

## Recovery and Determination of Boron by Magnesia Adsorption from El Max Saline Bittern Solution

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### Summary

The present study concerned with the feasibility of using magnesia, (MgO) as an adsorbent for recovering B (0.225g/L) from El Max saline bittern solution (TDS 530 g/L) via equilibrium batch technique. This adsorbent has been already prepared from the same bittern solution via direct precipitation using NaOH solution. Depending mainly on pH value, contact time and the quantity of added MgO, B was almost adsorbed. On the other hand, more than 95% of the adsorbed B was regenerated by using hot distilled H<sub>2</sub>O, (50°C) by stirring for 30min to yield B concentrated solution. The latter was used to prepare pure boric acid via gentle thermal evaporation.

### Introduction

Boron has been estimated to attain a value of approximately 10 ppm in the earth's crust from the chemical point of view. It is considered as a comparatively mobile element; however, it may reach a value of 4.6 ppm in the sea water. The famous world salt lakes rich in B and Mg are: Solar de Atacama (Chile). Xiao Qaidam Lake (China) and other 56 Lakes in China, Owens Lake, Searles Lake, California, Great Salt Lake-Utah, USA and Dead Sea at Jordan<sup>(1)</sup>. In Egypt many lakes and saline companies (Quaron Lake- Fayuom, EL Max, Borg El Arab- Alexandria and El Max Port Said) are also have bittern solutions containing high concentrations of B and Mg<sup>(2,3)</sup>.

Boron compounds (Borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·H<sub>2</sub>O and Boric acid, H<sub>3</sub>BO<sub>3</sub>) have been gained great importance due to their wide applications in many industries such as: borosilicate glasses, metal fluxing, rocket fuels and agriculture additives. Boron is used in the manufacture of control rods of nuclear reactors. Its isotopes <sup>10</sup>B and <sup>11</sup>B are characterized by their ability to absorb neutrons. <sup>10</sup>B has a large cross section for neutron absorption reached 3850 barn in comparison to 38 barns only for <sup>11</sup>B and 755 barns for the natural B. For this reason <sup>10</sup>B has a great importance in controlling the chain nuclear reactions as well as in shielding their nuclear radiations. <sup>11</sup>B can be used in the nuclear applications that require low neutron absorption<sup>(4)</sup>.

Recovery or removing of B from brines containing high concentrations of alkali and alkaline elements is always conducted by using the classical B selective resins and organic solvents. Boron selective resin, Amberlite IRA<sub>743</sub> has been used for recovering B from brines containing high concentrations of Mg salts<sup>(5-7)</sup>. On the other hand, many workers have been studied extraction and purification of B from different aqueous solutions using organic solvents. 50% 2-ethyl-1, 3-hexandiol (EHD) in kerosene was already used to recover B from different aqueous

solutions.<sup>(8-11)</sup> Also, B has been recovered from the brines of Searle Lake of California, USA assaying 36% total dissolved salts (Na, K, B, Cl<sup>-</sup>, ..SO<sub>4</sub><sup>2-</sup>) using polyalcohol dissolved in kerosene<sup>(1)</sup>.

Nowadays, some alkali oxides are used in the recovery or removing of B from aqueous solutions, the famous used one is MgO. Removing of B from irrigated water could be approached by adsorption on MgO. The adsorbent exhibited a high B adsorption capacity value of  $4.45 \pm 1.31$  mg of B / g of MgO<sup>(12)</sup>. Also the removing over 95% of B from the liquid waste of urban, agricultural or industrial origin by adsorption on MgO was attained. The removal process improves as the pH value ranged between 9.5 and 10.5 where B(OH)<sub>4</sub><sup>-</sup> anion predominates<sup>(13)</sup>.

Moreover, MgO can be effectively used at Mg / B mole ratio of 20 in recovering of 85% of B from the drainage waters of the Bigadic B mines of Turkey. But the consumption of 18,100 tons of MgO / year in the removal system makes this process uneconomical<sup>(14)</sup>. In addition, the removal of 90% of B from aqueous solutions via adsorption on MgO using batch technique was attained at pH 9.5<sup>(15)</sup>. On the other hand, up to 87% of B has been removed using 5 g/L MgCl<sub>2</sub>.6H<sub>2</sub>O at pH 11 and a temperature of 20°C from groundwater brought to the surface during oil and natural gas extraction at the Arroyo Grande Oil Field on the central coast of California, USA<sup>(16)</sup>. At least 50% and up to 95% by weight of the total B content from brine weighted of 400 g and assaying 52 mg/L of B was extracted with 20 g of adsorbent for 1h with a partially hydrated MgO adsorption<sup>(17)</sup>.

Finally, the present study is concerned with the preparation of pure adsorbent, MgO, from the bittern solution of El Max saline Company, in the northern Coast of Egypt to recover the toxic B content in the bittern solution.

## Experimental

### Materials

The present bittern solution was kindly provided from El Max Company, Alexandria, Egypt and has been physically and chemically characterized. The former includes mainly its density, pH value and its total dissolved salts, (TDS) while chemical characterization includes estimation of both major and trace elements.

### Analytical procedures

The physical properties such as: odour, colour, density, pH value and total dissolved salts (TDS) were investigated. For this purpose, a volume of 50 mL is weighted to calculate its density and thermally evaporated to estimate its TDS by subtracting the weight before and after the

evaporation process. On the other hand, different analytical techniques were performed to determine the chemical composition of the working bittern solution. The classical chemical analysis methods are used to determine the major cations and anions. Both Ca and Mg are analyzed by complexometric titration against EDTA standard solution, while  $\text{Cl}^-$  and  $\text{Br}^-$  anions are volumetrically determined by titration against  $\text{AgNO}_3$ . Also  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  anions are estimated by classical volumetric titration,<sup>(18)</sup>. While  $\text{SO}_4^{2-}$  anions are gravimetrically determined by using  $\text{BaCl}_2$ ,<sup>(19)</sup>. B and some other trace e.g. Zn, Sr, Mn...etc elements were estimated using Flame Atomic Absorption Spectrometry, (FAAS), Unicam 969 at their proper wavelengths.

The Flame Photometer (Sherwood Model 410) was used for the determination of Na and K at  $\lambda_{589}$  and  $\lambda_{766}$  nm, respectively. Where the pH values were measured by using a pH meter, (Digimed DM-21). The elemental structure of the obtained products was confirmed by X - Ray Diffraction, (XRD) analysis technique, PHILIPS.

### **Recovery procedures**

#### **Preparation of the activated adsorbent**

A volume of 500mL of the working bittern solution which assays 81 g/L of Mg and 0.225 g/L of B was treated with continues stirring with concentrated caustic NaOH solution. However, the complete precipitation of Mg ions was accomplished at pH 12.4. The produced  $\text{Mg}(\text{OH})_2$  was carefully washed with water to remove the adsorbed B and then ignited at  $650^\circ\text{C}$  for 1h to prepare pure MgO. The produced MgO was then stirred for 30 min with 1% NaOH solution, filtered and dried to prepare the activated adsorbent.

#### **Determination of Boron saturation capacity**

A weight of 1g sample portion of the prepared activated MgO was mixed with 40 mL of standard  $\text{H}_3\text{BO}_3$  acid which assays 1000 ppm of B and stirred at 225 rpm for 60 min at room temperature. After filtration, the remained B in the filtrate was analyzed to calculate the adsorbed B which indicates the saturation capacity of the working adsorbent dose.

#### **Optimization of Boron adsorption process**

The main objective of this study is to recover B from the present bittern solution by adsorption method using the prepared activated MgO adsorbent. For this purpose different operating variables such as: pH value of the bittern solution (3.8 – 8.5), contact time (30 – 90 min), quantity of adsorbent (0.1 – 0.25 g) and temperature ( $25 - 80^\circ\text{C}$ ) were investigated. All

adsorption experiments were carried out by mixing 0.1g of dry activated MgO adsorbent with 25 mL of the working bittern solution in a series of beakers via batch technique.

## Results & Discussion

### Characterization of the working bittern solution

#### Physical properties

Table (1) represents the physical properties of El Max bittern solution. From this table, it could be concluded the following:

- 1- The present bittern solution is transparent and has no odour.
- 2- It has high total dissolved salts (530 g/L) thus, it is a dense solution and its pH value could be increased by dilution with water.

**Table (1):** Physical properties of El Max bittern solution.

Issue	Property
Odour	Odour less
Colour	Colourless
Density	1.3 g/cm <sup>3</sup>
pH Value	6.8
TDS	530g/L

#### Chemical Composition

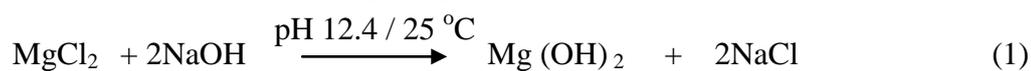
The chemical composition of the present bittern solution is represented by Table (2). This table shows the presence of high concentrations of Mg, Na, K, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> together with considerable concentrations of Ca, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and B as well as low concentrations of Fe, Zn, Sr and Mn.

**Table (2):** Chemical compositions of El Max saline bittern solution.

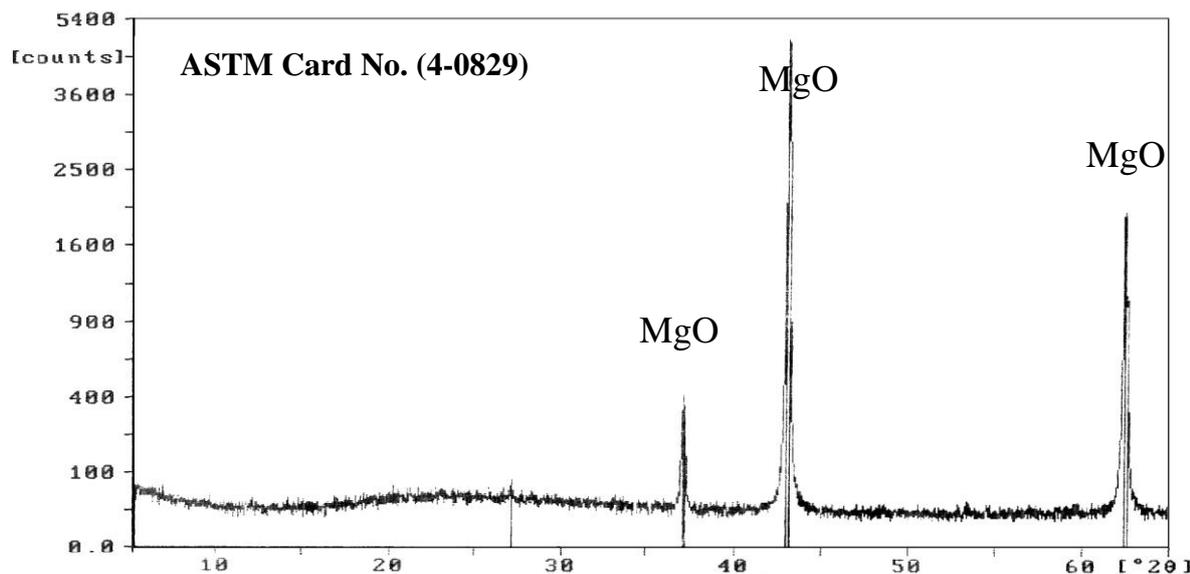
Major Elements	Conc., (g/L)	Trace elements	Conc., ppm
Mg	81	B	225
Na	70	Fe	54
K	12	Sr	40
Ca	7	Zn	10
Cl <sup>-</sup>	300	Mn	7
SO <sub>4</sub> <sup>2-</sup>	57	Co	4
CO <sub>3</sub> <sup>2-</sup>	2		
HCO <sub>3</sub> <sup>-</sup>	0.85		

### Preparation of the activated adsorbent MgO

A volume of 500 mL of the working bittern solution assays 81 g/L of Mg and 0.225 g/L of B was treated with continuous stirring with concentrated solution of caustic NaOH. However, the complete precipitation of Mg ions was accomplished at pH12.4<sup>(2)</sup>. After thickening, filtration, washing and ignition at 650°C for 1h, a weight of 66.34g of pure MgO was produced with achieved recovery of 99.3%., according to equations (1,2).



The produced MgO was carefully washed with distilled H<sub>2</sub>O to get rid of the adsorbed impurities and then dried. The prepared MgO was already investigated by means of XRD analysis to prove its chemical structure, (Fig.1). On the other hand, a weight portion of 1g is dissolved in 10 mL of conc. HNO<sub>3</sub> and closed up to a volume of 250 mL and was chemically analyzed to estimate its purity which achieved 99%, with low impurities of K, Ca, Na, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>. The produced MgO was then stirred with 1% NaOH solution for 30 min, filtered and dried to prepare an activated MgO adsorbent (hydrated MgO).

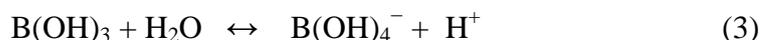


**Fig.(1):** XRD pattern for identification of pure prepared MgO

### Determination of practical adsorption saturation capacity

A weight 1 g of the prepared activated MgO was mixed with 40 mL of standard  $H_3BO_3$  acid which assays 1000 ppm of B and stirred for 60min at 225 rpm and at room temperature. After filtration and analysis of B in the filtrate, the obtained data emphasized that, 6700 ppm of B, (6.7 mg / g of MgO) was adsorbed onto the working dose of the activated MgO. This indicates that the activated MgO adsorbent has a total practical capacity of 6.7 g of B / Kg of MgO. It is very important to mention that, the practical capacity of MgO without pretreatment with an alkaline solution achieved only 4.8 g of B / Kg of MgO. The mechanism of the adsorption of B onto hydrated MgO is described in three steps<sup>(13,20,21)</sup>.

1-  $H_3BO_3$  acid is a very weak in aqueous solution, ( $K = 5.8 \times 10^{-10}$  at  $25^\circ C$ ) thus it behaves not as a proton donor ( Bronsted acid) but as a Lewis acid as in equation (3).



Because of its weak acidity, the non-dissociated  $H_3BO_3$  acid is present in neutral and acidic media but in the alkaline medium (pH value between 9.5 and 10.5) the predominant form are the  $B(OH)_4^-$  anions species.

2- Hydration reaction of MgO in the aqueous solution yields a gel  $Mg(OH)_2$ , over the surface of which the active sites for adsorption are situated. This reaction is slow, evolves with time and is hastened at high temperatures as in equation (4).

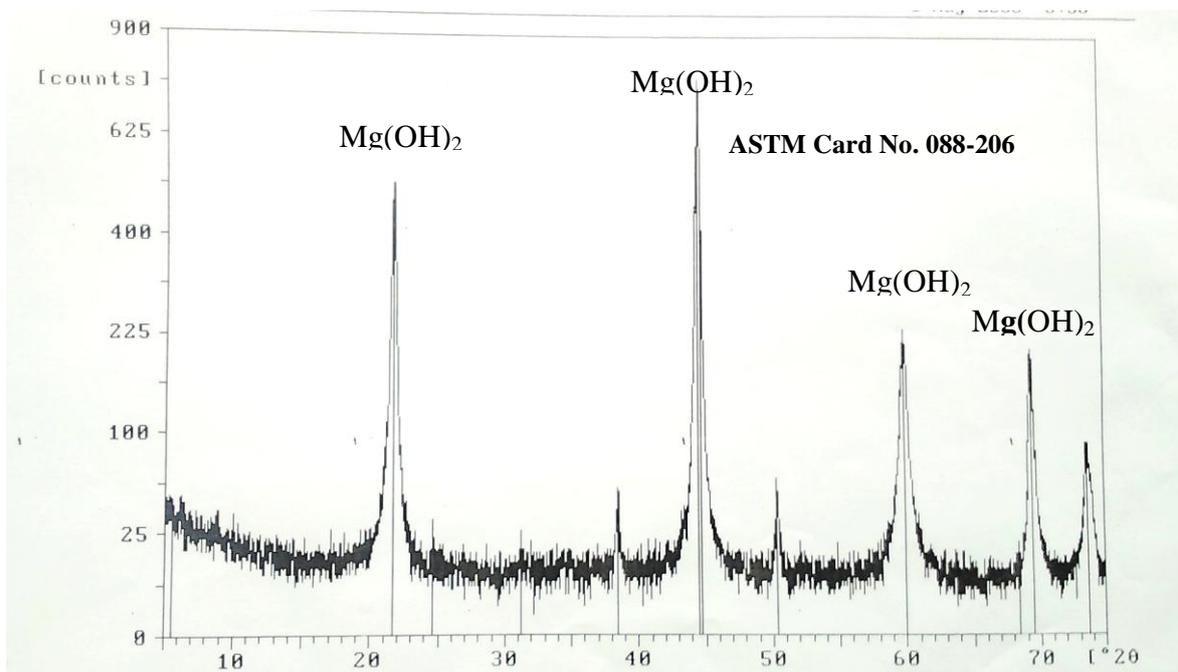


3- Stereo specific chemical reaction between  $B(OH)_4^-$  and  $(OH)^-$  can be described by means of the ligand exchange model in which the adsorbed species shifts the  $OH^-$  from the adsorbent, ions

of tetrahedral structure and the superficial hydroxide groups of  $\text{Mg}(\text{OH})_2$  are the active centers of adsorption as in equation (5).



The foregoing mechanism explained why the capacity of the adsorbent  $\text{MgO}$  increased from 4.8 g B / Kg to 6.7g B / Kg by performing a pretreatment process with 1%  $\text{NaOH}$  solution for 30 min where  $\text{Mg}(\text{OH})_2$  was already presented as confirmed with XRD, (Fig.2). Also, increase the pH value of the filtrate emphasized the liberation of  $(\text{OH})^-$  anions.



**Fig. (2):** XRD pattern of the hydrated  $\text{MgO}$  as an activated adsorbent.

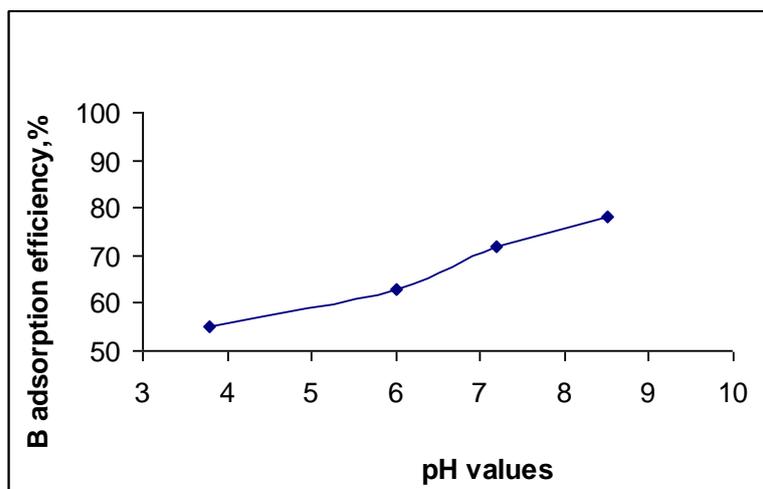
### Optimization of adsorption process

Optimization of the adsorption process of  $\text{B}(\text{OH})_4^-$  anions species from the working bittern solution required studying the following operating variables.

#### Effect of pH value

A series of adsorption experiments under controlled pH value were performed at different pH values ranged from 3.8 to 8.5. The pH values were adjusted by using diluted acidified or alkaline solutions. The mixtures were stirred for 30 min at  $25^\circ\text{C}$ . After filtration, the residual concentration of B in filtrates was determined to calculate its adsorption efficiency. The obtained data (Fig.3) indicates that, B adsorption efficiency increased from 55% up to 78% when the pH value of solution increased from 3.8 to 8.5. From the obtained data, it can be concluded that, in acidic and neutral media B exists in the form of  $\text{H}_3\text{BO}_3$  which decreases its uptake, while in alkaline media B exists as  $\text{B}(\text{OH})_4^-$  which increases its uptake, <sup>(13,15)</sup>. In the present work, at

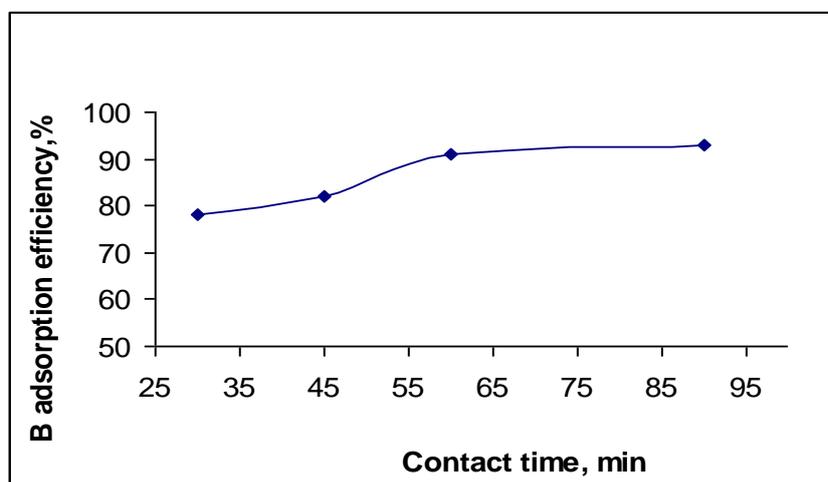
pH >8.5 a part of Mg ions in the working solution precipitated as  $Mg(OH)_2$  which adsorbs about 20% of B content.



**Fig. (3):** Effect of pH values upon B adsorption efficiency using MgO.

#### Effect of contact time

This factor was investigated at different periods of time ranged from 30-90 min at 25°C. After filtration and analysis, the obtained data, indicates that increasing the contact time from 30 min to 90 min has remarked influence upon B adsorption efficiency which increased gradually from 78% up to 93%, (Fig.4). Indeed, the suitable time was 60 min (91%) due little difference with the contact time of 90 min, (93%).

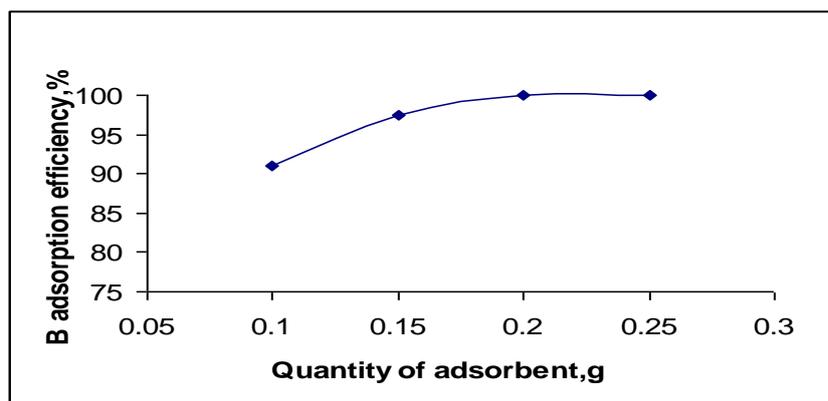


**Fig. (4):** Effect of contact time upon B adsorption efficiency using MgO.

#### Effect of adsorbent amount

This factor was investigated by mixing 25 mL of bittern solution at pH 8.5 with different amounts of dry activated MgO adsorbent ranged from 0.1 to 0.25 g and stirred for 60min at 25°C. The obtained results (Fig.5) revealed that B adsorption efficiency increases up to 100% with increasing the adsorbent amount to 0.2 and 0.25g. This is due to the presence of sufficient

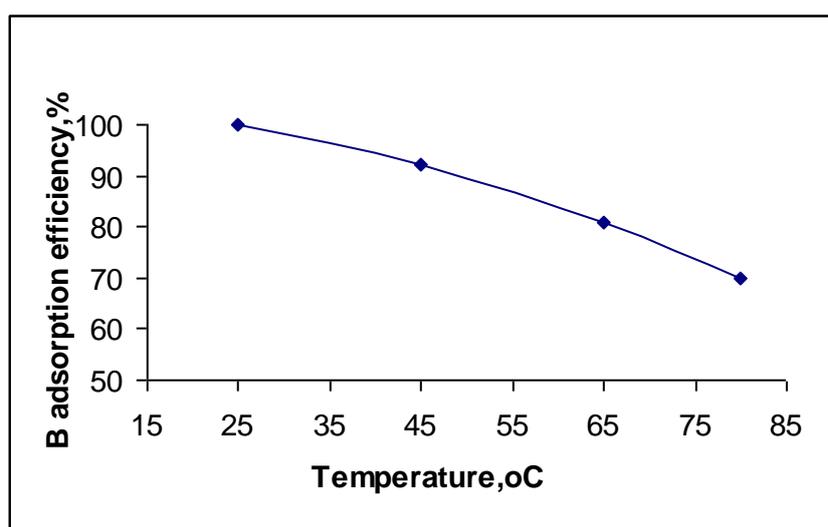
active sites for the adsorption of  $B(OH)_4^-$  anion species. The results also indicated that the adsorption of B with MgO was not affected with the presence of other ions, <sup>(14)</sup>.



**Fig. (5):** Effect of adsorbent quantity upon B adsorption efficiency.

### Effect of temperature

The adsorption efficiencies of  $B(OH)_4^-$  anions were investigated at different temperatures ranged from 25°C up to 80°C by mixing 0.2 g of dry MgO adsorbent with 25 mL of bittern solution at pH 8.5 and stirring for 60min. The adsorption data, (Fig.6) shows that B adsorption efficiency decreases from 100% to 70% as the temperature increases from 25°C to 80°C. This might be attributed to the fact that the interaction between  $B(OH)_4^-$  anions and the studied adsorbent is weaker at higher temperatures, <sup>(22)</sup>. Also, increasing of temperature leads to increase the pH value of the bittern solution which leads to precipitate of  $Mg^{2+}$  ions. The latter adsorbs  $B(OH)_4^-$  anions thus the adsorption efficiency decreased.



**Fig. (6):** Effect of temperature upon B adsorption efficiency using MgO.

From the foregoing adsorption study, it can be concluded that, the optimum adsorption conditions effective for the extracting 100% of total B content in the working bittern solution are as following:

pH value	: 8.5
Contact time	: 60min
Amount of adsorbent	: 0.2g
Temperature	: 25°C

### Elution process

The mentioned optimum adsorption conditions were applied upon 500 mL of the working bittern solution that containing about 0.113g of B. This solution was diluted with the same volume of diluted alkaline solution to adjust its pH value at pH 8.5 and mixed with 6g of dry prepared adsorbent. The mixture was then stirred for 60min at 25°C and left for settling and filtered. The loaded adsorbent was washed as rapid as possible with distilled H<sub>2</sub>O to get rid of the the remained adsorbed bittern solution. The loaded adsorbent was then stirred with 250mL of hot distilled H<sub>2</sub>O (50°C) for 30min to prepare B concentrated solution which assays 1.06 g/L of B realizing elution efficiency of 96.4%. The eluated B rich solution was adjusted to a gentel thermal crystallization process to prepare about 0.55 g of pure boric acid. The latter was identified by means of XRD technique, (Fig.7). The chemical specification of the product revealed that, it assays 16.2% of B with acheived purity of 95% together with some impurities e.g. 0.1% of Na, 0.3% of Cl<sup>-</sup>, 0.1% of SO<sub>4</sub><sup>2-</sup> and 0.33% of K.

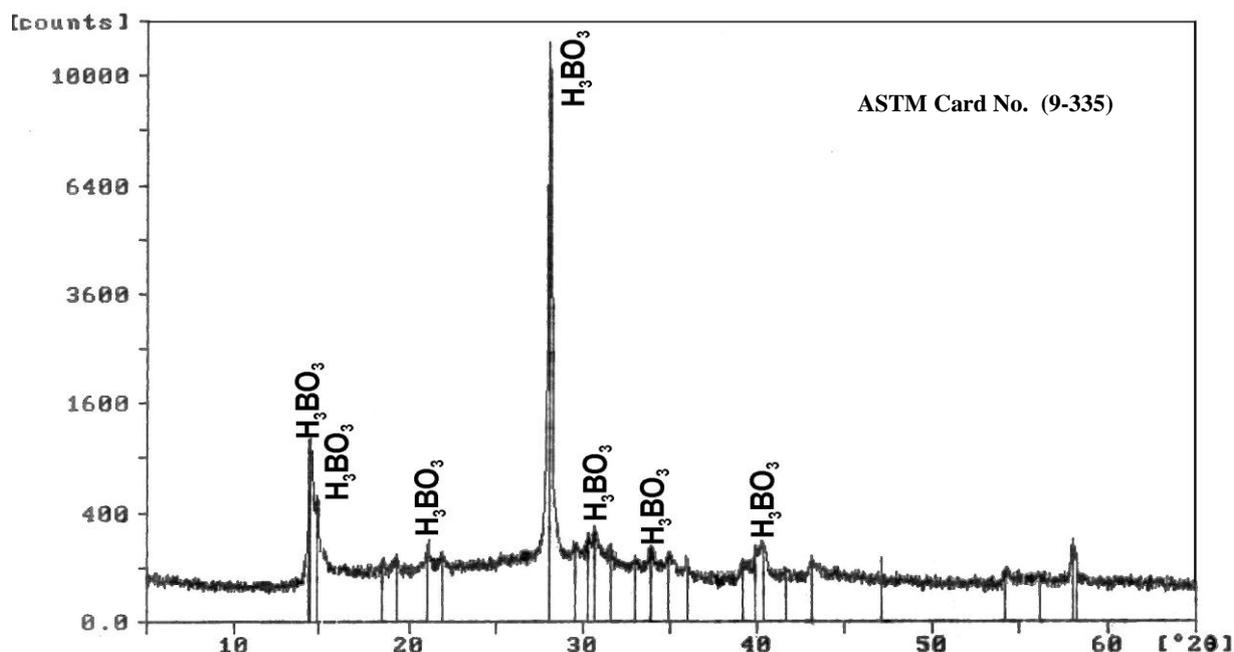


Fig. (7): XRD pattern for identification of the prepared H<sub>3</sub>BO<sub>3</sub>.

### Conclusion

Recovery of some strategic products such as MgO, H<sub>3</sub>BO<sub>3</sub> and NaCl from El Max saline bittern solution could be conducted by precipitation of Mg ions by using NaOH solution as Mg(OH)<sub>2</sub> at pH 12.4. The latter was washed and ignited at 650°C to prepare pure MgO which treated with 1% NaOH solution and dried to be available for using as an adsorbent.

The obtained results revealed that 100% of B adsorption efficiency was achieved at pH 8.5 and stirring time of 60min by using 6g of MgO / L of the working solution at room temperature. On the other hand, more than 95% of the adsorbed B was regenerated by using 250 mL of hot distilled H<sub>2</sub>O (50°C) by stirring for 30 min to prepare B concentrated solution. This solution was adjusted to a gentle thermal crystallization process where pure boric acid was prepared.

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