the concentration of Ca^{2+}, Na^+, $K^+$and Cl^- of 0 mg/L, 166,062 mg/L, 32.6 mg/L and 256,000 mg/L, respectively, while °BE amounts to 29. Compared with the previous studies in measurement sea water parameter, relatively high concentration of Ca^{2+}, Mg^{2+}, Na^+, and

Table 1. The physical parameters of the water samples

Sampling location	District/City	Sub-district	Village	°BE	pH	Salinity (ppt)
1	Sumenep	Dungkek	Lapa Taman	0	7.08	6.79
2	Sumenep	Gapura	Gersik Putih	0	7.7	10
3	Sumenep	Kalianget	Kalianget Timur	29	6.5	92.6
4	Sumenep	Kalianget	Kalianget Barat	0	8.3	4.09
5	Sumenep	Kalianget	Kalanganyar	4	7.25	31.9
6	Pamekasan	Pademawu	Bunder	0	8.35	10.1
7	Pamekasan	Tlanakan	Tlanakan	3	8.05	28.4
8	Sampang	Torjun	Ragung	8	6.75	57.4
9	Sampang	Camplong	Tamba'an	10	6.57	76.3
10	Bangkalan	Kwanyar	Pesanggrahan	5	7.35	38.6
11	Bangkalan	Sepulu	Maneron	3	7.7	20.8
12	Gresik	Manyar	Manyarejo	4	7.9	23.9
13	Gresik	Panceng	Campurejo	28.5	6.7	100
14	Lamongan	Brondong	Brengkok	4	8.3	33.7
15	Tuban	Palang	Pliwetan	11	7.3	77.2
16	Surabaya	Pakal	Benowo	10	7.1	69.9
17	Surabaya	Benowo	Romokalisari	5	7.4	39.3
18	Surabaya	Asemrowo	Tambak Langgon	5	7.45	34.6
19	Sidoarjo	Sedati	Tambak Segoro	0	6.8	26.9
20	Sidoarjo	Sedati	Gisik Cemandi	5	6.75	31.2

Table 2. The chemical characteristics of the water samples

Sampling location	Major ion (mg/l)												
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Br^-	NH_4^+	F^-	Cl^-	I^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
1	3.374	2.71	123	57	0.001	0.39	2.44	5.200	2.31	0.005	-	644	-
2	4.670	2.53	128	91	0.001	-	2.7	7.200	2.41	0.009	0.12	2.726	-
3	166.062	32.6	14.914	-	0.002	1	3.18	256.000	3.12	0.005	0.1	46.919	-
4	2.595	2.42	49	30	0.001	-	2.62	4.000	2.28	0.006	-	5.291	3.37
5	14.790	4.08	498	160	0.001	0.36	2.87	22.800	2.8	0.002	0.32	3.051	-
6	5.060	2.61	99	69	0.001	0.42	2.81	7.800	2.52	0.008	-	751	2.84
7	12. 975	3.28	399	171	0.001	0.51	2.96	20.000	2.61	0.004	-	2.618	-
8	6.490	2.53	3.300	1.714	0.001	-	2.42	10.000	1.83	-	0.15	9.544	-
9	86.826	35.55	6.986	1.786	0.003	0.3	3.86	28.800	3.08	-	0.32	8.964	-
10	7.005	2.58	2.751	1.014	0.001	-	2.48	10.800	1.96	-	0.23	7.581	-
11	3.244	2.01	1.440	800	0.001	0.45	2.18	5.000	1.48	-	0.13	5.178	-
12	17.640	5.75	1.766	286	0.05	0.51	1.58	27.200	3.63	-	0.12	5.167	0.03
13	181.640	23.23	28.714	-	0.03	-	5.09	280.000	14.13	-	0.27	17.717	0.76
14	19.720	8.12	1.903	486	0.18	0.45	2.18	30.400	4.06	-	0.31	4.676	-
15	77.846	17.89	6.429	1.286	0.24	0.68	3.62	120.000	6.56	-	0.29	12.100	0.01
16	62.277	16.26	6.343	1.143	0.11	0.86	3.56	96.000	11.7	-	0.14	9.384	0.01
17	21.530	9.62	2.280	1.257	0.21	0.61	2.51	33.200	6.02	-	0.2	5.464	0.03
18	21.537	8.39	2.143	543	0.06	0.64	2.24	33.200	4.04	-	0.15	3.859	0.01
19	12.974	3.3	1.817	229	0.001	4.57	2.92	20.000	2.09	-	0.22	5.285	0.38
20	15.569	3.96	2.143	114	0.003	13.13	3.08	24.000	2.57	-	0.3	6.865	0.78

Cl^- was observed in the present study. Literature data are listed in Table 3.

Trace metals concentrations of raw water

This work was conducted to characterize the trace metals as polluted matter. The aim of this work is to contribute to the decision regarding the pollutant removal method. Trace metals are represented by Pb^{2+}, Cu^{2+}, Hg^{2+} and As^{2+} concentration in the water sample. The results of the trace metal raw water samples are presented in Table 4. The concentration of Pb^{2+} and Cu^{2+} in all samples are varied from 0.07 to 0.42 mg/L and 0.08 to 1.56 mg/L, respectively. The $Hg^{2+}$and As^{2+} concentrations in twenty samples are not detected by Atomic Absorption Spectrometry method. The raw water for salt production process in East Java Province is polluted by Pb^{2+} and Cu^{2+}. The highest concentration of pollutants is found in sample from Campurejo Village, Panceng Sub District-Gresik District. The concentrations of Pb^{2+} and Cu^{2+} are 0.4 mg/L and 1.56 mg/L, respectively. The lowest Pb^{2+} and Cu^{2+} concentrations are found in Lapa Taman Village, Dungkek Sub District-Sumenep District.

Strategies to utilize sea water and treat waste by product from traditional salt production

a) Salt production

Traditional salt production is highly dependent on the season because the sea water evaporation process depends on the Sun. Susanto et al., (2015) reported that the salt traditional production was conducted by inserting gravity media filter (GMF) and black HDPE tarpaulin in the crystallization pond. GMF was installed between the concentration pond and crystallization pond. GMF was used for removing the suspended solid in sea water in the concentration pond. GMF consists of natural fiber, sand and gravel. Black HDPE was used for blocking sea water permeation into the soil in the crystallization pond. Sea water in the crystallization pond limited by 24–29 °BE. Sea water over 29°BE was circulated in the evaporation pond or concentration pond. Setyaningrum et al., (2014) reported that in order to improve the salt quality, the salt production process was conducted by physical treatment. The physical treatment involved the adding the carbonate or oxalate to precipitate the magnesium, sulphate and calcium in order to form a salt crystal with high purity NaCl. (Kasedde et al. 2014) reported that the nature, quality and quantity of salts are influenced by the chemical composition of the sea water as raw material to define appropriate processing.

b) Potential for bittern resources recovery and utilization in Indonesia

Magnesium concentration in bittern can reach 20–30 times of sea water, 1 m^3 of bittern is produced by 1 ton of salt produced (Hussein et al. 2017). Indonesia has traditional salt-works location spread over 44 districts with the total salt pro-

Table 3. The chemical and physical characteristics of sea water and bittern from a number of coastal and salt ponds

Sampling location	Major ion (mg/l)													BE	pH	Reference
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Br^{3+}	NH_4^+	F^-	Cl^-	PO_4^{3-}	NO_2^-	NO_3^-	SO_4^{2-}	HCO_3^{2-}			
SW Egypt	10.760	387	1290	413	67	-	-	19.350	-	-	-	2.710	-	-	-	Estefan 1983
Bittern. Egypt	18.729	15.280	95.120	-	3200	-	-	292.500	-	-	-	113.210	-	-	-	Estefan 1983
SW Singapore	8.850	565	1248	410	-	-	-	13.467	-	-	-	900	-	-	-	Liu et al. 2013
SW China	10.560	-	1.272	160	-	-	-	18.980	-	-	-	2.560	142	-	-	Yang et al. 2016
Bittern Lake Katwe. Uganda*	66.700–144.000	11.000–39.400	2.2–66.2	0.24–3.6	398–1.500	-	-	42.600–145.000	-	-	-	31.500–67.400	11.800–21.000	-	-	Kasedde et al. 2014
SSW India	10.880	394	1.311	423	-	0.63	-	19.655	1.73	0.47	5.38	2.742	-	3.5	8.15	Tewari et al. 2003
Bittern India	77.890	7.630	31.740	150	-	1.5	-	191.160	1.0	0.21	0.22	43.230	-	28.5	6.95	Tewari et al. 2003
SW East Java Indonesia	2.595–86.826	2.01–35.55	49–6.429	30–1.786	0.001–0.24	0.3–13.13	1.58–3.86	4.000–120.000	0.01–3.37	0.002–0.009	0.1–0.32	644–12.100	-	0–1 1	6.57–8.3	Present study
Bittern East Java Indonesia	166.062–181.640	23.23–35.55	14.914–28.714	-	0.002–0.03	0–1	3.18–5.09	256.000–288.000	0–0.76	0.005	0.1–0.27	17.717–46.919	-	28.5–29	6.5–6.7	Present study

Table 4 Trace metals concentrations of raw water

Sampling location	Trace metal (mg/l)		Sampling location	Trace metal (mg/l)	
	Pb^{2+}	Cu^{2+}		Pb^{2+}	Cu^{2+}
1	0.07	0.17	11	0.12	0.08
2	0.21	0.18	12	0.1	0.51
3	0.42	0.28	13	0.4	1.56
4	0.08	0.28	14	0.15	0.52
5	0.28	0.23	15	0.32	1.32
6	0.18	0.16	16	0.28	1.09
7	0.24	0.21	17	0.16	0.6
8	0.18	0.16	18	0.14	0.53
9	0.26	0.22	19	0.09	0.26
10	0.16	0.17	20	0.12	0.41

duction of 2,915,461.17 ton/year by 2016. Indonesia has 2,915,461.17 m^3/year of bittern which has a potential as a less expensive and more abundant magnesium source. The Indonesian government has to take advantage of the local conditions to develop the mineral recovery from bittern as raw material with abundant availability.

Bittern could constitute a promising, cheap source of magnesium from sea minerals (Estefan, 1983; Liu et al., 2013). As a by-product from salt production, bittern was explored as a magnesium source to recover nitrogen and phosphorous from wastewater. It reported that ammonia and phosphate could be removed with high efficiencies using bittern as magnesium resources at treated wastewater to produce struvite (Li & Zhao 2002). Utilization of bittern into Nigari which serves as food/drink supplement is widely patented by some people in Japan, Indonesia and USA. Cardiofit or nigarin is an isotonic liquid processed from bittern that has been granted a patent in Indonesia on behalf of Suwarno and Sembiring. In Japan, a product from bittern called Nigari as "Siotakijiinotennennigari" is producted by Yuriya-seienjyo Ltd., Nagasaki and "Sesanonigari" producted by Nihon-kaisui Co., Ltd. Tokyo (Haga et al., 2005). J.Q. Dickinson salt work in USA produced nigari from salt work in liquid form besides a variety of salt products.

Lozano & Sanvicente (2002) conducted the experiment to recover bittern as Mg-K-PO_4 salt also containing B. Mg-K-PO_4 fertilizer is characterized by low solubility and has advantages for use in acidic tropical soil. In addition to the use as a fertilizer, bittern can also function as a liquid-desiccant cooling for green house cooling system. Bittern containing $MgCl_2$ can be utilized for supporting cooling system (Lychnos et al., 2010).

c) Removing trace metal

On the basis of the obtained results, all samples contaminated by heavy metal are represented by lead (Pb^{2+}) and copper (Cu^{2+}). Water contaminated by toxic heavy metals cause health problems. Lead is one of the most toxic metals. Lead and copper can accumulate in the environment and human body, cause hypertension, nervous disease and kidney failure (Blais et al., 2008).

The techniques for heavy metal remediation are coagulation-precipitation (Blais et al., 2008; Aziz et al., 2008; Fu & Wang, 2011), activated-carbon adsorption and ion-exchange (Blais et al., 2008), membrane separation (Hajdua et al., 2012) and electrochemical (Fu & Wang, 2011).

The success of metal removal in the coagulation-precipitation method is determined by the pH conditions appropriate for each type of metal (Apriani et al., 2016). Coagulation-precipitation method is cheap and simple to operate. However, the coagulation-precipitation method produces a large amount of sludge that requires processing (Kurniawan et al., 2006; Fu &Wang, 2011). Activated-carbon adsorption is one of the cheap and easy methods, while its ion selectivity is low (Babel & Kurniawan, 2003; Fu & Wang, 2011). Ion exchange has been widely applied for metal removal in wastewater. Ion exchange is a relatively expensive method for applying large amount of metal removal in wastewater. Membrane separation principle uses monovalent and divalent separation. Membrane separation has a high selectivity for metal removal while requiring high operating cost (Kurniawan et al., 2006). The electrochemical method requires low chemicals dosage and produces less sludge. However, the electrochemical method is expensive in terms of investment and operation especially taking into account the electrical needs (Fu & Wang, 2011).

Technology approach for pure magnesium recovery

The common method of solids and liquid separation is precipitation, which is a combination of coagulation-flocculation or flotation process for the separation of solids and solutions (Blais et al., 2008). The separation of solids and liquid through precipitation results in the production of sludge which requires advanced treatment. Crystallization technology is the separation between solids and liquids, through the formation of dissolved crystals from solution into pure solid crystals. This makes crystallization an effective technique for the recovery of useful and economically valuable compounds from waste (Lu et al., 2017). The crystallization technique that can be used for inorganic ion recovery is reaction crystallization (RC) (Lu et al., 2017). The RC technique is crystallized through the reaction between several solutions or between gas and solution which can produce a dissolved substance. This technique is one of the separation technologies that can produce products with high purity (Huang et al., 2014). RC can produce crystals in the form of hydroxides, carbonates or sulfides (Chen et al., 2015). Technology developments apply crystallization using fluidized beds for the removal of pollutants and recovery of reusable products. Separation through fluidized bed can reduce the problem of sludge disposal. The application of fluidized bed crystallization (FBC) has been widely developed to eliminate hardness, fluoride and phosphate from waste and heavy metal recovery. FBC produces less sludge than chemical precipitation and has the potential for cost recovery. The hydrodynamic behavior to be observed on the FBC is the initial contact of the reaction and stirring which is essential for controlling the quality of the formed solids (Su et al., 2014). The application of FBC on RC techniques that produces crystals of $PbCO_3$, $BaHPO_4$, $Mg_3(PO_4)_2$ has been developed (Chen et al., 2015; Su et al., 2014a, bs). FBC uses seed material which is a medium where crystal growth occurs. The existence of seed material can help form larger crystals and serve as a driving force in the crystal growth (Pervov, 2015).

CONCLUSIONS

The chemical characteristic of Na^{+}, Cl^{-}, Mg^{2+} and Ca^{2+} from sea water and bittern in East Java Indonesia were 2,595–186,826, 4,000–288,000, 49–28,714 and 0–1,786 mg/L, respectively. The trace metals for Pb^{2+} and Cu^{2+} parameter were 0.07–0.42 and 0.08–1.56 mg/L. The highest concentration of Na^{+}, Cl^{-}, and Ca^{2+} in seawater were found in Camplong-Sampang District. The measured concentrations were obviously greater than in the case of the seawater from Egypt, China, India, Singapore and Uganda. The highest concentration of Mg^{2+} in bittern was 28,714 mg/L that was found in Panceng-Gresik District. This concentration was smaller than the bittern from Egypt and India. The highest concentration of trace metal was measured in Panceng-Gresik District.

Traditional salt production in East Java has high potential to utilize the bittern as cheaper mineral from sea. Bittern can be used as magnesium sources for magnesium carbonate hydrate product, mineral supplements for drink/food, struvite, supporting fertilizer and cooling system.

The technology for magnesium recovery with high purification degree and less sludge production was crystallization through fluidized bed crystallization.

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REFERENCES

1. Aziz H.A., Adlan M.N. and Ariffin K.S. 2008. Heavy metals (Cd , Pb , Zn , Ni , Cu and Cr (III)) removal from water in Malaysia: Post treatment by high quality limestone. Bioresource Technology, 99, 1578–1583.
2. Apriani M., Masduqi A. and Hadi W. 2016. Degradation of organic, iron, color and turbidity. ARPN Journal of Engineering and Applied Sciences, 11(13), 8132–8138.
3. Babel S. & Kurniawan T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials, B97, 219–243.
4. Blais J.F., Djedidi Z., Cheikh B.R., Tyagi D. and Mercier G. 2008. Metals Precipitation from Effluents: Review. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 12(3), 135–149.

5. Chen C.S., Shih Y.J. and Huang Y.H. 2015. Remediation of lead (Pb(II)) wastewater through recovery of lead carbonate in a fluidized-bed homogeneous crystallization (FBHC) system. Chemical Engineering Journal, 279, 120–128.
6. Estefan S.F. 1983. Controlled phase equilibria for the chemical utilization of sea-bitterns. Hydrometallurgy, 10(1), 39–45.
7. Fu F. and Wang Q. 2011. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 92(3), 407–418.
8. Haga M., Niino Y., Nishimura H. and Seki H. 2005. Quality of bittern products. Journal of Cookery Science of Japan, 38, 281–285.
9. Hajdu I., Bodnár M., Csikós Z., Wei S., Daróczi L., Kovács B., Györi Z., Tamás T. and Borbély J. 2012. Combined nano-membrane technology for removal of lead ions. Journal of Membrane Science, 409– 410, 44–53.
10. Huang H., Xiao D., Pang R., Han C. and Ding L. 2014. Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined with struvite crystallization. Chemical Engineering Journal, 256, 431–438.
11. Hussein A.A., Zohdy K. and Abdelkreem M. 2017. seawater bittern a precursor for magnesium chloride separation: Discussion and assessment of case studies. International Journal of Waste Resources, 7(1), 1–6.
12. Kasedde H., Kirabira J.B., Bäbler M.U., Tilliander A. & Jonsson S. 2014. Characterization of brines and evaporites of Lake Katwe, Uganda. Journal of African Earth Sciences, 91, 55–65.
13. Li X.Z. and Zhao Q.L. 2002. MAP Precipitation from Landfill Leachate and Seawater Bittern Waste. Environmental Technology, 23(9), 989–1000.
14. Liu B., Giannis A., Zhang J., Chang V.W.-C. and Wang J-Y. 2013. Characterization of induced struvite formation from source-separated urine using seawater and brine as magnesium sources. Chemosphere, 93, 2738–2747.
15. Lu H., Wang J., Wang T., Wang N., Bao Y. and Hao H. 2017. Crystallization techniques in wastewater treatment: An overview of applications. Chemosphere, 173, 474–484.
16. Lozano J.A.F & Sanvicente L. 2002. Multinutrient phosphate-based fertilizers from seawater bitterns. Interciencia, 27(9), 496–499.
17. Lychnos G., Fletcher, J.P. and Davies, P.A. 2010. Properties of seawater bitterns with regard to liquid-desiccant cooling. Desalination, 250(1), 172–178.
18. Ministry of Maritime Affairs and Fisheries. 2017. KKP news about *World Ocean Summit Panel* "*What Comes Next: A Call for Commitments on February, 24 2017.*available from: http://news.kkp.go.id (accessed 12.12.17).
19. Ministry of Maritime Affairs and Fisheries, 2013. Profil keluatan dan perikanan Propinsi Jawa Timur untuk mendukung industrialisasi kelautan perikanan (East Java marine and fishery profile to support marine and fishery industrialization), Center for Data Statistics and Information Secretariat General of the Ministry of Maritime Affairs and Fisheries.
20. Pervov A.G. 2015. Precipitation of calcium carbonate in reverse osmosis retentate flow by means of seeded techniques–A tool to increase recovery. Desalination, 368, 140–151.
21. Rodrigues C.M., Bio A., Amat F. and Vieiral N. 2011. Artisanal salt production in Aveiro/Portugal-an ecofriendly process. Saline Systems, 7(1), 3.
22. Setyaningrum R., Suprijono H., Anomsari A. and Hartini E. 2014. Pengembangan Model PUGAR Berbasis Sustainable Manufacturing Untuk Mensukseskan Swasembada Garam Industri (PUGAR model development-based sustainable manufacturing to succeed salt industry self suffiency), Report for competitive research grants Ministry of Education and Culture, Indonesia.
23. Su C., Dulfo L.D.D., Dalida M.L.P. and Lu M.C. 2014. Magnesium phosphate crystallization in a fluidized-bed reactor: Effects of pH, Mg, P molar ratio and seed. Separation and Purification Technology, 125, 90–96.
24. Su C., Reano R.L., Dalida M.L.P. and Lu M.C. 2014. Barium recovery by crystallization in a fluidized-bed reactor: Effects of pH, Ba/P molar ratio and seed. Chemosphere, 105, 100–105.
25. Susanto H., Rokhati N. and Santosa G.W. 2015. Development of traditional salt production process for improving product quantity and quality in Jepara District, Central Java, Indonesia. Procedia Environmental Sciences, 23, 175–178.
26. Tewari A., Joshi H.V., Raghunathan C., Trivedi R.H. and Ghosh P.K. 2003. The effect of sea brine and bittern on survival and growth mangrove Avicennia marina (Dicotyledones: Avicenniaceae). Indian Journal of Marine Sciences, 32(1), 52–55.