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Extraction and characterization of magnesium chloride from different brackish water sources in Rivers state

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Magnesium chloride, an important source of magnesium, chlorine and other related products was extracted from brackish water obtained from Kaa, Eagle Island, Opobo and Iwofe water fronts in Rivers State using conventional methods. This involved the concentration of the sea water from 10 L to below 1 L before reacting with CaO to precipitate $Mg(OH)_2$.The precipitates were washed, filtered and dissolved in 200 ml of 1.0 M HCl to form $MgCl_2$ solution. The solution was evaporated to dryness in order to crystallize $MgCl_2.6H_2O$ salt. The different yields of the salts obtained were 0.79, 0.73, 0.4 and 0.2 g/L for the Kaa, Eagle Island, Opobo and Iwofe brackish waters, respectively. Physicochemical parameters such as pH, conductivity and total salinity of the salts obtained followed the same trend of Kaa> Eagle Island>Opobo>Iwofe. The salts were characterized using XRD and XRF. The XRD gave major reflections of hydrated magnesium chloride salt while the XRF showed the elemental compositions indicating the presence of magnesium as the major component of the salt.In addition, high sulphur content as well as significant presence of Sn, Sb, Al, Si, P, Fe, Cu, Zn, W and Mo were also observed on the XRFcharts of all the four salts.

Key words: $MgCl_2.6H_2O$, Rivers State, Brackish waters (Kaa, Eagle Island, Opobo, Iwofe), XRD, XRF.

INTRODUCTION

The exploitation of seawater for minerals appears to have garnered less attention in comparison to efforts put in search for crude oil in various on- and off- shore finds around the world. However, the sea in addition to supporting marine flora and fauna is also a sink to numerous minerals or salts of economic value from weathering. Minerals found in seawater (brines) include salts of Na, Mg, Ca, Ba, Li, K, Al, S, Si, Fe, Sn, Mn, Mo, Zn, Ni, Co, Cr, Cu, V, Ti, Cd, Pb, Au, Th, U, etc. (Al Mutaz and Wagialia, 1990; Bardi, 2010).

Magnesium and calcium chlorides rank second and third respectively to sodium chloride in terms of relative abundance in seawater. Ca and Mg chlorides find applications in road construction as dust control agents, road de-icing, drying agents (hygroscopic), etc. However, there is renewed interest in $MgCl_2$ because of

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its applications as catalyst support for Ziegler Natta catalyst (used in the petrochemicals/plastic industries for the production of Polyethylene or polypropylene products), Grignard reagents, borates and carnallites. This translates to added commercial value (Tripp, 2009; Rojanotaikul, 2012; Podder et al., 2013; Derun, 2013; Kipcak et al., 2013).

Brines currently serve as major commercial sources of magnesium and its products. For instance, major exporters like Norway, United States of America and Union of Soviet Socialist Republic, mined Mg from brines (Al Mutaz and Wagialia, 1990; WTIC, 1997; Maddan, 2001). Hydrated magnesium chloride, $MgCl_2x$ H_2O exists as $MgCl_2.12$ H_2O in seawater (0.55%) and in other hydrated forms, $MgCl_2.x$ (H_2O), where x=1,2,4,6,8 and 12 due to its hygroscopic nature (Kipouros and Sadoway, 2001). The hexahydrate, $MgCl_2 6$ H_2O, on the other hand is the stable form at room temperature. Production of anhydrous or high purity grades and crystal modifications of magnesium chloride have also been reported (Rojanotainul et al., 2011; Zhang et al., 2012).

The conventional method used for the extraction of $MgCl_2$ from seawater is by the Dow method. This method exploits the low solubility of the precursor, magnesium hydroxide compared to that of calcium hydroxide since solubility of the salts of bi negative ions increases down the group. The precipitated magnesium hydroxide reacts with HCl to form the hydrated chloride salt according to Equation 1:

$$Mg(OH)_2(s) + 2HCl \rightarrow MgCl_{2(aq)} + 2H_2O(l) \quad (1)$$

In general, a litre of seawater is said to contain over 1.0 g of magnesium ions (Bhatti et al., 1984; Atkins and Shriver, 2009). However, it could be less with brackish water due to possible river-brackish water mix.

There is currently no available report on the magnesium chloride content of Nigerian waters despite similar report in North Africa (Behij et al., 2013). This project therefore investigates the presence, yield and characterization of crude magnesium chloride extract obtained from some brackish waters (Kaa-BoriOgoni, Eagle Island Rumueme-Oroakwo, Opobo and Iwofe) in Rivers state of Nigeria. This study would also provide some useful information on the elemental composition of unrefined salts from brackish waters in River State.

MATERIALS AND METHODS

Collection and concentration of brackish (brine) water

Brackish water samples from four selected locations namely: Kaa-BoriOgoni, Eagle Island Rumueme- Oroakwo, Opobo and Iwofe in Rivers state of Nigeria were collected in a 10 l dry plastic container each, prewashed with detergent and rinsed with deionise water. All samples were collected at high tide at each location. This was done because salinity is usually higher at high tides than at low tides. The 10 L was heated at 100ºC in a clean 20 L steel pot and later transferred to a 2 L beaker where it was finally reduced to 1 L saturated salt solution *via* evaporation.

Precipitation of $Mg(OH)_2$ and crystallization of $MgCl_2.6H_2O$

The precipitation of $Mg(OH)_2$ precipitates was done by the reaction of 200 Ml of a 11.2 g (0.2 M) CaO with 200 mL of the saturated brackish (brine) water to form white gelatinous precipitates of $Mg(OH)_2$. The reaction was allowed for a day for proper aging before separation by decantation of the clear supernatant. The precipitate was further heated to remove any remaining supernatant liquid present (but not to dryness). The recovered $Mg(OH)_2$ precipitate was reacted with (dissolved in) 200 mL of 1 M HCl to form the magnesium chloride solution. Evaporation of the resultant solution crystallized the hydrated magnesium chloride salt: $MgCl_2.6H_2O$.

The triple function conductivity meter was used to record the pH, conductivity and salinity of the salt solutions. A 5 min flux of nitrogen gas into a second magnesium chloride solution was done in order to investigate possible reaction of the Mg^{2+} ions in solution with free nitrogen for confirmation. The sample with the highest yield was chosen for X-ray diffraction characterization (on a Siemens D5000 Diffractometer) while X- ray fluorescence analyses were donefor only two samples due to cost.

RESULTS AND DISCUSSION

The XRD pattern of the extracted salt is shown in Figure 1a. The three major peaks (27.7, 32.05 and 46.25º) reflect at 2-theta angles reported previously for $MgCl_2$ (Zhang et al., 2014).The particle size estimated using Scherrer's formula was 63.23 nm. The unlabeled minor peaks could be those of associated impurity phases not indexed due to insufficient data from available literature. This was confirmed by the X-ray Fluoresce (XRF) data which indicated the presence of impurities like S (Major), Sn, Sb, Al, Si, Fe, P, Ni, Cu, Zn, W, Mo, V, Rb and Nb. Figure 1b,c and d for the XRF charts of $MgCl_2.6$ H_2O salts from Kaa, Nitrogenated (Kaa) and Opobo brackish waters, respectively.

The high concentration of sulphur suggested that most of the impurity phases were sulphates or that the salt was a mixture of Magnesium chloride and sulphates but confirmation will be done in further studies. S counts on the XRF of $MgCl_2.6$ H_2O from Kaaand Opobo (Figure 1b and d respectively) were slightly higher than those of magnesium. However, the Mg peak on the nitrogenated $MgCl_2.6H_2O$ chart diminished to less than half of its original peak before nitrogenation. This could be due to possible reaction of Mg^{2+} ions with free nitrogen to form Mg_3N_2 but would be confirmed in future studies. However, the reaction confirmed the Mg peak being one of the characteristic reactions of Mg^{2+} ions.

The XRF also confirmed significant presence of toxic elements like Pb,Sn and Sb in all the samples. This report would help to create public awareness of the dangers of using brackish water salts as table salts. The common occurrence of these toxic elements in both areas investigated reflects the impact of heavy

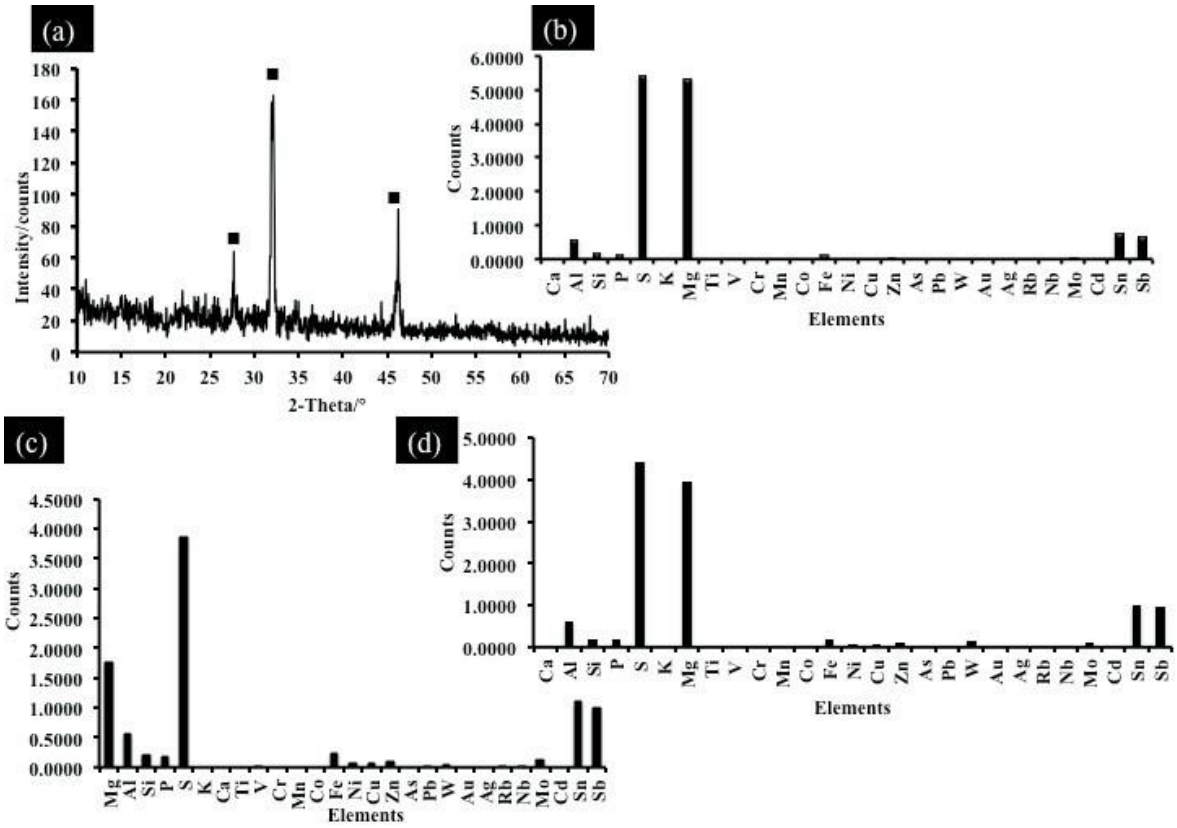

Figure 1. (a) XRD patternof $MgCl_2.6H_2O$ (Kaa); (b) XRF of $MgCl_2.6H_2O$ (Kaa); (c) XRF of $MgCl_2.6H_2O$ (Kaa) fluxed with N_2. (d) XRF of $MgCl_2.6H_2O$ (Opobo) extracted from the respective brackish waters.

Table 1. Showing the brackish water location, Yield, pH, Conductivity and Salinity of each solution of extracted $MgCl_2.6H_2O$.

S/N	Location	Yield (g/L)	pH	Conductivity (mS/cm)	Salinity (ppt)
1	KAA	0.79	9.75	101.10	67.20
2	ISLAND	0.73	9.64	79.40	49.30
3	OPOBO	0.40	9.62	69.20	43.60
4	IWOFE	0.20	9.62	56.50	34.20

environmental pollution due to oil spills. The metals including sulphur are inorganic components of crude oil.

The yields in grams of $MgCl_2.6H_2O$ extracted from the four brackish waters were 0.79, 0.73, 0.40 and0.20 g/L for Kaa, Eagle Island, Opobo and Iwofe respectively. Similarly, the physicochemical properties like pH, conductivity and salinity also followed the same trend as shown in Table 1. The lower salinity of Opobo and Iwofe brackish waters could be due to dilutions from river water unlike Kaa that empties into the Bonny high sea.

Conclusion

The extraction and characterization of magnesium chloride, $MgCl_2.6\ H_2O$ salt obtained from brackish water obtained ofKaa, Eagle Island, Opobo and Iwofe in Rivers State has been reported for the first time. The XRD showed three major reflections of $MgCl_2.6H_2O$ salt while the XRF indicated the presence (higher counts) of Mg as well as S with lower counts for Sn, Sb, Al, Si, P, Fe, Cu, Zn, W and Mo on the XRF charts of all the four salts. However lower counts were also recorded for Mg on the XRF chart of the pre-nitrogenated $MgCl_2.6H_2O$ sample indicating possible conversion of the Mg to nitride. The yields of the salts were 0.79, 0.73, 0.4 and 0.2 g/L for the Kaa, Eagle Island, Opobo and Iwofe brackish waters, respectively. This report recommends that the use of extracted salt from brackish waters for food seasoning should be discouraged due to the possible presence of

toxic elements in such salt.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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