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Treatment of Hardness and Heavy Metals from Red Sea by using Zeolites

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Abstract: ***This study was conducted to analyze water samples collected from Red sea at the shore of Port Sudan City. The study was undertaken to determine the concentration of heavy metals (Cu, Pb and Zn) and metals that cause hardness (Ca and Mg) in Red Sea shore water. The study samples are taken from a location at the eastern side of Port Sudan (Segala area). This area is the main source for sea water to desalination plant, which supplies the city with drinking water. Samples were taken from two depths (1 meter and 3 meters) at distance of 7 meters from the shore. Zeolite is practically prepared from crude materials (e.g K-feldspar, Clay, Trona and Bi $(HCO_3)_2$ by certain ratio. All analysis results of elements measured in this study assured that synthetic zeolite is better than natural zeolite in treatment process, although the weight of natural zeolite used for treatment process is double synthetic zeolite.***

Keywords: Water Treatment, Zeolite, Heavy Metals

1. Introduction

The Red Sea is a basin, a semi-enclosed open on the Mediterranean through the Suez Canal and the proportion of the small estuaries and valleys where the surface salinity in the Red Sea is generally high within the range 36-46 % due to high evaporation, precipitation, and the lack of a major river inflow (Fig 1a). Salinity is usually lower in the southern region due to the inflowing waters from the Gulf of Aden and it increases in northwards due to evaporation (Sofianos and Johns, 2003). Salinity known as the total amount of solids in grams per kilogram of sea water after the transformation of each carbonate to the oxide and replacing the bromide and iodide by chloride, and all organic materials are oxidized completely. The high salinity in the waters of the Red Sea reaches 41% per thousand . There are some factors affect the rate of salinity, such as the amount of water gained by rainfall and rivers compared with the amount of water lost due to evaporation process. Salinity increases with depth (Fig 1b) and the bottom of the halocline is marked by the 40.5 % isohaline (Sofianos and Johns, 2003. The United States Center for Public Health recommends that the degree of salinity in drinking water must not exceed 500 ppm.

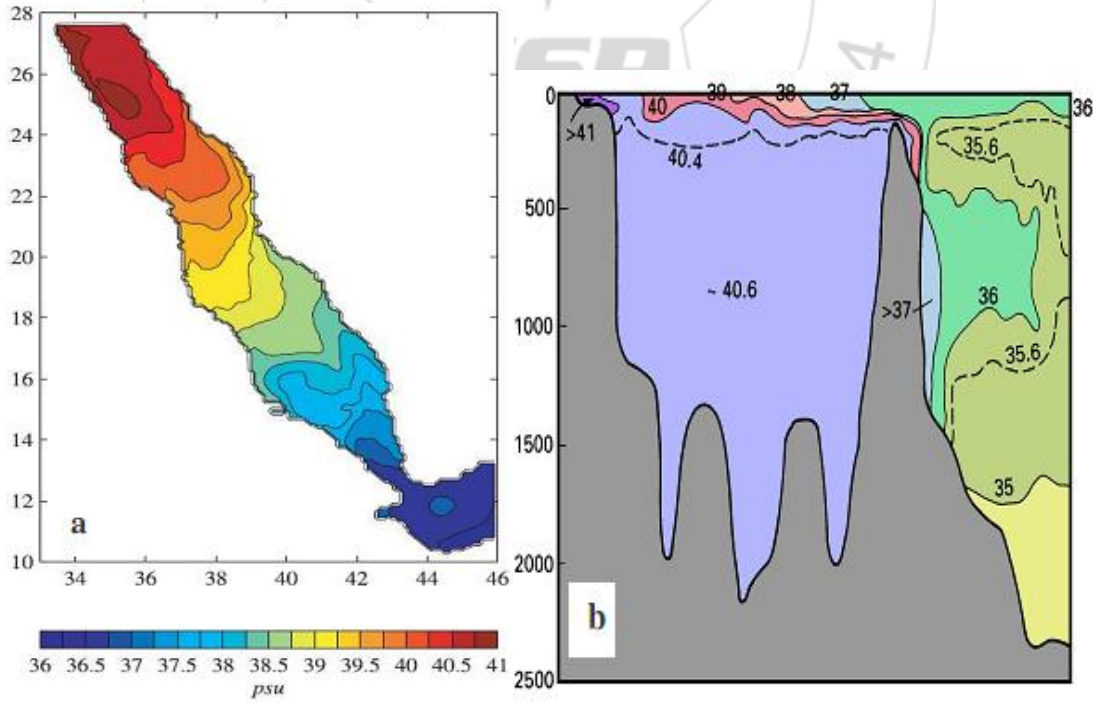

Figure 1: Salinity distributions in the Red Sea (a) surface water (b) water column (Sofianos and Johns, 2003)

Sea water containing dissolved calcium, magnesium, and iron salt is known as hard water .The negative ions present in hard water are usually chloride, sulfate, and hydrogen carbonate. Hardness in water is objectionable for two reasons:

1. The calcium, magnesium, and iron ions form insoluble soaps in reaction with soluble soaps such as sodium stearate.

$$2\ C_{17}H_{35}COO^- + 2\ Na^+ + Ca^{+2} \longrightarrow Ca(C_{17}H_{35}COO)_2 + 2Na^+$$

Insoluble soaps have no cleaning power, and due to their sticky nature adhere to fabrics giving dingy appearance. Insoluble soaps make up the ring in the bathtub.

2. Hard water is responsible for the formation of a tightly adherent scale in boilers. At high temperatures, much of the mineral matter dissolved in hard water is precipitated as scale (Nebergall et al., 1976).

Marine pollution occurs as a result of chemicals, industrial, agricultural and residential particles of waste, or the spread of invasive organisms. (Mark and Bhatia, 2007; Mason et al ., 1996).

Heavy metals are defined as the elements that increase the intensity of five times the density of water of 5 g /cm^3 and have negative impacts on the environment when used excessively (Mason et al., 1996), and these elements which exist in abundance in nature is initiated through the courses Geochemical to the environment and spread some of these metals in the air in the form of fine particles with dust, and some remain stuck in the air in the form of aerosols, some may reach into the soil and be absorbed by plant roots. Among the most important of these metals: lead /mercury /arsenic manganese / nickel / cadmium. The danger of these elements is in the following:

- They are not decomposed and eliminated by bacteria in nature.
- They change type of compound and increase concentration of the metal gradually.
- When increasing concentrations heavy metals move to distant places (Mason et al., 1996).

Zeolite is a Greek word that means "boiling stone" as naturally occurring zeolites are minerals that absorb water which subsequently boils when heated. Zeolite (hydrated alumino silicates minerals) is one of the alkaline and alkaline –earth metals . About 40 natural zeolites have been identified during the past 200 years, and more than 150 zeolites have been synthesized. Zeolites consist of three – dimensional frameworks of (Si, Al)O_4 tetrahedra where all oxygen ions of each tetrahedron are shared with adjacent tetrahedra. The presence of Al^{+3} in place of Si^{+4} in the structure gives rise to a deficiency of positive charge in the framework. The net negative charge is balanced by cations, principally Na^+, K^+, and Ca^{+2}, less frequently Li^+, Mg^{+2}, Sr^{+2}, and Ba^{+2} which are situated in cavities within the structure.

Synthetic Zeolite In the 1930 Richard Barrer Started Systematic Studies into zeolite synthesis under high pressure and temperature. The most common are zeolites A, X, Y . In 1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. Today synthetic zeolites are used widely throughout petroleum refining and chemical process industries as selective adsorbents, and etc… (Bekkum et al.,2001).

Structure of zeolite are crystalline alumino silicates of group IA and group IIA elements such as: Na, K, Mg, and Ca. Chemically, they are represented by the empirical formula: $\mathbf{M_{2/n}\ O\ .\ AL_2O_3\ .\ y\ SiO_2\ .\ wH_2O}$

Where: y: is 2 to 10 / n: is the cation valence / w: represents the water contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline in organic polymers based on an infinitely extending components including:

- A three – dimensional frame work of tetrahedral occupied more than 50 % by Si and Al .
- An "open" structure with a framework density lower than 20 and hence enclosing cavities connected by windows larger than regular six-membered rings .
- An extra frame work content represented by cations and water molecules (Jackson et al., 1988).
- The general formula of a zeolite permits a large chemical variability, the only constraint being Lowenstein's rule (Si $\geq$ Al).
- Natural and synthetic zeolites are used commercially because of their unique adsorption, ion exchange and catalytic properties.

2. Materials and methods

Samples Sources
The water samples were collected from 1 meter and 3 meters at distance 7 meters from the shore of Port Sudan City (Segala area).

Equipments and Instruments
Beakers 1000, 500 ml were cleaned and dried, stands, measuring cylinder 1000, 500, 100 ml, conical flasks 500 ml, thermometer, mortar and pestle, glass column with length of 7 cm and diameter 5 cm , electronic balance, furnace (model ELF 11\6B -1200 ^{0}C) drying oven, Atomic Absorption Spectroscopy, Refractometer**,** pH meter

Kind of zeolite:
Natural zeolite from Doka ElGalabat mountains is known as K- mordnite
Synthetic zeolite prepared in labfrom :

The row material such as clay (29%), K- feledspar (60 %) , Trona (10% and Bi(HCO_3)$_2$ 1 %.

Laboratory preparation of zeolite
The basic materials in the composition of zeolite are clay, K - feldspar and Trona . Clay, and K- feldspar which are characterized by high content of silica and alumina.

The burning of these materials results in a united form of the zeolites rock.

Method

- Required quantities of Crushed Samples which contain K-feldspar 60%, 29% Clay, 10% Trona , 1% Bi$(HCO_3)_2$ are weighed.

- The mixture in ceramic crucibles is put in electric furnace and exposed for an hour to gradually increasing temperature that reached 950 - 1000 degrees Celsius.
- Controlled in the electric furnace at 1100 degrees Celsius for 6 hours and then left to cool down.
- Stored in desiccator until broken down to appropriate size with the experience.

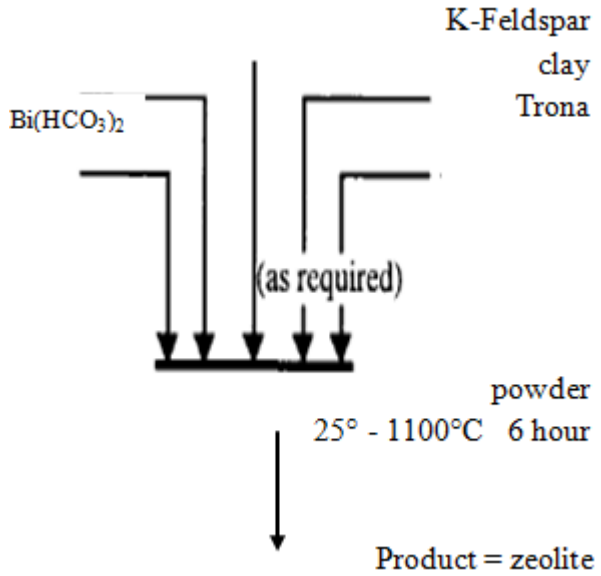

Figure 2: Schematic representation of synthesis method for zeolite synthesis.

pH measurement
The pH of the oceans waters considered as buffer solutions with pH arranged 8.3

Temperature and Salinity measurement
The temperature is measured by Thermometer Mercury and the Salinity is taken immediately by Refractometer.

Determination of calcium in water by titration method
When calcium ions are titrated with EDTA calcium complex is formed:

$$Ca^{+2} + H_2Y^{-2} \rightleftharpoons CaY^{-2} + 2H^+$$

With calcium ions alone,a sharp end point and transition from red to blue can be obtained when E.C.B.T indicator is used (Vogel, 1989).

Determination of magnesium by titration method

When magnesium ions are titrated with EDTA somewhat less stable complex is formed:

$$Mg^{+2} + H_2Y^{-2} \rightleftharpoons MgY^{-2} + 2H^+$$

Consequently , during the titration of solution containing magnesium and calcium ions with EDTA in the presence of E.C.B.T the EDTA reacts first with the free Ca^{+2} , then with the free Mg^{+2} , and finally with the Mg – indicator complex . Since the Mg – indicator complex is wire red in colour and the free indicator is blue between pH 7 – 11, the colour of the solution changes from wine red to blue at the end point (Vogel, 1989) :

$$Mg\,D^{-}\,(red) + H_2Y^{-2} \rightleftharpoons MgY^{-2} + H\,D^{-2}\,(blue) + H^+$$

Determination of Zinc, Lead, and Copper in sea water
Determination of Zinc, Lead, Copper, and Cadmium in sea water is done by atomic Absorption Spectrophotometric method.

3. Results

The zeolite prepared in laboratory at a temperature of 1100 ^oC is brown, solid and has a coherent structure.

Treatment results of Red Sea water

Table 1: Physical properties of Red Sea water

Parameter	Sample
pH	8.22
Temperature	34.3°C
Salinity	39

The following tables showing the results of analysis of Red Sea water before and after treatment by zeolites.

Table 2: The analysis of Red Sea water before the treatment with zeolite

Element	Sample mg / ml
Cu	0.063
Pb	0.818
Zn	1.4
Ca	0.189
Mg	1.887

Table 3: The analysis of Red Sea water after treatment by **Natural zeolite (NZ)**
Weight of zeolite = 250 gm
Volume of sample = 1000 mls
Temperature of room = 34.2° C

Element	Sample mg/ml
Cu	0.041
Pb	0.373
Zn	0.033
Ca	0.120
Mg	1.258

Table 4: The analysis of Red Sea water after treatment by synthetic zeolite (SZ)
Weight of zeolite = 125 gm
Volume of sample = 1000 mls
Temperature of room = 34.2° C

Element	Sample mg/ml
Cu	0.060
Pb	0. 6450
Zn	0.046
Ca	0.184
Mg	1.829

4. Discussion and Conclusion

The pH of sample is 8.2 this is attributed with high content of dissolved salt.

The Salinity of sea water sample is about 39. Generally, it is high within the range 36-46 due to high evaporation, low precipitation, and the lack of a major river inflow.

The exchange of multivalent metal ions can be achieved over pH range between 3-6.

The influence of pH is very important for efficient removal of heavy metals by ion exchange. In this study efficient low because of high pH.

Treatment of heavy metals (Cu , Zn , Pb , Cd) and hardness (Ca^{+2} and Mg^{+2}) from Red sea water was possible by using natural zeolite and synthetic zeolite is prepared from (K-Feldspar , Clay and Trona) .

Lead ions are the best to be sorbeted, then Zinc ions and finally Copper ions in seawater by sorbent natural zeolite and synthetic zeolite.

All result show that, the synthetic zeolite contents Mg and Cu ions which are present in raw material as well.

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