

Research

## Seawater Desalination - Removal of Boron Rests From Desalinated Seawater: Boron Adsorption by Composite Magnetic Particles

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### Historic Background

The Middle-East geography puts Israel, latitude around 32° (31.771959, 35.217018) north of the equator, on the border of the desert.

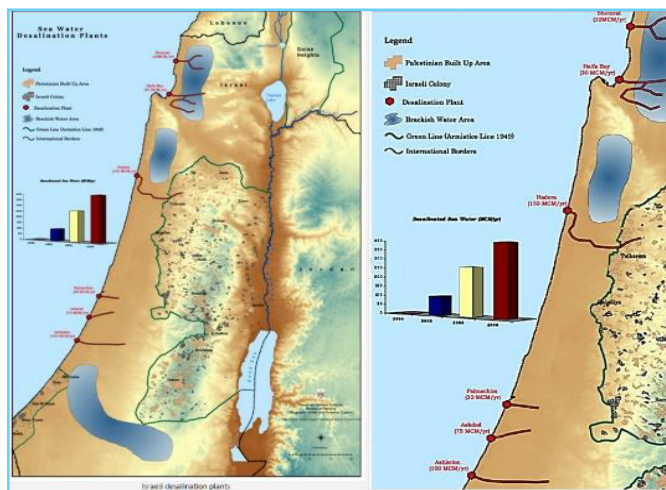


**Figure 1 :** Israel from the north (below, green forest) to south (above, yellow desert) as seen from a satellite.

### Israel From the North (Below, Green Forest) To South (Above, Yellow Desert) as Seen From a Satellite

The northern part gets an average of about 600 mm of rain annually, this can produce mineral water wells and drinking waters to a population of about 3-4 million humans. One of the major sweet water sources relies on Mt.

Hermon (highest peak 2200 above sea level, see diagram below), where the snow melts and rain precipitates produce the Jordan River, lake of Galilee.



**Figure 2:** Seawater desalination along the Israeli coast

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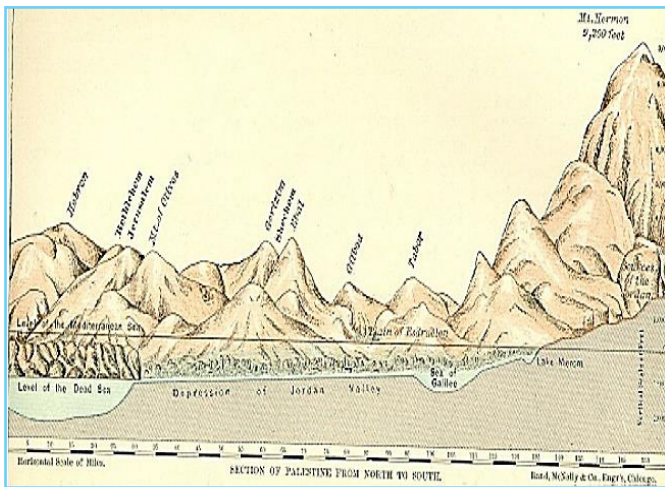


Figure 3: A cut along the Jordan River valley, Mt. Hermon, sea of Galilee and dead sea

One of the plans to eliminate Israel and siege her people eraze her from the map of the world, was to divert the Jordan River from Israeli territory to the Golan Heights and from there to the Dead Sea in the Arab (Syria, Jordan) territory. This annoyed Israel and the legend is that Mr. David Ben-Gurion, Israel first prime minister initiated the project of applying the infinite water reservoir, the Mediterranean sea which could if the proper technology is perfected, provide drinking water to a large Israel with many millions of citizens. This was about 70 years ago, now the technology is available and Israel uses about 80% of its sweet drinking waters from desalination plants along the shores of her Mediterranean Sea coast [1].

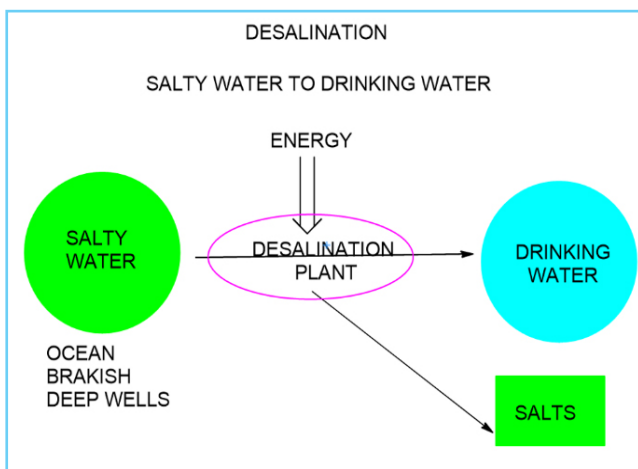


Figure 4

Is such circumstances, the Golan as the place in which the “Arab” Jordan diversion canal should flows, lost its importance. It continues to be a military asset, but the desalination technological project renovated it live threatening importance.

Nowadays, large amount of these ocean waters can be used for irrigation and human consumption [2] through desalination.

There is a lot of water on Earth [3], but more than 97% of it is salty and over half of the remainder is frozen at the poles or in glaciers. Meanwhile, around a fifth of the world’s population suffers from a shortage of drinking water and that fraction is expected to grow. Industrial production of water by desalination will be the main source of drinking water starting today and soon.

### 3. Removal of Salts from Salty Waters

- 1) Reverse Osmosis (RO).
- 2) Evaporation – Condensation

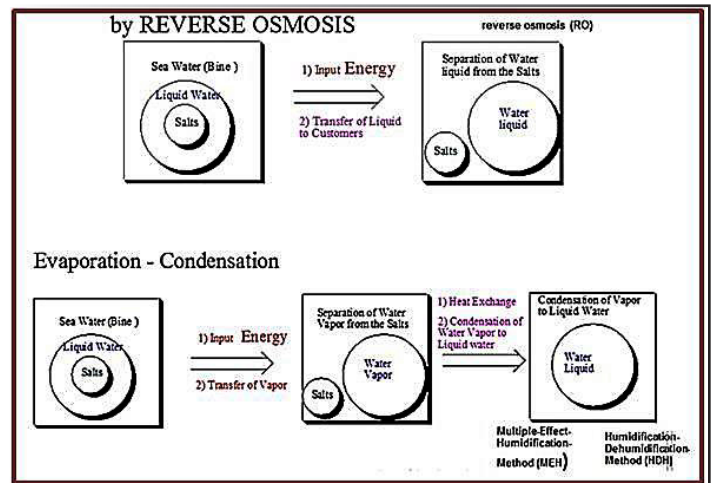


Figure 5

The most commonly used desalination technologies are reverse osmosis (RO) and thermal processes (evaporation – condensation methods) such as multi- stage flash distillation (MSF)[4a] and multi-effect distillation (MED)[4b]. The advantage of reverse osmosis (RO) is in the fact that the heating of the brine is omitted, saving thereby energy which is invested in the evaporation methods.

We live in an area where the shortage of water is a concern; processes have been developed to obtain water from seawater and brackish waters by means of reverse osmosis (RO) technology. Desalination is carried out in mega scale amounts. The advanced technology provides processes that present Percentages of elimination of salts superior in most cases to 98%. However, due to the chemistry of boron [5], at normal pH of operation of these plants, the boron, which is a cumulative toxin, is in the form of boric acid. However, the elimination diminishes to values only around 43%.

In Europe, reverse osmosis, due to its lower energy consumption, has gained much wider acceptance than its thermal alternatives. The presence of boron in drinking water facilities based on natural waters sources comes from brackish surface waters or ground water and can be traced back to either residual from 4 waste water treatment plants (mainly borate from detergent formulations) or to leachable from subsurface strata.

Today, more than 50% of the fresh waters in Israel are produced in Seawater desalination plants purified brackish waters applied for the agriculture.

However, Environmental Protection Agency estimated that the annual consumption of washing powder in Israel is greater than 40,000 tons. These amounts find their way to the desalination plant and corrupt the desalination columns.

The desalination industries are facing a few public health problems Boron [6], Magnesium [7] and other trace elements [8] that are not yet under health desired control.

### The Salts in Seawaters

Seawater is brine with a lot of salts and minerals dissolved in it in a very long process that lasts for eons. Most of the seawater differs dramatically from river water as indicated in the table:

PRINCIPAL CONSTITUENTS OF SEAWATER		COMPARISON BETWEEN OCEAN WATER AND RIVER WATER		
Chemical Constituent	Content (parts per thousand)	Chemical Constituent	Percentage of Total Salt Content	
			Ocean Water	River Water
Calcium (Ca)	0.419	Silica (SiO <sub>2</sub> )	—	14.51
Magnesium (Mg)	1.304	Iron (Fe)	—	0.74
Sodium (Na)	10.710	Calcium (Ca)	1.19	16.62
Potassium (K)	0.390	Magnesium (Mg)	3.72	4.54
Bicarbonate (HCO <sub>3</sub> )	0.146	Sodium (Na)	30.53	6.98
Sulfate (SO <sub>4</sub> )	2.690	Potassium (K)	1.11	2.55
Chloride (Cl)	19.350	Bicarbonate (HCO <sub>3</sub> )	0.42	31.90
Bromide (Br)	0.070	Sulfate (SO <sub>4</sub> )	7.67	12.41
Total dissolved solids (salinity)	35.079	Chloride (Cl)	55.16	8.64
		Nitrate (NO <sub>3</sub> )	—	1.11
		Bromide (Br)	0.20	—
		TOTAL	100.00	100.00

Figure 6

Sea salt, NaCl. Is the major component in sea waters, whereas Calcium carbonates are in abundance in River waters? Desalinated seawater [9] (from the Ashkelon facility) out of a desalination facility is poor in salts in particular Magnesium: various elements in the water is not yet optimized Magnesium [10] and Boron as reflected below:



Figure 7: The Ashkelon Desalination Facility produces about 5 percent of Israel's total water needs.

### India water quality compared with Ashkelon

The Ashkelon water (left table) contains less ions. It is totally deficient in Mg.

WATER-QUALITY PARAMETERS AFTER DESALINATION			Drinking Water standards recommending agencies and unit weight		
Parameter	Water from Ashkelon desalination plant	Recommendation for domestic and agricultural usage	[All values except pH is in mg/L]		
			Standards	Recommended Agency	Unit Weight
EC (dS/m)	0.2-0.3	<0.3	6.5 - 8.5	ICMR / BIS	0.2190
[Cl <sup>-</sup> ] (mg/liter)	15-20	<20	120	ICMR	0.0155
[Na <sup>+</sup> ] (mg/liter)	9-10	<20	300	ICMR / BIS	0.0062
[Ca <sup>2+</sup> ] (mg/liter)	40-46	32-48*	500	ICR / BIS	0.0037
[Mg <sup>2+</sup> ] (mg/liter)	0	12-18	75	ICMR / BIS	0.025
[SO <sub>4</sub> <sup>2-</sup> ] (mg/liter)	20-25	>30	30	ICMR / BIS	0.662
[B] (mg/liter)	0.2-0.3	0.2-0.3	250	ICMR	0.0074
Alkalinity (mg/liter as CaCO <sub>3</sub> )	48-52	>80*	45	ICMR / BIS	0.0413
CCPP (mg/liter as CaCO <sub>3</sub> )	0.7-1.0	3-10*	150	ICMR / BIS	0.0124
pH	8.0-8.2	<8.5*	5.0	ICMR / BIS	0.723
			5.0	ICMR	0.3723

\*Value based on the new Israeli recommendations for desalinated water.  
<http://www.techon.ac.il/pdf/Professors/Dr. Lahav/14.pdf> [http://www.cesjournal.org/wp-content/uploads/2012/07/wellno2\\_4\\_12.pdf](http://www.cesjournal.org/wp-content/uploads/2012/07/wellno2_4_12.pdf)

Figure 8

The low metal ion concentrations are achieved by the reverse osmosis technology-based on DOW Film Tec Seawater RO Membrane Elements (SWRO) for Seawater Desalination [11,12].

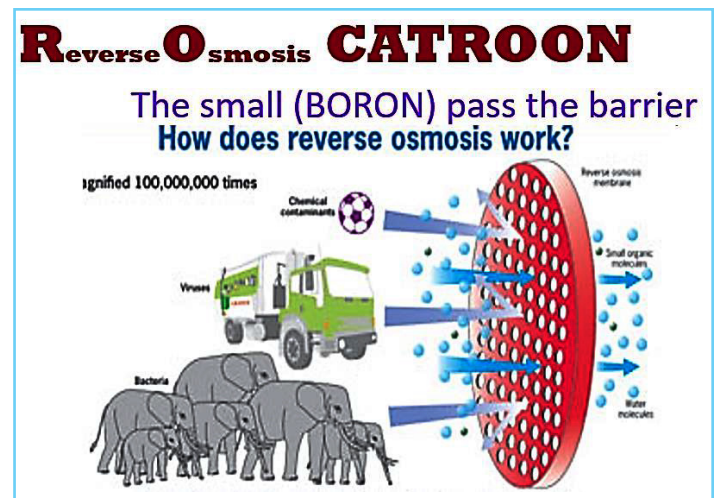


Figure 9

Although the boron amounts in the Ashkelon desalinated seawater is low far below the values approved (1,0) by the European authorities, we thought that toxicity of boron, in application to field agriculture watering, should be even lower than achieved in the desalination Plants [13]. In irrigation, the soil gets poisonous due to accumulation. It is reported that efficient removal of boron needs additional treatments based on the small atomic radius of the element [14]. These low boron concentrations are critical for allowing the use of the treated municipal wastewater for agricultural irrigation, since many crops are sensitive to boron concentrations above 0.7 ppm and municipal water use adds, mostly through detergents, about 0.4 ppm to the water supply's background concentration. To achieve such limits, all the large seawater desalination plants use a two-pass design, which reduces not only boron but also chloride and sodium concentrations.

Water Use	Guideline (Total B)
Drinking Water	5.0 mg/L
Aquatic Life Freshwater Marine	1.2 mg/L 1.2 mg/L
Wildlife	5.0 mg/L
Irrigation	0.5 - 6.0 (depends upon crop. See Table 2)
Livestock Watering	5.0 mg/L

Table 1 : Recommended Guidelines for Boron Credit Ref. [4]

Boron compounds in water at high concentration are known to be toxic to humans and plants. The World Health Organization (WHO) has limited boron concentration in drinking water to less than 0.5 ppm. Because of the increased use of desalinated seawater and underground water for drinking water and a lot of boron emissions via wastewater from the manufacturing process, the removal of boron from aqueous solutions has been an important issue in recent years. There are several methods used for boron removing from aqueous solutions, such as precipitation, adsorption, solvent extraction and ion-exchange method. Since small amounts of boron have to be removed from very large amounts of water, we have explored the feasibility of applying magnetic Nanoparticle-bound complexation for the removal of boron.

The general concept is adopted [15] from medical diagnostics as follows based on the general scheme for the capture and removal of the boron by applying the curcumin-magnetite magnetic conglomerate particles is depicted in the figure:

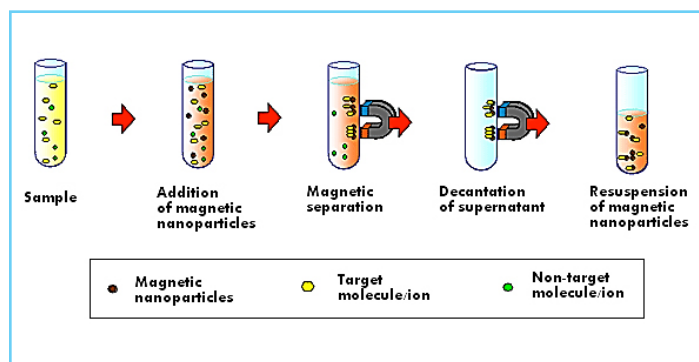


Figure 10 : the general protocol for the capture and removal by magnetic field the water soluble boron applying the magnetite-curcumin nanoparticles composite

Tolerance	Boron in Irrigation Water (mg/L)	Agricultural Crop
Very sensitive	< 0.5	Blackberry
Sensitive	0.5 - 1.0	Peach, cherry, plum, grape, cowpea, onion, garlic, sweet potato, wheat, barley, sunflower, mung bean, sesame, lupin, strawberry, Jerusalem artichoke, kidney bean, lima bean
Moderately sensitive	1.0 - 2.0	Red pepper, pea, carrot, radish, potato, cucumber
Moderately tolerant	2.0 - 4.0	Lettuce, cabbage, celery, turnip, Kentucky bluegrass, oat, corn, artichoke, tobacco, mustard, clover, squash, muskmelon
Tolerant	4.0 - 6.0	Sorghum, tomato, alfalfa, purple vetch, parsley, red beet, sugar beet
Very tolerant	6.0 - 15.0	Asparagus

Table 2

For the capture and removal of the boron by applying the curcumin-magnetite conglomerate is depicted in the following figure. The in high dilution water-soluble boron removal, applying the magnetite-curcumin nanoparticles composite. The feasibility of recycling the magnetic conglomerate is also checked.

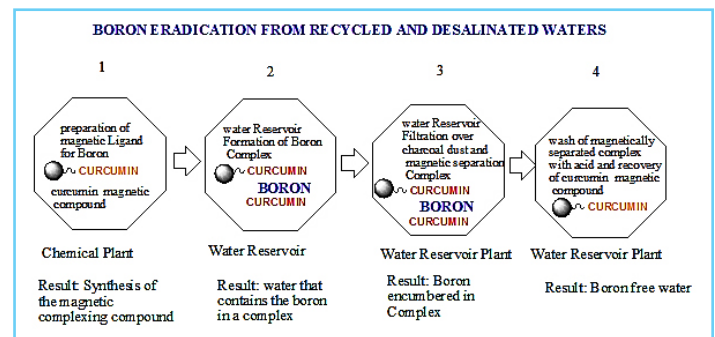


Figure 11 : General concept for boron extraction in large water reservoir

### Abstract

We prepared Fe<sub>3</sub>O<sub>4</sub> (magnetite nanoparticles) coated covalently with curcumin other curcuminoids. In this research, novel prototype boron quantification/removal technique, based on curcumin method and magnetic separation was developed and evaluated under different conditions to the most efficient and cost-effective methods of boron determination/removal.

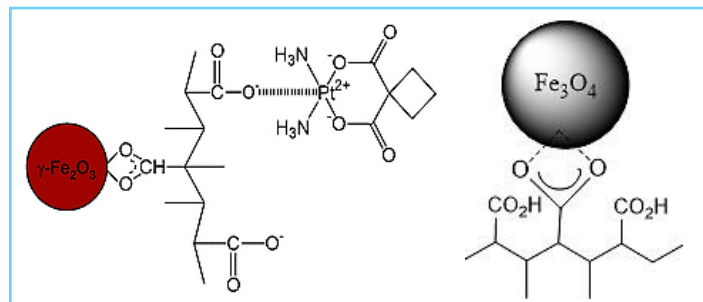
This technique is based curcuminoid synthesis which comprises functional di-ketone coupled to phenol on each side that complexes boron (ROSOCYANINE RED COMPLEX). This molecule is attached to a handle that will connect the Curcumin and the particle. The linker is connected to the phenol moiety on one side and on the other will be the amino group to bind it with a carboxylic acid, which is the functional

group on the particle surface forming amide- stable group under drastic conditions.

The curcumin unit forms the well-known Rosocyanine complex with boron which enables the removal of the boron from the water vis its complex with the magnetite basis to immobilize the curcumin by covalent5 bonding to the coated surface of a magnetic particle to enable the formation of a Rosocyanine complex with the boron.

**Abstract**

We prepared Fe<sub>3</sub>O<sub>4</sub> (magnetite nanoparticles) coated covalently with curcumin other curcuminoids. It is believed that Fe<sub>3</sub>O<sub>4</sub> particles can form a polar- covalent bond with one of the carboxylates of the poly-methyl-metacyclic acid coating. We applied the protocols of conglomerate synthesis of Ref[7] for the coating of the magnetite nanoparticles.



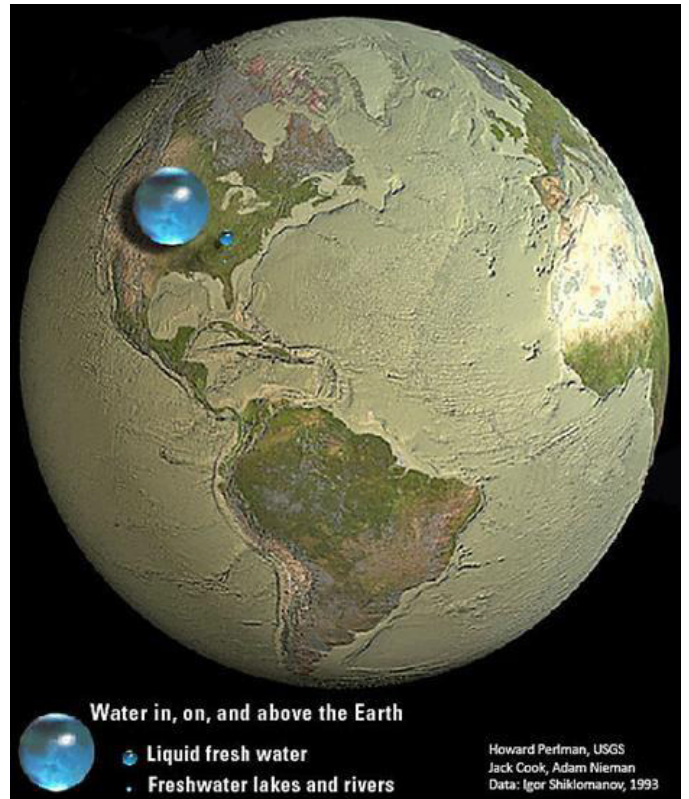
**Figure 12 :** poly (methacrylic acid) (PMAA) coated magnetite nanoparticles [16] **Figure 13**

On this basis, in this research work, novel prototype boron quantification-removal technique, based on curcumin and on magnetic separation, was developed and evaluated under different conditions to the recyclable, most efficient and cost-effective methods of boron determination/removal.

**Introduction**

Water, the essential element for the existence of life, carries in it many ingredients that are the centers of the multi enzyme systems on which life is based. Such as trace minerals and other elements building units of enzymatic multi systems.

This central role makes modern water economy a major issue in most of the countries around the world. Although 2/3 of our planet is covered with water, only a small fraction of the water is used for humans and plants [17]. Drinking water supply is becoming a major topic in the modern economy and access to it determines relations between states and countries are based on it.

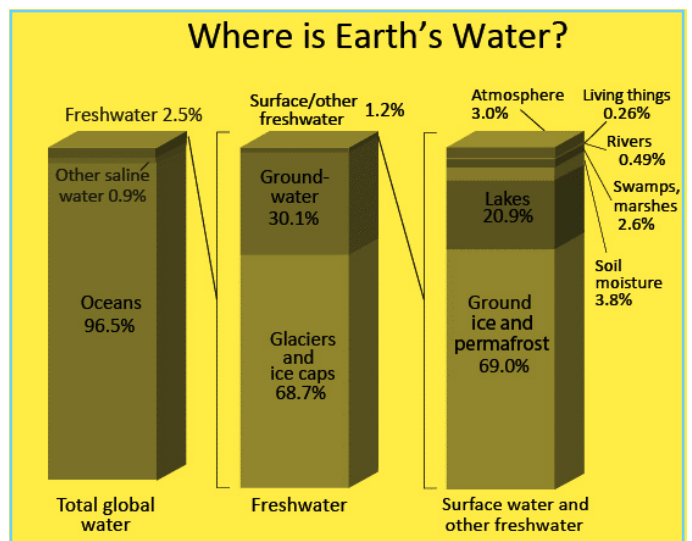


**Figure 14 :** The World's Water

Spheres showing:

- (1) All water (sphere over western U.S., 860 miles in diameter)
- (2) Fresh liquid water in the ground, lakes, swamps, and rivers (sphere over Kentucky, 169.5 miles in diameter), and
- (3) Fresh-water lakes and rivers (sphere over Georgia, 34.9 miles in diameter).

Credit: Howard Perlman, USGS; globe illustration by Jack Cook, Woods Hole Oceanographic Institution (©); Adam Nieman.



**Figure 15**

There are a few routes to achieve the goal - safe drinking water supply. The major approach is the of sea water desalination as the most modern technology to access drinking waters from salty oceans.

Nowadays, a large amount of these ocean waters can be used for irrigation and human consumption [18] through desalination. There is a lot of water on Earth [19], but more than 97% of it is salty and over half of the remainder is frozen at the poles or in glaciers. Meanwhile, around a fifth of the world's population suffers from a shortage of drinking water and that fraction is expected to grow. Industrial production of water by desalination will be the main source of drinking water starting today and in the near future.

### Removal of salts from salty waters

- 1) Reverse Osmosis (RO).
- 2) Evaporation – Condensation

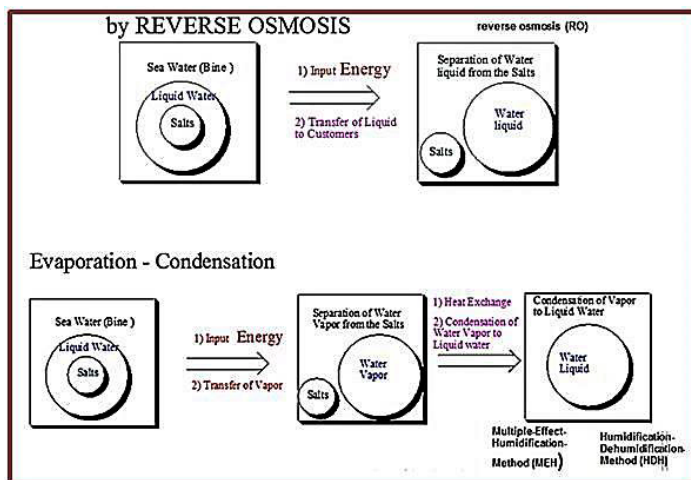


Figure 16

Two main approaches for desalination, both require energy

The most commonly used desalination technologies are reverse osmosis (RO) and thermal processes (evaporation – condensation methods) such as multi- stage flash distillation (MSF)[5a] and multi-effect distillation (MED)[5b]. The advantage of reverse osmosis (RO) is in the fact that the heating of the brine is omitted, saving thereby energy which is invested in the evaporation methods.

We live in an area where the shortage of water is a concern; processes have been developed to obtain water from seawater and brackish waters by means of reverse osmosis (RO) technology. Desalination is carried out in mega scale amounts. The advanced technology provides processes that present percentages of elimination of salts superior in most cases to 98%. However, due to the chemistry of boron[20], at normal pH of operation of these plants, the boron which is a cumulative toxin is in the form of boric acid. However, the elimination diminishes to values only around 43%.

In Europe, reverse osmosis, due to its lower energy consumption, has

gained much wider acceptance than its thermal alternatives. The presence of boron in drinking water facilities based on natural waters sources comes from brackish surface waters or ground water and can be traced back to either residual from waste water treatment plants (main borate from detergent formulations) or to leachable from subsurface strata.

Today, More than 50% of the fresh waters in Israel are produced in Seawater desalination plants purified brackish waters applied for the agriculture. However, environmental Protection Agency estimated that the annual consumption of washing powder in Israel is greater than 40,000 tons. These amolunts find their way to the desalination plant and corrupt the desalination columns.

The desalination industries are facing a few public health problems in particular Boron[21], Magnesium[22] and other trace elements[23] that are not yet under health desired control.

Under these circumstances, the boron remains a focus as the most sensitive element regarding agriculture and crop production. Since crops are very sensitive to the boron concentration in the soil and waters, and the brackish waters contain boron in much higher concentration that is allowed. Its presence corrupts both vegetation's, reduces quality and amounts of crops and poisoning the soil due to its cumulative nature. This presence of boron is resulting from household sources, like laundering for example. Great effort is being invested in the rejection of boron from brackish waters [24]. For the time being, the remedy is still needed. Post treatment for boron removal by RO is the practical way. However, the situation in the brackish waters may need a better treatment for boron removal [11]. The post treatment by a second RO desalination leaves about 10% of the small unwanted boron ions that pass the membrane used for removal of the salts (see cartoon) in the desalinated sea waters and further treatments to remove these rests.

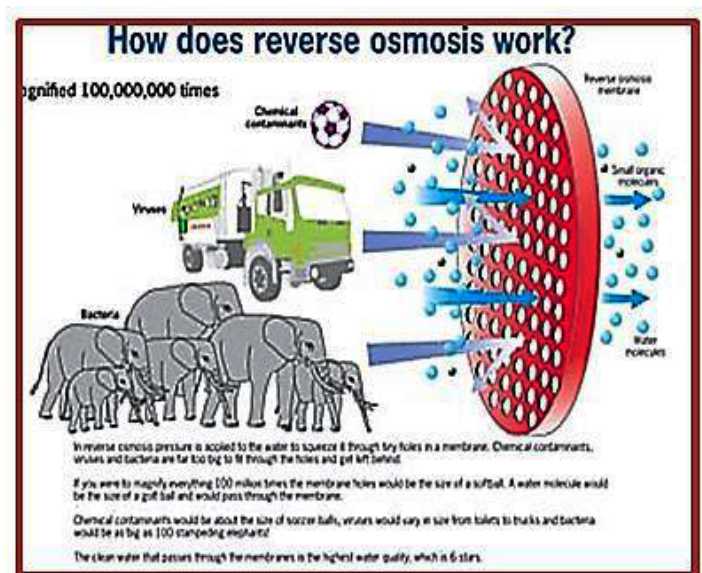


Figure 17

The strainer ignores the “small (refers to a short atomic radius) ions (boron for example)

This further purification is needed to avoid physiological damage in animals and plants. Plants are extremely sensitive to Boron, although this element, in traces, is essential to their metabolism. Water for irrigation and the soil should keep boron in that quality[25].

Tolerance <sup>Note</sup>	Concentration of boron in soil water (mg/L) <sup>Note2</sup>	Agricultural crop
Very sensitive	<0.5	Blackberry
Sensitive	0.5-1.0	Peach, cherry, plum, grape, cowpea, onion, garlic, sweet, potato, wheat, barley, sunflower, sesame, strawberry
Moderately sensitive	1.0-2.0	Red pepper, pea, carrot, radish, potato, cucumber
Moderately tolerant	2.0-4.0	Lettuce, cabbage, celery, turnip, oat, corn, arlchoke, lobacco, mustard, squash
Tolerant	4.0-6.0	Tomato, alfalfa, purple, parsley, sugar-beet
Very tolerant	6.0-15.0	Asparagus

**Table 1:** Optimal Boron C concentrations for irrigation waters for some plants

Boron removal with RO alone is done at pH 9. At this pH, the boron is partially negatively charged and the rejection can be up to 90% with seawater RO and 75% with brackish water RO elements. To achieve a limit of below 0.5 mg/l boron in the permeate; an additional RO treatment of the first permeate is necessary (by a two pass or partial two pass system). The pH adjustment is done in front of the second pass in such a case. Therefore,

Boron removal in seawater RO desalination systems is usually done by a second desalination pass, operating at high pH (pH>10). This method is not economical for reduction of boron content in permeates of brackish water desalination [15].

Why should Boron be removed from drinking water?

The human body contains approximately 0.7 ppm of boron, an element that is not considered as a dietary requirement. Still, we absorb this element from food, because it is a dietary requirement for plants. Daily intake is approximately 2 mg. The amount of boron present in fruits and vegetables is below the toxicity boundary.

At a daily intake of over 5 g of boric acid, the human body is clearly negatively influenced, causing nausea, vomiting, diarrhea and blood clotting. Amounts over 20 g are life threatening. Boric acid irritates the skin and eyes.

A possible correlation exists between the amount of boron in soils and drinking water, and the occurrence of arthritis among people.

The World Health Organization recommends a Boron concentration in

drinking water below 0.5 mg/L. EU Standards require a boron level below 1 mg/L

Boron can be toxic at very low concentration levels. Boron concentration lower than 1mg/L is essential for plant development, but higher levels can cause problems in sensitive plants. Most plants exhibit toxicity problems.

Source: Extracted from the Australian Water Quality Guidelines for Fresh & Marine Waters (ANZECC)

Note. Tolerance will vary with climate, soil conditions, and crop varieties. Maximum concentration tolerated in irrigation water without a reduction in yield is approximately equal to soil water values.

Boron level in drinking waters and waters used for irrigation should be constantly monitored and kept within the required limits.

**The main options for boron removal are: 1 single pass RO with high boron rejection membranes. 2 SWRO (seawater reverse osmosis ) followed by BWRO (brackish water reverse Osmosis). 3 SWRO followed by boron selective ion exchange resin (BSR). 4 SWRO followed by a hybrid process of BSR and BWRO. 5 SWRO followed by electro dialysis reversal (EDR)**

**Figure 18:**

How can Boron remove be achieved from desalinated water? (See below) [26]

A very often applied removal procedure is based on post treatment of the desalinated waters to remove the rests od the Boron by an additional RO removal procedure as shown below[27]:

Depending on the water salinity, boron concentration, and temperature, two main processes are used to produce drinking water below 0.5 mg/L of Boron:

- **Process A 2-pass SWRO:**

2nd-Pass RO with caustic soda addition to raising pH around 9.5. Some of the pass-1 permeate can be by-passed in order to keep some minerals in the water.

The 2nd pass RO can be made of Seawater Low Energy membranes if temperature and salinity are high or Brackish Water High rejection membrane in case of milder conditions.

- **Process B SWRO+ IX:**

Selective Boron Ion Exchange Resin with or without bypass, depending on the residual boron concentration needed. The selective resin must be on-site regenerated with caustic soda and hydrochloric acid. A double column system is often required to ensure a continuous production.

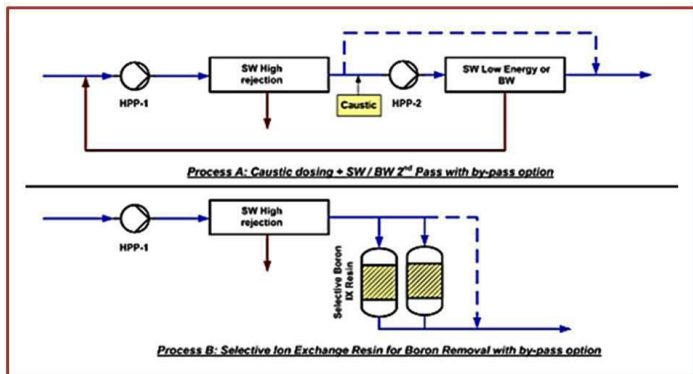


Figure 19

Comparison Parameters	Process A	Process B
Boron residual concentration	0.3-1.0 mg/L	0-1.0 mg/L
Energy costs	Higher - HPP2 power consumption	
Investment costs	Higher - Second Pass RO	
Chemicals costs		Higher - Resin Regeneration by NaOH, HCl
Footprint	Larger	
Water quality	Poor mineralization without by-pass, low sodium chloride content	High mineralization with or without by-pass due to resin selectivity, high sodium chloride content
Recommendations	Cost efficient for drinking water production at 0.5 mg/L Boron residual max.	Cost efficient for irrigation water for sensitive crops with Boron residual tolerance between 0.5 and 1.0 mg/L

LENNTECH engineers design and size the most cost-efficient Boron Removal Process that matches your water requirement.

Figure 20

As one can see from the tables above. The value of 0.5 mg/Lit. is tolerated by both mammals and many plants. However, Process B requires a second RO process which is expensive in energy and needs its own facility suited to treat huge volumes of desalinated waters.

<http://www.lennotech.com/processes/desalination/post-treatment/post-treatments/boron-removal.htm#ixzz47tiffBVgh>

Many researchers have investigated to remove the rest of boron by various chemical and absorption on polymers and naturally occurring minerals, a few examples of attempts for such post treatments are cited therein [28].

## Introduction

Modern water economy is a major issue in most of the countries around the worlds. Although 2/3 of our planet is covered with water, only a fraction of a large amount of this resource can be used for irrigation and human consumption [29]. There is a lot of water on Earth, but more than 97% of it is salty and over half of the remainder is frozen at the poles or in

glaciers. Meanwhile, around a fifth of the world's population suffers from a shortage of drinking water and that fraction is expected to grow [30]. It is clear that Industrial production of water will be the main source of drinking water starting today and in the near future. There are a few routes to achieve the goal for safe drinking water supply the major approach is the of sea water desalination.

Most of the salts in the seas can be removed by frequently applied the filtration technique Reverse osmosis (RO) as basic technology. In many cases, almost all cations and anions are removed from the saline leaving about 10% of the problematic Boron element in the desalinated water.

Boron is essential for life in low concentration but may be poisonous at higher than 0.3 mg/1000cc of drinking water [31].

An economically useful and simple way has yet to be found for the complete removal of the rests of boron element which are still present in the Reverse Osmosis desalinated drinking waters[32].

In this paper, we suggest the development of our results from a laboratory research project. Boron containing natural products is rare, for example, the antibiotic macrolide Boromycin [33]. Other boron containing antibiotic macrolides related to Boromycin. Can bind boron by forming covalent bonds between boron and adjacent hydroxyl groups of the antibiotic. This general type of strong binding is realized also in the binding of Boron by curcumin.

Curcumin in was applied to eradicate Boron from water by Malaysian [34] researchers, However, The pure curcumin spice fate is to become a waste product. With a view on a recycling possibility for the curcumin having environmental considerations in mind, we investigated the possibility of application of immobilized curcumin on magnetic nanoparticle to affect the eradication of the Boron from the water.

This work is based on covalently immobilized curcumin by a 4-step synthesis, boron capture by complex forming reaction (Rosocyanin or Rubocurcumin moiety formation in bulk), separation and isolation by the magnet of the composite that contains the water soluble boron and recycling to the magnetic composite, and recycling of the free immobilized curcumin material.

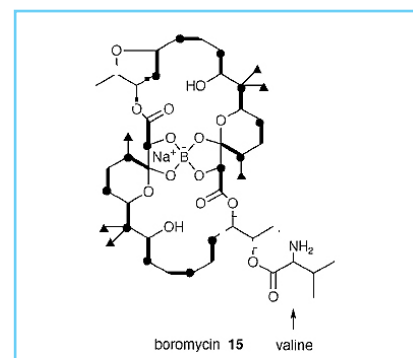


Figure 21 : Boromycin[5b]



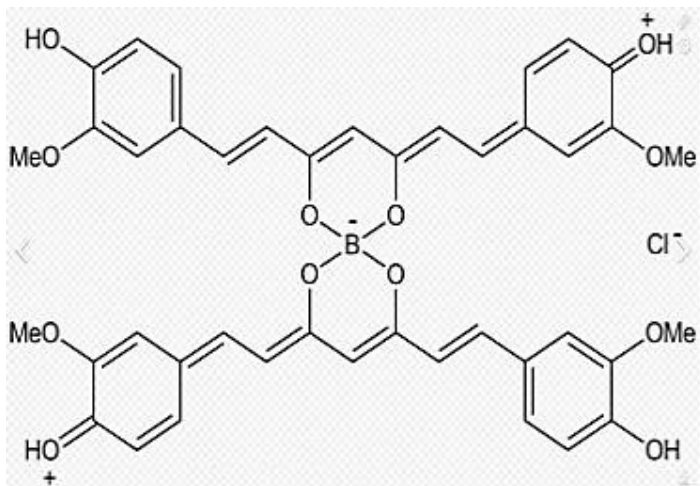


Figure 22 : Rosocyanine

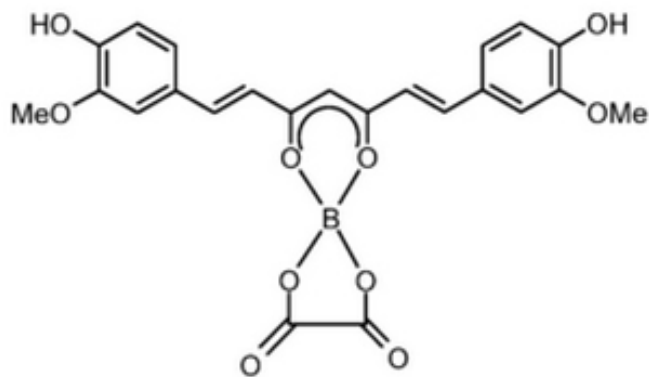


Figure 23 : Rubrocurcumin

Our findings may give a way to improve currently applied technologies and remove possible obstacles presently present in the currently used procedures for removal of boron from industrially manufactured waters.

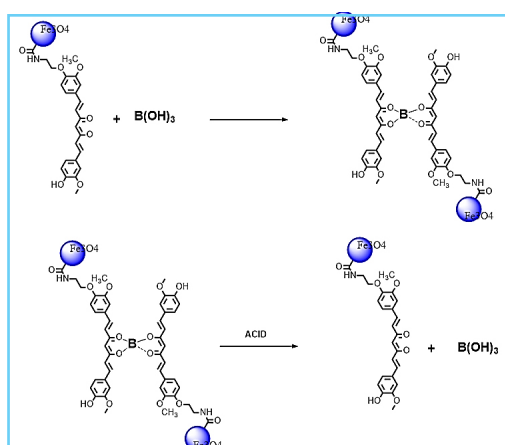


Figure 24

Capture and recycle of boron by immobilized curcumin on Fe3O4 nanoparticles and recycling of the immobilized curcumin.

Turkish scientists [35] applied boron-specific resin Amberlite IRA-743 in free-amine form (see chart below) is also uneconomical due to expensive regeneration steps.

The capacity of this resin in salt-form was found to be 1.5 mg boron ml<sup>-1</sup> resin at 10% boron leakage. The possibility of reuse of 90% of the regenerate and production of 4400 tons of boric acid in the removal system with salt-form boron-specific resin, compensate the annual cost of chemicals and also bring in some profit. The complexing organic unit of the resin is recyclable.

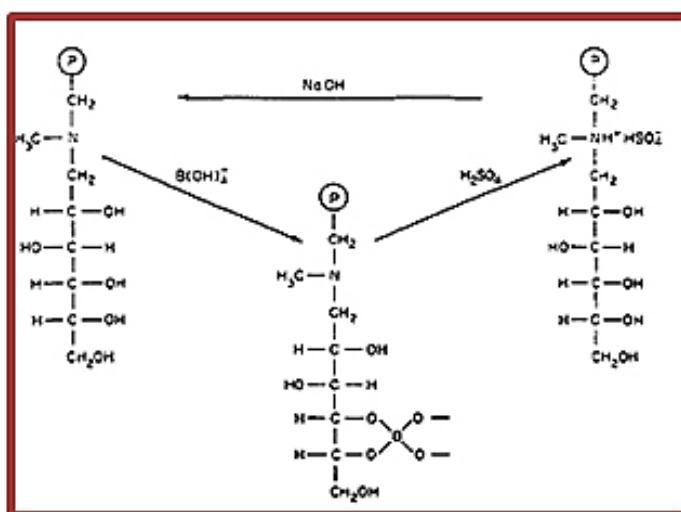


Figure 25 : Resin: Amberlite Chart: capture of boron and recovery of complexing polyol under acidic conditions

With the view on a recycling possibility for the curcumin and having environmental considerations in mind, we investigated the possibility of application of immobilized curcumin on magnetic nanoparticle to affect the eradication of the Boron from the water (inspect Turkish Chart above).

## Methods

### Synthesis Strategy and Synthesis of Conglomerate

A CH<sub>2</sub>-CH<sub>2</sub> (from 2-Bromo Ethan amine) tether will connect the curcumin unit to the covalently integrated carboxylate moiety of the Carboxyl group (-CO<sub>2</sub>H) functionalized ferromagnetic iron oxide 5 via the robust amide group formation. For this, the modified curcumin was prepared in 4 synthetic steps. The strategy for the synthesis of the complexing agent is depicted in Scheme 2 as follows:

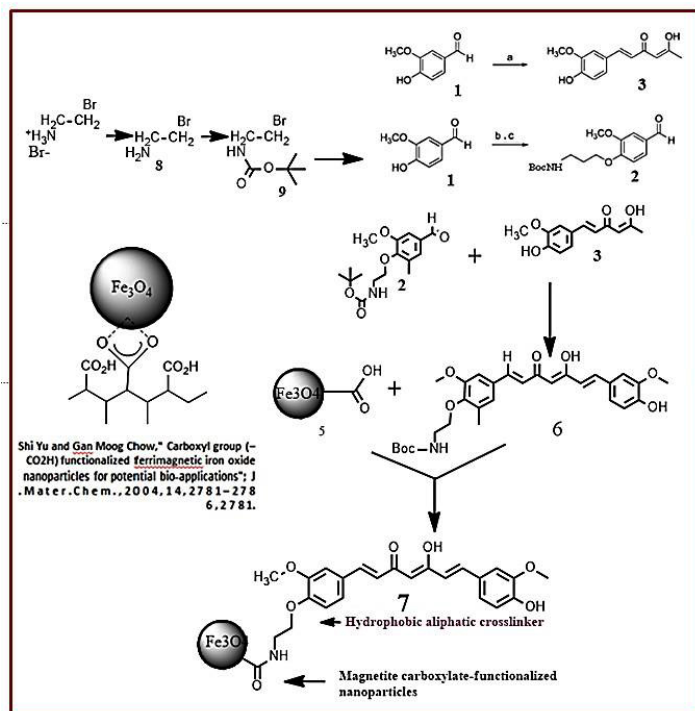


Figure 26

Scheme 2: Overview on the synthesis of the boron capturing agent 7 based on the polyacrylic acid coated Fe<sub>3</sub>O<sub>4</sub> bound to curcumin via a hydrophobic linker

### Reactions

1) The reaction of vanillin with acetyl acetone in the presence of B<sub>2</sub>O<sub>3</sub> afforded the dienone 3.

2) The reaction of 2 with n-Boc protected 2-Bromo Ethan amine gave the aldehyde 4.

3) Aldol type Condensation of 3 in the presence of Et<sub>3</sub>B gave the N-protected curcumin derivative which upon acidic removal of the Boc group in 30% aqueous TFA afforded the target organic moiety of the expected product 6.

4) Reaction of the magnetic nanoparticles of 5 either in water (method #1, the formation of (LCC1-MP1) or in methanol/water solution (method #2, the formation of LCC1-MP2) as follows:

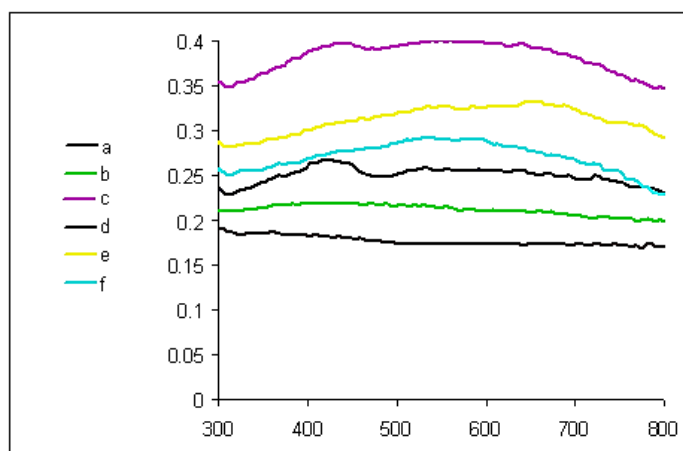
Method #1: water as reaction medium (formation of 7).

1 ml suspension of the Carboxyl group (-CO<sub>2</sub>H) functionalized ferrimagnetic iron oxide 5 in water (contains the composite in amounts of 10 mg/ml), 2 ml water the solid rinsed and another amount of 1 ml water was added. 10 mg EDC (1-Ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride) was then added and the reaction was shaken for 5 min. then 10 mg of the unprotected amino compound 6 were added and the reaction was allowed to continue under shaking overnight at room temperature. Then the solvents removed, washed twice with 5 ml of

water dried under reduced pressure at room temperature and subjected to spectral identification. Yield 20 mg of magnetic material.

Method #2: water -methanol 1:1 as reaction medium (formation of 7).

1 ml suspension of the Carboxyl group (-CO<sub>2</sub>H) functionalized ferrimagnetic iron oxide 5 in water (contains the composite in amounts of 10 mg/ml), 2 ml water was added to the reactor, the solid rinsed and an amount of 1 ml of water-methanol 1:1 was added to the wet solid. 10 mg EDC (1-Ethyl-3-(3-dimethyl aminopropyl)carbodiimide hydrochloride) was then added and the reaction was shaken for 5 min. then 10 mg of the unprotected amino compound 6 were charged and the reaction was allowed to continue under shaking 3 hours at room temperature. Then the solvents removed, washed twice with 5 ml of water dried under reduced pressure at room temperature and subjected to spectral identification. Yield 20 mg of magnetic material.



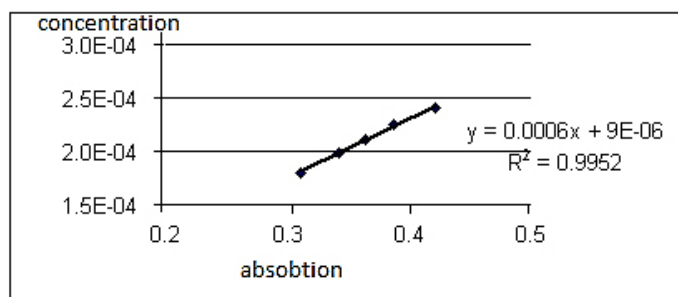
**Graph 1 :** UV/VIS spectra of Magnetic Nanoparticle bound to Curcumin 7 prepared in method #1 and method #2 as compared to curcumin derivative 6 (not connected to magnetic nanoparticle)

The spectra were taken on samples of 0.25 mg/ml of 1:1 methanol -water solution the above graphs were obtained:

- Magnetic nanoparticle connected to carboxylate (LCC1-MP1) type 1,
- Magnetic nanoparticle connected to carboxylate (LCC1-MP2) type 2.
- Conglomerate 7 in coupling method #1 (water as solvent),
- Conglomerate 7 on MP1 coupled in 1:1 methanol -water (method #2).
- Conglomerate based on magnetic nanoparticles carboxylate type 2 methods #1.
- Conglomerate based on magnetic nanoparticles carboxylate type 2 (method #2)

The graphs indicate the connection of the curcumin derivative by covalent bonding to the carboxylate moiety of the magnetite nanoparticles. The estimation of the amount of curcumin coating on the magnetite was done as follows:

We have carried out a comparative measurement to be able to estimate which composite contained more curcumin moiety bound to the surface. We were able to calibrate by the calibration graph. (See below graph 2)



Graph 2

The actual absorption at 420 nm (graph 1) is a superimposition of mainly two contributions:

- The curcumin bound to the magnetic nanoparticle.
- The free curcumin-linker unit and

It is possible, by application of the calibration curve to estimate the contribution of the free curcumin-linker unit (graph 2). Subtracting this contribution from the absorption of the bulk will give an estimation of the magnitude bound curcumin).

The table below summarizes the contributions of the suspension of the nanoparticles bound curcumin[36] and the unbound curcumin-linker molecules in solution respectively.

the particle	amount of coating on magnetite
LCC1-MP1	$1.286E^{-4}$ mol/mg
LCC1-MP2	$5.24E^{-5}$ mol/mg
LCC2-MP1	$3.49E^{-5}$ mol/mg
LCC2-MP2	$5.40E^{-5}$ mol/mg

Figure 27: Conglomerates: estimated curcumin bound covalently to magnetite particles.

TOTAL ABSORPTION OF CURCUMIN IN SUSPENSION	CONCENTRATION OF CURCUMIN NOT BOUND TO MAGNETITE
LCC1-MP1	$1.286E^{-3}$ M
LCC1-MP2	$5.24E^{-4}$ M
LCC2-MP1	$3.49E^{-4}$ M
LCC2-MP2	$5.40E^{-4}$ M

Figure 28: concentrations of curcumin-linker and curcumin bound to the magnetite respectively

Subtraction of data from the table affords the estimation of magnetically bound curcumin (table)

This indicates that the highest degree of binding to the magnetite is resulting by application of method 1 (water as reaction solvent) the concentration of curcumin bound covalently to the surface of the magnetite nanoparticles is more than twice as compared to the results in method 2.

### Experimental Section

For the quantitative determination of boron and curcumin in aqueous solutions

A calibration graph was created as follows:

- Preparation of the basic standard solution of Curcumin-oxalic acid:

40 mg of pure curcumin and 4 gr of oxalic acid were dissolved in a 100 ml. analytical volumetric flask and dissolved in 80 ml. of absolute ethanol to this,

4.2 ml. of concentrated hydrochloric acid were added and the pure ethanol was added to fill the calibrated 100 ml. volumetric flask. This standard solution remained stable for 3 days.

The creation of the calibration plot was done as follows: a) 0.0 , b) 0.25 , c) 0.5 , d) 0.75 , e) 1.0mg of solid B(OH)<sub>3</sub> were diluted in 1 ml. volumetric flask and water was added to the calibration line. To each sample of the standard solution and the UV/VIS spectra of the red solution were taken

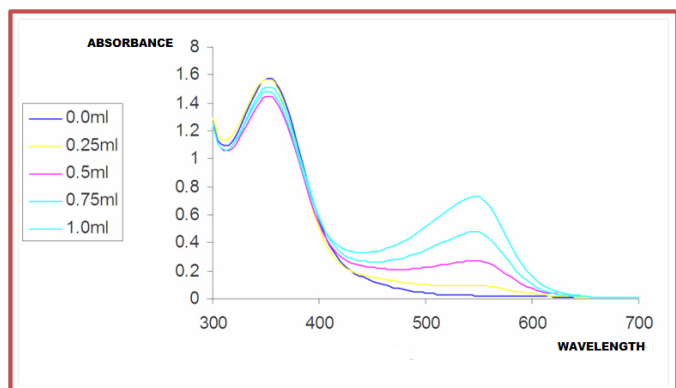
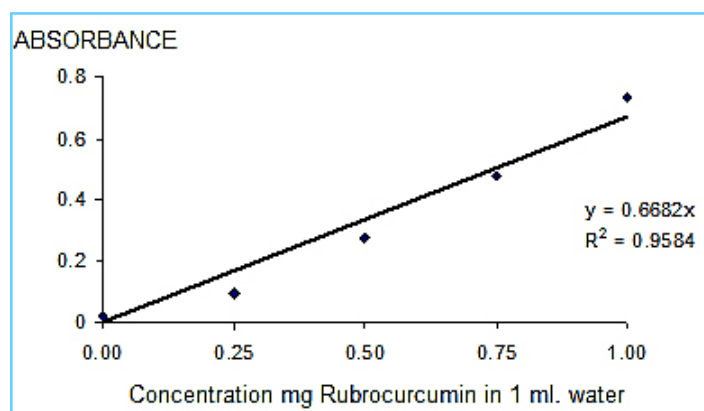


Figure 29: UV/Vis of the aqueous solutions a-e for the variety of B concentrations

The 540 nm wavelength shows the highest sensitivity to Rubrocurcumin concentrations on this basis. Graph 8 was plotted to indicate a linear relation (Beer-Lambert law) of Rubrocurcumin concentration and the absorbance,



Graph 3: calibration curve based on 540 nm absorbances of rubrocurcumin for the quantitative determination of boron in the aqueous medium.

The synthesis of (1E,4Z,6E)-1-(4-(2-aminoethoxy)-3-methoxyphenyl)-5-hydroxy-7-(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-trien-3-one 6.

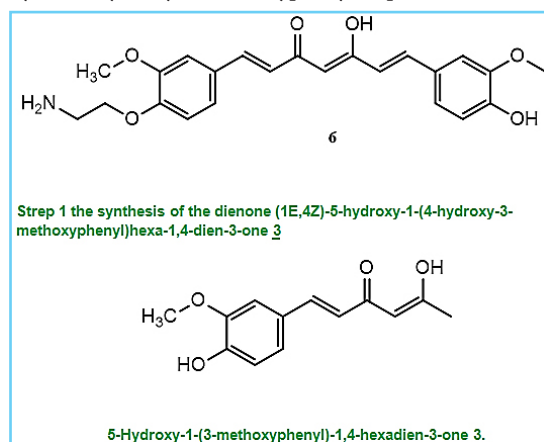


Figure 30

Charge 0.0145 mol (2.05 gr) acetyl-acetone, 0.013 mol (1.92 gr) B<sub>2</sub>O<sub>3</sub> into a 3-necked flask under N<sub>2</sub> atmosphere. Add 15 ml dry ethyl acetate. Heat to 80°C for 30 minutes. A solution of 0.0068 mol (1 gr.) of vanillin, triethyl borate 0.0027 mol (0.466 ml) in 30 ml. dry ethyl acetate was then added drop wise at 80°C over another 30 min. Then, n-butyl amine (-.54 ml, 0.0026 mol) was added and the reaction was warmed and placed under reflux for 1 hour. The color changed from white to dark orange. The reaction was cooled to 50°C, 18 ml of 1N of aqueous hydrochloric acid were added and allowed to stir for 10 more minutes. 50 ml. ethyl acetate was then placed into the reaction and the organic phase washed twice with water, dried (Na<sub>2</sub>SO<sub>4</sub>). The solvents removed under reduced pressure and the crude material was purified by filtering over Silica gel column eluting with a mixture of 70% Ligroin and 30% ethyl acetate. The collected pure fractions were collected, solvents removed and recrystallized from water and ethanol mixture to yield 896 (56%) pure 3.

<sup>1</sup>H-NMR: 2.15(s, 3H); 3.93(s, 3H); 5.62(s, 1H); 5.84(s, 1H); 6.32(d, J=15.2Hz, 1H);

7.09(s, 1H); 7.19(d, J=8.1Hz, 1H); 7.53(d, J=15.2Hz, 1H) 27

Preparation of the linker 9 1-Bromo-ethylene amino-Boc

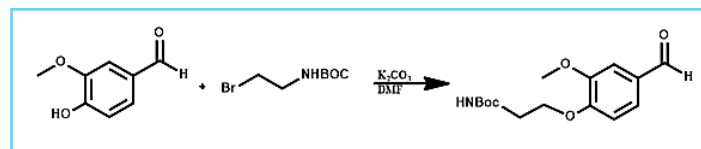


Figure 31

The linker was prepared from Bromoethyleneamine hydrobromide according to the literature as follows: The commercially available hydrobromide (1.65 gr. 8.04 mmol) was dissolved in Dioxane (10 ml) water (10 ml) were then added and 18 ml. of 2N NaOH were added at 0-4°C. To this, Boc anhydride (22ml. 9.64 mmol) was added dropwise. The cooling bath was then removed and the reaction was allowed to stir at room temperature overnight. The liquids were removed under reduced pressure and acidified with a KHSO<sub>4</sub> solution (2 N) to pH 2-3. The slightly acidic aqueous solution was washed with ethyl acetate (4x25 ml). The combined organic solution was dried over MgSO<sub>4</sub> anhydrous, filtered and the solvent removed under reduced pressure to afford an oily crude material (1.33 gr, 74% yield. With the following <sup>1</sup>H-NMR: <sup>1</sup>H-NMR: 1.44(s, 9H); 3.42(J=5.5Hz, 2H); 3.46(t, J=5.5Hz, 2H); 4.98(bs, 1H)

This material was applied without further purification for the next synthetic step.

4-(3-amino(Boc)proxy)-3-methoxy benzaldehyde

225 mg vanillins were mixed with 1 gr. Of the N-Boc protected Bromoethyleneamine, 10 ml dry DMF under nitrogen atmosphere. K<sub>2</sub>CO<sub>3</sub> (414 mg, 3 mmol) was then added and the reaction was allowed to stir vigorously for 2 hours at 80°C. The reaction was cooled to 0°C

and neutralized with 20 ml 1N HCl. The product was extracted with ethyl acetate and washed 2x20 ml with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and the solvents removed under reduced pressure. The solid was purified on a silica gel column using Ligroin/Ethyl acetate as eluent. The white solid obtained in this manner yield 68%.

<sup>1</sup>H-NMR: 1.44(s, 9H); 3.46(t, J=5.2Hz, 2H); 3.54(t, J=5.2Hz, 2H); 3.98(s, 3H);

7.10(d, J=8.4Hz, 1H); 7.26(s, 1H); 7.46(d, J=8.4Hz, 1H), 9.87(s, 1H)

The synthesis of modified curcumin with linker:

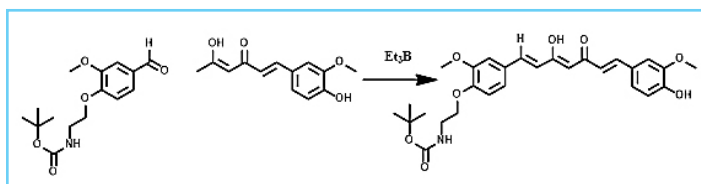


Figure 32

1-[4-(3-amino(Boc)propoxy)-3-methoxyphenyl]-5-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-1,4,6-heptatrien-3-one

The dienone (1E,4Z)-5-hydroxy-1-(4-hydroxy-3-methoxyphenyl)hexa-1,4-dien-3-one

(0.45 gr, 192 mmol) and B<sub>2</sub>O<sub>3</sub> (0.196 gr, 2.82 mmol) was dissolved in 5 ml. dry ethyl acetate and mixed with the protected vanillin 2 (0.35 gr, 1.13 mmol) and min during which an intensive red coloration of the reaction took place. The reaction was true OC for 30 min. and then with 0.4 N HCl for 30 more min at 50°C. The reaction was extracted with 3x20 ml ethyl acetate and washed 2x20 ml. water. The organic layer was dried Na<sub>2</sub>SO<sub>4</sub> filtered and the solvents removed under reduced pressure. The gummy material was purified over silica gel eluting with 7:3 Ligroin-ethyl acetate. 0/43 gram of an orange substance was obtained yield 75%.

MS m/z calc. 513.38 found 511.2 MH<sup>+</sup>

<sup>1</sup>H-NMR: 1.44(s, 9H); 3.56(t, J=5.1Hz, 3H); 3.95(s, 3H); 3.98(s, 3H); 4.11(t, J=5.1Hz,

2H); 5.81(s, 1H); 5.87(bs, 1H); 6.48(d, J=15.8Hz, 1H); 6.50(d, J=15.8Hz,

1H); 6.94(d, J=8.4Hz, 2H); 7.07(s, 2H); 7.13(d, J=8.4Hz, 2H); 7.59(d, J=15.8Hz, 2H)

Removal of the Boc protection: synthesis of the amino compound 6.

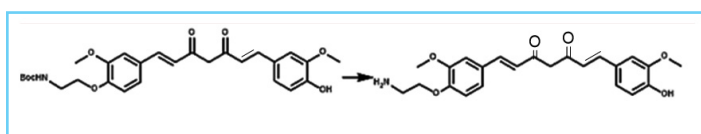


Figure 33

1-[4-(3-aminopropoxy)-3-methoxyphenyl]-5-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-1,4,6-heptatrien-3-one

The Boc carbamate was dissolved in 10 cc Dichloromethane and cooled in an ice bath. To this 3 ml. of trifluoroacetic acid was added and the reaction was followed by TLC analysis. Eluent 100% methanol. After all starting carbamate reacted; the solvents were removed under reduced pressure. Methanol was added and evaporated several times repeatedly. The solid obtained was purified on a silica gel column using methanol/ethyl acetate 1:1 as eluent. The orange product was obtained in 90% yield.

<sup>1</sup>H-NMR DMSO-d<sub>6</sub>: 3.24(t, J=7.0, 2H); 3.84(s, 3H); 3.86(s, 3H); 4.22(t, J=7.0, 2H);

6.09(s, 1H); 6.83(m, 2H); 7.07-7.42(m, 6H); 7.56(d, J=15.8Hz, 1H);

7.58(d, J=15.8Hz, 1H); 8.07(bs, 2H); 9.78(bs, 1H)

<sup>13</sup>C-NMR: δ38.5, 69.9, 73.4, 105.1, 117.0, 118.8, 124.6, 127.0, 133.2, 143.3, 144.8

M.S ES<sup>+</sup>: calc. 412, found 412.152.6, 159.1, 185.7, 193.1

Binding of the carboxylate Nano particle 5 to the modified curcumin 6.

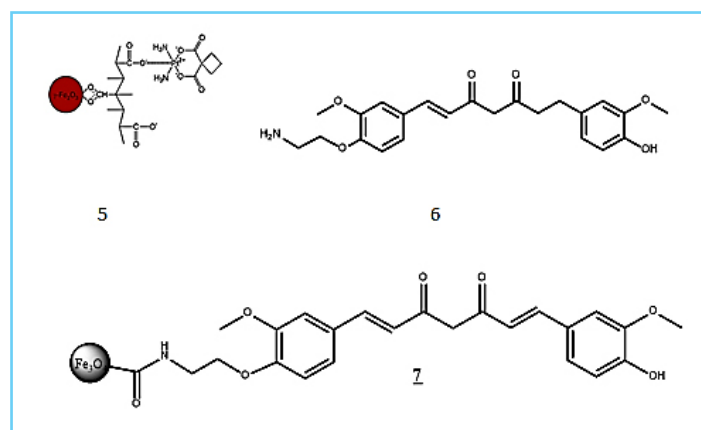


Figure 34

Building blocks (5 and 6) and magnetic reagent (7) for the eradication of Boron from Desalinated sea waters

Method #1: Synthesis of 7 in water

The magnetic nanoparticle was prepared according to the literature<sup>7</sup>. The binding to the curcumin derivative was done as follows:

10 mg of coated magnetite nanoparticle were charged into 10 ml. reaction flask together with 1 ml. of water. The solid was rinsed twice with 2ml of water. Then, 10 mg of EDC was added and the reaction was shaken for 5 min. 10 mg of 6 were then charged to the reaction and shaken overnight at room temperature. The liquid phase was tested for curcumin applying the calibration curve created as above, and the solid was dried and tested for binding of curcumin spectroscopically.

Method #2: Synthesis of 7 in water-methanol 1:1

The magnetic nanoparticle was prepared according to the literature<sup>7</sup>. The binding to the curcumin derivative was done as follows:

10 mg of coated magnetite nanoparticle were charged into 10 ml. reaction flask together with 1 ml. of water-methanol 1:1. The solid was rinsed twice with 2ml of water-methanol 1:1. Then, 10 mg of EDC was added and the reaction was shaken for 5 min. 10 mg of 6 were then charged to the reaction and shaken overnight at room temperature. The liquid phase was tested for curcumin applying the calibration curve created as above, and the solid was dried and tested for binding of curcumin spectroscopically.

For every procedure, 2 batches (different particle size) of coated nanoparticle were tested having in mind the optimal choice of particle size to be a more effective coating of the curcumin. The following graph represents the UV/vis absorption of the coated nanoparticle. It is clear that the carboxyl coated nanoparticle bind the tethered curcumin and that the uncarboxylated do not show any absorption spectrum.

Recovery of complexing agent 7 after removal of boron from the water.

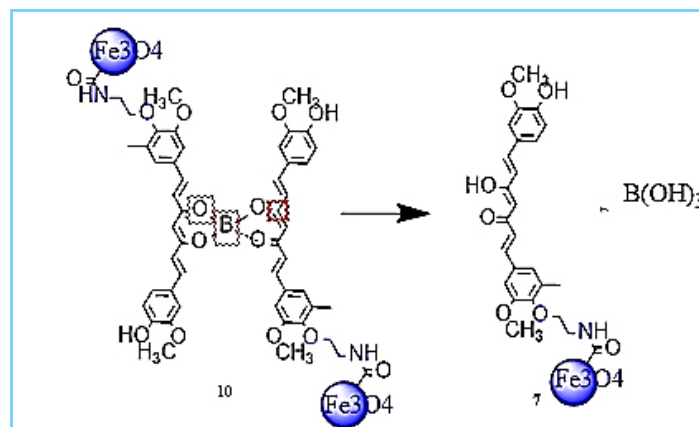
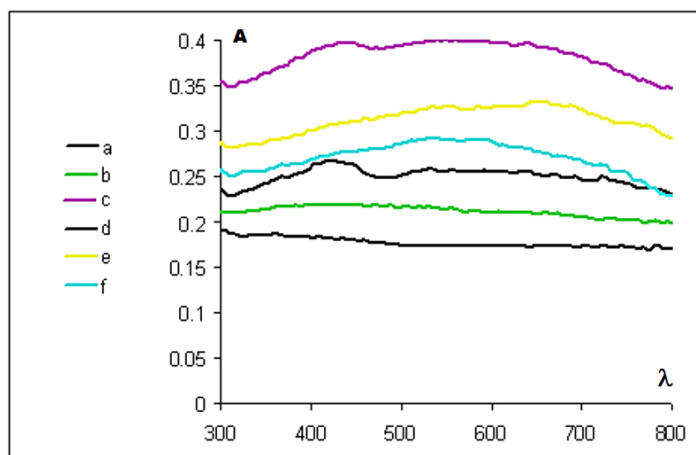


Figure 35

Finally, 1.3 gr of 10 were shaken with a 10% solution of aqueous acetic acid to 33 afford 0.23 gr boron and 1.02 gr of immobilized curcumin 7 which was recycled in the boron eradication process.



Graph 4 : UV/VIS spectra of Magnetic Nanoparticle bound to Curcumin 7 prepared in method # 1 and method # 2 as compared to curcumin derivative 6 (not connected to magnetic nanoparticle)

The spectra were taken on samples of 0.25 mg/ml of 1:1 methanol -water solution the above graphs were obtained: a) magnetic nanoparticle connected to carboxylate (LCC1-MP1) type 1, b) magnetic nanoparticle connected to carboxylate (LCC1-MP2) type 2. c) Conglomerate 7 in coupling method #1 (water as solvent), conglomerate 7 on MP1 coupled in 1:1 methanol -water (method #2). E) Conglomerate based on magnetic nanoparticles carboxylate type 2 methods# 1. f), conglomerate based on magnetic nanoparticles carboxylate type 2 (method #2)

The graphs indicate the connection of the curcumin derivative by covalent bonding to the carboxylate moiety of the magnetite nanoparticles.

The highest absorption was perceived in graph c - coupling in water as reaction solvent preferred from graph c - water as the reaction solvent.

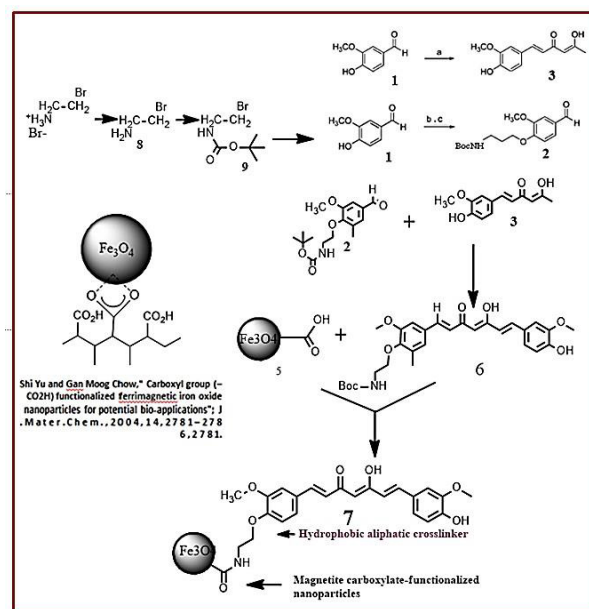


Figure 37 : acid coated Fe3O4 bound to curcumin via a hydrophobic linker Scheme: Overview on the synthesis of the boron capturing agent 7 based on the polyacrylic

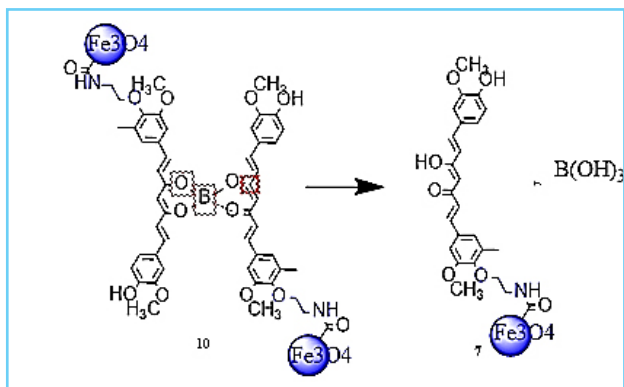


Figure 36 :

Recovery of complexing agent 7 after removal of boron from the water. Finally, 1.3gr of 10 were shaken with a 10% solution of aqueous acetic acid to shaken afford 0.23 gr boron and 1.02 gr of immobilized curcumin 7 which was recycled in the boron eradication process.

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