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Clay's Ability to Remove Iron and Manganese from Brackish Groundwater in Comparison to Cation Exchange Risen

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ABSTRACT

Having available, safe, and continuous access to potable water resources is one of the most important targets for nations nowadays. The situation in Egypt becomes harder every year with a threat of water scarcity in the future, since the river Nile is the main and almost the only water resource. Other available resources such as rainfall, groundwater, domestic sewage treatment, seawater desalination and brackish groundwater only contribute with low percentages to the total water resources in Egypt. Obstacles hindering the wide use of groundwater refer to the high cost of desalination and contamination of ground water with some heavy metals like iron and manganese. Two main methods of desalination technologies have been considered in the technological evolution (evaporation and membrane technologies). Research is rapidly running to enhance the characteristics of different membrane materials and adsorbents. Since clay minerals are considered as a natural filter by removing and accumulating contaminates in water passing through it, clay with its promising characteristics has been tested through this paper to desalinate seawater and remove iron and manganese from brackish groundwater. A comparison between different materials (adsorbents and ion exchange desalination based) will be discussed. Samples of (local clays and ion exchange resin) were prepared. A dead end setup was designed for the experiment to take place. Raw seawater of TDS 36,966 ppm and brackish groundwater solution was also prepared in lab, contaminated with iron and manganese of 50 ppm concentration, separately. Results were good as local clay achieved around 20% raw seawater desalination which could be useful for low saline brackish water desalination, local clay also achieved very promising results in iron removal of 62% from 50 ppm concentrated solution in the time that manganese removal was around 53% from same concentration. This proofs local clay future in water treatment.

Keywords:
Water scarcity, brackish groundwater treatment, clay minerals, ion exchange, adsorption, FE and MN removal

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1. Introduction

Potable water is an essential life need; each person in the world needs at least 20 to 50 liters per day of clean, safe water, for daily life usage [1]. People's access to water resource and sanitation are considered by the United Nations as human rights, being one of the life's fundamentals. Lack of access to safe, sufficient and affordable water, sanitation and clean facilities has severe effects on health, dignity and prosperity of nations, and contributes for the realization of other human rights [2].

Water scarcity is a global concern for our world these days, due to increasing population, people's behaviour in water consumption, and climate change, the challenge to keep water consumption at sustainable and considerable levels is becoming even more difficult in the coming years [3].

It is estimated that potable water resources in the world is approximately equal to 326 million cubic meters. Fresh water from rivers, lakes and underground water contributes to around 2.5% of the total water on earth. While the seas and oceans water contributes to 97% of total earth's water. And about one third of world's fresh water is underground water [4]. According to these numbers, looking for non-conventional freshwater resources such as brackish groundwater treatment and sea water desalination to solve water scarcity problems in many places is the most logic solution regardless the economical and regional issues.

Egypt is one of those countries where people started to experience water scarcity problems, Water scarcity indication is always defined with value of 1000 cubic m^3/capita/year, unfortunately Egypt has passed this limit already in the 19's, threshold of absolute water scarcity is 500 m3/capita/year, according to current situations, and population predictions for 2025, this average will exceed such a threshold down to 500m^3/capita/year [5]. "The water shortage is the main constraint and a major limiting factor facing the implementation of the country's future economic development plans"[6].

Although using non-conventional water resources in Egypt such as brackish groundwater treatment and seawater desalination is considered very promising to overcome water scarcity, there are still many difficulties referring to the expensive technologies and high energy usage.
Hence, the study performed here in has focused on finding low cost techniques to treat brackish groundwater using available local material; knowing that it's highly recommended to conduct research in this solution, to help decrease the cost of desalination treatment [6].

2. Literature Review

2.1 Water resources in Egypt

Egyptian share from River Nile is 55.5 BMC/year. Rainfall share is very low with almost 1 BCM/year [5]. The non-traditional water resources available in Egypt include groundwater, sewage water treatment, seawater desalination and brackish groundwater treatment [6]. Domestic waste water Reuse in Egypt was estimated to be 2.5 BCM/year in 2009 and it's used mainly for irrigation. Agriculture drainage water reuse could be considered as recycling of water used from river Nile for irrigation and returned back as irrigation drainage waste, which is estimated to be around 25% of the total irrigation water [7].

Egypt has various sources of ground water aquifers located in the Nile valley and delta zone and those are renewable ones, and other non-renewable aquifers located in the western desert and Sinai [7]. Nile valley and delta aquifers have an average salinity of 800ppm, while the salinity in non –renewable aquifers of western desert and Sinai ranges from 2000 ppm to 9000 ppm. [11].

2.2 Desalination in Egypt

"Desalination is the process of removing salt and other dissolved solids from water in order to produce water suitable either for human consumption or agricultural purposes and industrial processes"[8]. As shown in Table 1, water salinity ranges from fresh water to brine water according to the following total dissolved solids (TDS) concentrations:

Table 1
Water salinity range [8]

Water	TDS ppm
Fresh	< 1,000
Brackish	1,000 – 15,000
Saline water	15,000 – 30,000
Sea water	30,000 – 40,000

Greater than 40,000 ppm TDS is considered as Brine. According to (IDA report, June 2015), there are 300 million people who rely on desalination for some or daily needs, in 150 countries, with a total capacity of 150 MCM/day, through 18,426 desalination plants. The two main major technologies for desalination include membrane and thermal technologies. The first is widely used for its low energy consumption but has a high cost. The second includes multi-effect distillation MED, multi-stage flash MSF 26.8% of global capacity, membrane distillation MD, mechanical vapor compression MVC [8].

There are two critical parameters in desalination processes:

Quality of produced water: it depends on desalination process, for distillation processes, the outflow concentrate around 20 ppm TDS, when the membrane processes produce 100-500 ppm TDS. [10].

Energy consumption: its high intense energy consuming process, could reach 50% of the overall cost. [10].

Great potentials of potable water could be achieved from brackish ground water treatment and sea water desalination as mentioned before. Brackish ground water recorded presence of iron and manganese, there are many methods to remove these two metals, but the research will not stop exploring cheaper and better techniques. Although the world health organization doesn't consider iron and manganese contamination in potable water as health hazards, but they are considered as ethical and technical problems. Presence of iron in water makes turbidity and gives yellow brown colour adding this to the damage of plumbing systems that could happen because of iron precipitations, while manganese presence is able to give water unpleasant appearance and taste.

Since there is an abundant amount of ground water available in Egypt that could contribute toward solving the water scarcity problem, this study has focused on using low cost, effective technique to treat Fe and MN presence in brackish groundwater and removal of TDS from sea water. According to The world health organization, accepted levels of iron and manganese in potable water must be less than 0.3 mg/l and 0.1 mg/l respectively, while the Egyptian authorities' states that accepted level of iron and manganese have to be less than 0.3 mg/l and 0.4 mg/ l respectively [12].

Hence, a model was developed to test the effect of local clay minerals and cation exchange resin to iron and manganese present and to measure their effect in removal.

3. Experimental Work

The water treatment work was divided into two stages. The Preliminary step was to experiment the local clay abilities for water treatment, then a designed apparatus was developed and used for the further experiments.
Step A: was held to experiment the local clay abilities to desalinate raw sea water with a column setup that is usually used for constant head permeability test.
Step B: was held to experiment the new specially made column filtration setup to remove heavy metals (iron and manganese) out of synthesised brackish groundwater

3.1 Apparatus set up
3.1.1 Set up A

Constant head permeability test column with inner diameter 10cm, and height of 30cm, was used, with one inlet and one outlet, atmospheric pressure was used as the setup doesn't resist more pressure, attached with 3 head pressure piezometers, inlet for feed water was introduced first to porous stone, followed by a clay layer, held by layers of sand stone, as shown in Figure 1.

Fig. 1. Setup A

3.1.2 Set up B

Aluminium was the suitable material to build the new apparatus as its planned to use flow under pressure up to 10 bars during future steps for this research, the apparatus consists of 1 litre feed water tank, connected with easy connection pipes size #8, directly connected to the upper base of the setup, one attached valve will be used for the gauge pressure during future experiments, then the cylinder of inner diameter of 11.5 cm and outer diameter of 12.7 cm and thickness of 0.6 cm, and 7.8 cm height, then lower base of same material that has the outflow filtered water as illustrated in Figures 2 and 3. Three screws 1cm diameter for each was used to connect three parts together.

A capsule of aluminium base and acrylic cap was designed specially to uniformly distribute the water feed to the filter, to insure the same flowing rate entering the sample, and to confirm the sealed system, that no flowing water escape out of the filter layer.
The capsule aluminium base has outer diameter of 11.5 cm, contains 38 openings of 0.35cm diameter for each while the top cap contains 32 openings, presented in Figure 4.

Fig. 2. Components of the used apparatus

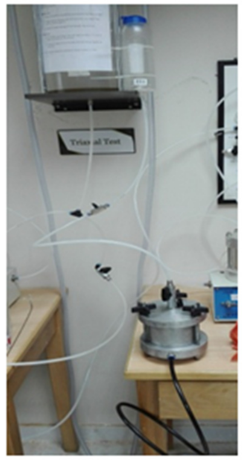

Fig. 3. Feeding tank

Fig. 4. Capsule holding the membrane

3.2 Samples used for testing

3.2.1 Seawater samples.

Raw seawater sample was extracted from the Red sea at Hurghada city. The sample salinity was measured in the lab and showed salinity concentration of 36,696 ppm.

3.2.2 Synthesize of brackish water samples

Two elements were chosen to be removed from brackish groundwater, as mentioned before, brackish groundwater in Egyptian deserts an Sinai has low salinity but includes iron and manganese, the synthetic sample represented was made of distilled water contaminated with (iron ııı and manganese), (iron standard solution 1000ppm, iron ııı nitrate nonahydrate in nitric acid 0.5 mol/l) and (manganese standard solution 1000 ppm, manganese nitrate in nitric acid 0.5 mol/l) produced by *Scharlau*.

Two diluted solutions were made from these standards, 50ppm concentration for each –iron and manganese – to be subjected to the membranes. By adding 50ml of those standards and the volume was completed to 1L with distilled water. 50 ppm is away greater than average concentrations in nature brackish groundwater in Egypt that has extreme values around 9ppm and average values around 4ppm, but this value was chosen for clear result investigation.

3.3 Materials preparation

3.3.1 Experiment A

Clay sample of high monmorolonite composition, known with its high exchange capacity and adsorption abilities, which is very promising in water treatment. [13]. Clay was chosen from district DAR EL SALAM in Cairo, two different samples were prepared to be tested as follows:
Sample 1: was dried in oven @210°c for 24 hours, then compacted under pressure of 7 ton/cm^2
Sample 2: was dried in oven @210°c for 24 hours, then compacted under pressure of 6.5 ton/cm^2

3.3.2 Experiment B
3.3.2.1 Local clay

Figure 5 shows a set of photos taken during the preparation of the clay sample to be used in the experiment. Samples were taken of constant weight of 20 gm, prepared by grinding clay sample, then sieving

Fig. 5. Local clay sample preparation

3.3.2.2 Cation exchange resin

Samples were taken of constant weight of 50 gm of Cation exchange resin, produced by morgan specialty Chemicals Company as shown in Figure 6.

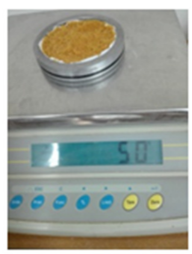

Fig. 6. Cation exchnage resin

3.4 Methodology
3.4.1 Method of experiment A

A volume of 1.5 litres of raw seawater was flowing through the local clay layer of 1cm height under the atmospheric pressure, outflow water was stored in coded bottles and subjected to salinity tests.

3.4.2 Method of experiment B

One litre of each prepared synthetic solution was used in each experiment (iron water and manganese water sample), under atmospheric pressure, and with constant flow rate of 11ml/minute through all trials. In each experiment, three outflow water samples have been taken, one every 30 minutes. Result water samples were coded and set ready to be tested for removal percentage of iron and manganese.

4. Results and Discussion

Step A: preliminary experiments showed that local clays has filtration abilities to partially remove saline from seawater as showed in **Table 2**, leaks through the clay particles and not enough sealing was mostly the reason of low percentages of removal, and also showed a need to design and create column setup that's very sealed and with ability to resist pressure as well. It also showed a very slow flow rate due to excessive compaction, which needs using high pressures and sealed system to maintain the desalination process to be occurred.

Table 2
Preliminary experiments of local clay against seawater

	Raw Seawater	**Clay Sample 1**	**Clay Sample 2**
TDS (ppm)	36,696	32,132	29,832
Tested flow rate	--	18.75 ml/hr	8.3 ml/hr
Clay compaction	--	7 ton/cm^2	6.5 ton/cm^2
% Removed	--	13%	19%

Clay sample permeability was so low, the difference sizes of particles helped to decrease permeability as void ratio going decreases. These issues were considered in step B of the experiment. From experiment step A, clay sample 2 was chosen for its higher adsorption abilities and exchange capacity, to be used for next steps

Step B: The sealed system helped to assure that flow totally passes through filtration samples, uniformity of flow was maintained by the capsule, its perforated from both in (38 openings) and out (32 openings) sides, that assures uniform flow of synthetic water.

Grinding clay samples helped to increase the surface area, increasing adsorption abilities of clay. The samples were subject to sieve #200 and shaken for 15 min before each experiment. Heavy metals including iron and total manganese were measured using Inductively Coupled Plasma Optical Emission Spectrometer (ICP) in Fayoum central lab. Results were very promising for local clays in Egypt specially in removing iron as shown in Tables 3 and 4 and Figures 7 and 8.

Table 3
ICP results for experiment step B (Fe solution 50 ppm)

Sample no./30 min interval	**Fe (ppm)**	**Membrane**	**% removed**
1 @30 MINS	20.51	Local clay	63.05%
2 @60 MINS	21.41	Local clay	61.19%
3 @90 MINS	25.31	Local clay	54.11%
4 @30 MINS	5.21	Cation exch. Resin	90.55%
5 @60 MINS	6.72	Cation exch. Resin	87.82%
6 @90 MINS	14.92	Cation exch. Resin	72.95%
Fe Reference	55.16	--	

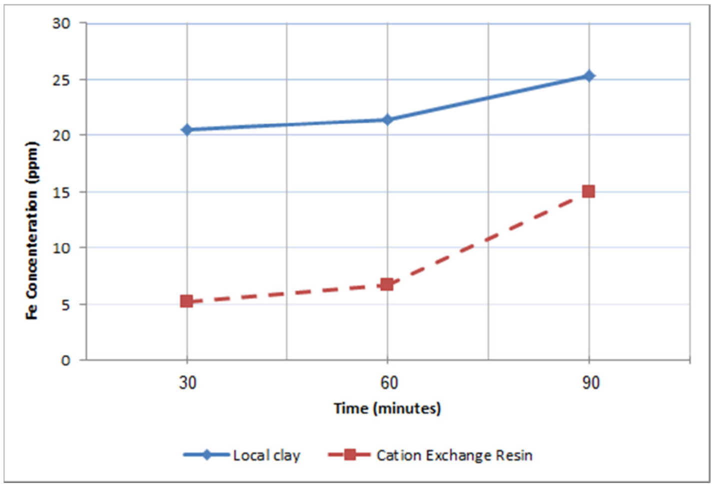

Fig. 7. Fe concentration vs time for both local materials and Cation exchange resin membranes

Comparing results of local clay to cation exchange resin samples against FE synthetic solution is showing some similarities in shapes regardless the values, as shown Figure 4; there's a gap between results, to be achieved by next experiments and enhancements of existence clay samples. Percentage removal after 30, 60 and 90 minutes for local clay sample and ion exchange resin were also displayed in table 3.

Moreover, the results indicate similar reaction comparing local clay and cation exchange resin against Mn, as cation exchange resin's percentage removal decreased from 90.55% in case of Fe after 30 minutes to 76.45% in case of Mn after the same duration, the local clay shows the same decrease in values as shown in table 4.

Table 4
ICP results for experiment step B (Mn solution 50 ppm)

Sample no./30 min interval	Mn (ppm)	Membrane	% removed
1 @30 MINS	23.48	Local clay	53.66%
2 @60 MINS	41.78	Local clay	17.54%
3 @90 MINS	50.60	Local clay	0.1%
4 @30 MINS	11.93	Cation exch. Resin	76.45%
5 @60 MINS	8.97	Cation exch. Resin	82.29%
6 @90 MINS	9.02	Cation exch. Resin	82.20%
Mn Reference	**50.67**	--	

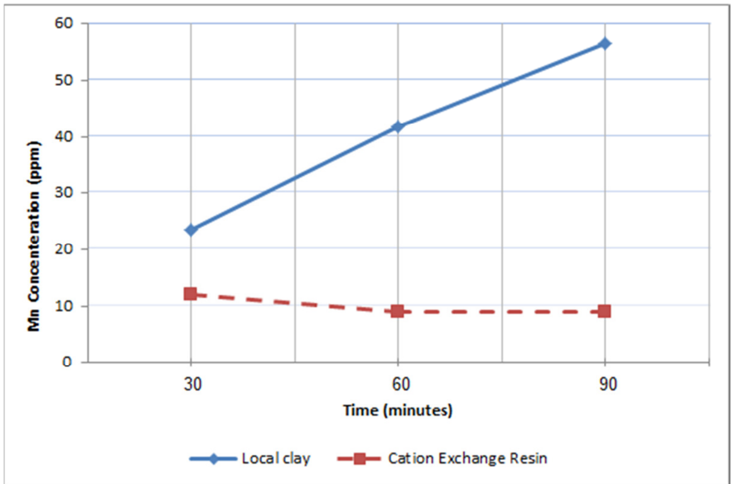

Fig. 8. Mn concentration against time for both local materials and Cation exchange resin membranes

5. Conclusion

This paper presents new, promising and low cost membrane material for treated of seawater and removal of iron and manganese from brackish groundwater. Egyptian local clays with its exchange capacities and adsorption abilities showed very promising results despite the fact that experiments used local clay without any additives or activation, which expects higher treatment percentages with enhancing local clay characteristics [14]. Local clay has desalinated seawater by around 20% of raw seawater salinity, which gives potential for treatment of low saline brackish ground water that ranges between 1000 to 15000 ppm TDS, and it has removed FE from synthetic extremely high concentration solution of 50 ppm by 62.82 % and the least result was for removing Mn from synthetic sample of 50ppm concentration by 53.67 %. Enhancing local clay characteristics and examining more factors will be further investigated during the next research steps.

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