



Boron Removal by Adsorption onto Different Oxides

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ABSTRACT

A research was conducted to determine the feasibility of using adsorption process to remove boron from aqueous solutions using batch technique. Three adsorbent materials; magnesium, aluminum and iron oxide were investigated to find their abilities for boron removal. The effects of operational parameters on boron removal efficiency for each material were determined.

The experimental results revealed that maximum boron removal was achieved at pH 9.5 for magnesium oxide and 8 for aluminum and iron oxide. The percentage of boron adsorbed onto magnesium, aluminum and iron oxide reaches up to 90, 42.5 and 41.5% respectively under appropriate conditions. Boron concentration in effluent water after adsorption via magnesium oxide comply with the allowable concentration according to WHO and the Iraqi drinking water guidelines, i.e. below 0.5 mg/l. Aluminum and iron oxide yield effluent water with boron concentration more than allowable limits. Accordingly, magnesium oxide is more suitable as adsorbent for boron removal from water; for its high adsorbent capacity and high removal ability for boron compared with aluminum and iron oxide.

Key words: Adsorption, Boron, Magnesium oxide, Aluminum oxide, Iron oxide

أزالة البورون بالامتزاز بعدة أكاسيد

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أستاذ

الخلاصة

تم إجراء البحث لدراسة إمكانية استخدام عملية الامتزاز في إزالة البورون من الماء بنظام النمط الدفعي (Batch process) باستخدام ثلاث مواد ممتزة هي أكاسيد المغنيسيوم، الألمنيوم والحديد ودراسة مدى تأثير الظروف التشغيلية على كفاءة الأزالة. أظهرت التجارب المختبرية أن أعلى نسبة ازالة للبورون تم الحصول عليها بدرجة حامضية للمحلول هي 9.5 باستخدام أكسيد المغنيسيوم كمادة ممتزة ودرجة حامضية 8 باستخدام أكاسيد الألمنيوم والحديد كمادة ممتزة . وجد أن أعلى نسبة ازالة للبورون وصلت إلى 90%، و42.5% و41.5% لأكاسيد المغنيسيوم، الألمنيوم والحديد على التوالي. أن تركيز البورون في الماء الخارج من عملية الامتزاز باستخدام أكسيد المغنيسيوم كمادة ممتزة يتطابق مع النسبة المسموح بها من قبل منظمة الصحة العالمية (0.5 ملغم / لتر) بينما تكون نسبة البورون في الماء الخارج من عملية الامتزاز باستخدام أكاسيد الألمنيوم والمغنيسيوم كمادة ممتزة أعلى من النسبة المسموح بها من قبل منظمة الصحة العالمية ، لذلك يعتبر أكسيد المغنيسيوم مادة مناسبة لأزالة البورون بعملية الامتزاز لقابليته العالية لأزالة البورون وسعته الامتزازية العالية.

الكلمات الرئيسية: الامتزاز، البورون، أكسيد المغنيسيوم، أكسيد الألمنيوم، أكسيد الحديد

1. INTRODUCTION

Boron is a naturally occurring element that is widely distributed at low concentrations in the environment. Recently its concentrations in some areas of Iraqi surface water increased significantly due to the reduction in the Tigris and Euphrates Rivers average flow rates. Sea water, from the Arabian Gulf, with high concentration of boron, is dispersed into Shatt-Alarab River causing its concentration to be as high as 5 mg/l. This is 10 times the allowable drinking water concentration for boron according to WHO and the Iraqi drinking water guidelines.

Boron takes two forms in water (depending on pH value), boric acid and borate ion. Boric acid dissociation is a function of pH, above pH 9.24 the anion $B(OH)^-$ is predominant, while below pH 9 the uncharged species are predominant (Marek et al., 2009; Jeffrey and Marc, 2005).

Boric acid and borate salt have extensive industrial uses in the manufacture of glass and porcelain, in wire drawing, production of leather, carpet and photographic chemicals. The most economically important compound of boron is sodium tetraborate decahydrate $Na_2B_4O_7 \cdot 10H_2O$, or borax, used for insulating fiberglass and sodium perborate bleach. Boric acid is an important compound used in textile products. Compounds of boron are used in organic synthesis, in the manufacture of a particular type of glasses, and as wood preservatives. Boron filaments are used for advanced aerospace structure.

Although boron is essential for plant growth, in excess of 2.0 mg/l in irrigation water, it is deleterious to certain plants species. Boron deficiencies cause growth problems and difficulties in sugar mobilization. Other plants may be affected adversely by concentration as low as 1.0 mg/l (Andrew et al. 2005). High levels of boron are found in sea water (4.7 mg/l), domestic waste water (0.5-2 mg/l) and reach to 8 mg/l in ground water in Italy, Cyprus and Greece. The human body contains approximately 0.7 ppm of boron, an element that is not considered a dietary requirement. Still, human absorb this element from food stuffs, because it is a dietary requirement for plants. Daily intake is approximately 2 mg. The amount of boron presents 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, diarrhoea and blood clotting. Amounts over 20 g

are life threatening. Boric acid irritates the skin and eyes. Skin contact with boron trifluoride may cause corrosion (Polat et al., 2004; Kabay et al., 2008; Yoshinari et al., 2004).

Plant adsorbs boron from the ground and through plant-consuming animals can end up in food chains. Boron has been found in animal tissue, but it is not likely to accumulate. When animals absorb large amounts of boron over a relatively long period of time through food or drinking water the male reproductive organs will be affected. When animals are exposed to boron during pregnancy their offspring may suffer from birth defects or delayed development. Furthermore, animals are likely to suffer from nose irritation when they breathe in boron (Polat et al., 2004; Kabay et al., 2008; Yoshinari et al., 2004).

Food and agriculture organization in United Nations (FAO) imposed a regulation on the concentration of boron in irrigation water to be in the range of 0.7-3 mg/l (FAO, 1985).

Boron has virulence for reproduction, it causes male reproductive impediments when overdosed, and therefore removal of hazardous boron from water is important for environment control (Polat et al., 2004; Kabay et al., 2008; Yoshinari et al., 2004). The World Health Organization (WHO) recommends maximum boron concentration as low as 0.5 mg/l for drinking water. Iraqi drinking water guideline uses the same value (0.5 mg/l) (Iraqi drinking water standard, 2009).

Various technologies were used to reduce boron concentration in water and wastewater mainly as listed in Table 2.1 where the removal efficiency and the evaluation for each process are listed (Xu and Jia, 2008; Xu et al., 2009):

Table 1.1: Different technologies of boron removal

Technology	Removal efficiency (%)	Evaluation
Chemical precipitation	60%	Causes high salinity and produces a voluminous amount of sludge
Ion exchange	> 99 % at pH 12	High cost
Reverse osmosis	43-78% Single stage	Producing large brine wastewater,



Technology	Removal efficiency (%)	Evaluation
	40-100% (Two stages with pH adjustment)	membrane scaling and fouling problems
Liquid-liquid extraction	High removal ability	High cost, environmental risk
Electro dialysis	80% at pH 10	Expensive
Electro-coagulation	Multistage is >99%	Expensive and effective for high Boron concentration
Adsorption onto Activated Carbon	12.7% for non-impregnated carbon and 69.7 % for activated carbon impregnated with mannitol	High investment

1. The Aim of Research

-Study the efficiency of adsorption technology to reduce or remove boron from water using several kinds of oxides (magnesium, aluminum and iron Oxide).

-Study the influence of operating parameters: pH, adsorbent dosing and resident time on boron adsorption.

2. EXPERIMENTAL WORK and PROCEDURE

3.1 Materials

Adsorbate

Boric acid (H_3BO_3) reagent used in this study to prepare synthetic water with the required feed concentration of boron. It was procured from Reidel-de Haen Company (Germany).

Adsorbents

Three types of materials were used as adsorbents. These are magnesium oxide (MgO), iron oxide (Fe_2O_3), and alumina (aluminum oxide) (Al_2O_3) was procured from Fluka Company (Switzerland).

3.2 Analysis of Boron Concentration

The concentration of boron was analyzed by means of HACH DR2000 spectrophotometer (carminic method).

3.3 Experimental Procedure

Batch adsorption was carried out to obtain equilibrium data and investigate the effect of pH, stirring time and adsorbent dose on boron removal at the temperature held at 30°C in a laboratory batch unit.

Boron stock solution (5mg/l) was prepared by dissolving an appropriate quantity of boric acid (H_3BO_3) in such a manner that the initial boron concentration was held at 5 mg/l. All solutions were prepared with distilled water.

To investigate the effect of pH of boric acid solution, a set of 15 samples were prepared. The pH of these boric acid solutions were adjusted to values in the range of (5-11) using dilute hydrochloric acid or dilute sodium hydroxide solution. The pH of solution was kept constant during the adsorption process in all the experiments. Samples of 100 ml of these solutions were mixed with 1g of adsorbent (5 samples for each adsorbent) and are shaken by means of mechanical stirrer at 220 r.p.m for 1h. After one hour of mixing the solution was separated from the solid adsorbent by filtration using Whatman-31filter paper. The filtrate was analyzed for boron concentration.

Using the best pH value (that gives maximum boron removal which was 9.5 for magnesium oxide and 8 for aluminum and iron oxide), to study the effect of adsorbent dose on boron removal, adsorption experiments with different amounts of adsorbents were conducted. 100 ml boron stock solution with 5 mg/l boron concentration was shaken with adjusted amount of adsorbents at 220 r.p.m by means of mechanical stirrer for 1h. After that the solution was separated from solid adsorbent by filtration using Whatman31filter paper and the filtrate was analyzed by HACH DR2000 spectrophotometer (carminic method).

To investigate the effect of stirring time, 18sample with 100ml boric acid solution (5 mg/l boron concentration)were mixed with 1g of adsorbent (magnesium, aluminum and iron oxide) at best pH (which were 9.5 for magnesium oxide and 8 for aluminum and iron oxide). The samples were shaken by using a mechanical stirrer at 220 r.p.m with stirring time (20, 30, 45, 70, 140, 180 and 240) minute respectively for samples containing magnesium oxide, (10, 35, 45, 63, 75

and 90)min respectively for samples containing alumina and (11, 30, 60, 90, 120) min respectively for samples containing iron oxide. The solution was then separated from the solid adsorbent by filtration using Whatman-31 filter paper and the filtrate was analyzed to determine the percentage of boron in solution after adsorption.

3. Mechanism of adsorption

4.1 Aluminum oxide

Boric acid adsorption on both crystalline and amorphous aluminum oxide increased with increasing pH up to an adsorption maximum between pH 6 to 8 (Sims and Bingham, 1968; McPhail et al., 1972; Goldberg and Glaubig, 1985; Su and Suarez, 1995). After reaching the maximum, boric acid adsorption decreases with increasing pH. Hatcher et al. (1967) and Sims and Bingham (1968) have found that boric acid adsorption was greatest on freshly precipitated minerals and the adsorptivity decreases as minerals become more crystalline due to aging. On a per mass basis, boric acid adsorption is much greater on aluminum oxide than on iron oxide (Sims and Bingham, 1968; Goldberg and Glaubig, 1985).

The mechanism of boric acid adsorption on aluminum oxide mineral is considered to be ligand exchange with reactive surface hydroxyl groups (Sims and Bingham, 1967; McPhail et al., 1972; Goldberg et al., 1993; Su and Suarez, 1995). Ligand exchange mechanism is often characterized by a shift in the point of zero charge (PZC) of the mineral as the adsorbent become specifically adsorbed on mineral surface. Boric acid adsorption has been documented to shift the PZC to a more acidic pH value (Beyrouthy et al., 1984; Goldberg et al., 1993; Su and Suarez, 1995).

4.2 Iron oxide

Boric acid adsorptive behavior on iron oxide is akin to its behavior on aluminum oxide. The adsorption of boric acid on Fe oxides increased with increasing pH up to an adsorption maximum pH 7 to 9 (Bloesch et al., 1987). Beyond pH 9, boric acid adsorption decreased with increasing pH. Similar to boron adsorption on aluminum oxide, the greatest adsorption was found on freshly prepared minerals (Sims and Bingham, 1968).

4.3 Magnesium oxide

The mechanism of boron adsorption onto magnesium is that:

-The hydration reaction of magnesium oxide when it is in touch with the aqueous solution to yield a magnesium hydroxide gel, over the surface of which the active sites for adsorption are situated. It has been experimentally observed that this reaction is slow, evolves with time and is hastened at high temperatures. These aspects agree with the consulted bibliographical data dealing with the reactivity of magnesium oxide. This process has an enormous influence on the availability of active centers and will rule the development of the process with time.

- The alkalization reaction of the solution due to the acid–base reaction between the magnesium oxide and water. The pH value is between 9.5 and 10.5. Under these conditions the equilibrium between the orthoboric acid and borate ions is shifted to the right. Therefore, $B(OH)_4^-$ ions, the other species involved in the process, predominate in the solution. -The stereospecific chemical reaction between $B(OH)_4^-$ and OH^- -This reaction 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 the magnesium hydroxide are the active centers of adsorption. (Del la Fuente and Eugenio, 2006).

4. RESULTS and DISCUSSION

5.1 Effect of Water pH on Boron Adsorption

Figures 1- 3 show the effect of solution pH on boron removal by adsorption onto magnesium, aluminum and iron oxide respectively. The maximum boron removal by magnesium oxide occurs at pH 9.5 (Figure 1). At this pH value the surface of magnesium oxide is positively charged (Pzc=12) (point of zero charge is the pH where the surface charge density is zero) and the borate anions are the dominating boron species in solution (Konstantinou et al., 2006). Up to pH 12 the surface remains positively charged and borate anions are the dominating species in solution, however, the removal efficiency of boron is decreasing almost linearly between 10.5 and 11, reaching a minimum value of about 8%.

The best pH for the removal of boron by aluminum (Figure 2) and iron oxide (Figure 3) is found to range from 7 to 9 with a maximum value at pH 8. This pH value is close to the Pzc value of aluminum and iron oxide (Mc Bride, 1994;



Konstantinou et al., 2006) which indicates that the best conditions for boron removal are given when the surface has no charge and boric acid is the predominant species in solution. These results support the mechanism suggesting proton dissociation of H_3BO_3 at the surface of the adsorbent and subsequent reaction of the dissociated protons with surface hydroxyl groups of neutral sites to form water which is then displaced by the anion. Less than pH 7.9 the surface sites become protonated, dissociation of the boric acid at the surface is unlikely to occur and thus the efficiency of boron removal is decreasing. At pH > 9.2, the surface is negatively charged and repels borate anions at this pH value which is dominating at this area for the species in solution, resulting in lower boron removal efficiency.

The result is that maximum removal ability for magnesium oxide to remove boron occurs at pH 9.5 (Figure 1), while for aluminum and iron oxide was at pH 8 (Figures 2 and 3). This corresponds with that reached by Del La Fuente and Eugenio, (2006) and Bouguerra et al., (2008) that maximum boron removal was achieved at pH value between (9.5-10.5) for adsorption onto magnesium oxide and pH (8-8.5) for adsorption onto aluminum and pH 8 for adsorption onto iron oxide. Magnesium oxide is more favorable to remove boron; it has a more removal ability than aluminum and iron oxide.

5.2 Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of boron is representatively shown in Figures (4 to 6). These figures show the percent of boron removal increase with increasing adsorbent dose, as a result of the increases in the total available surface area of the adsorbent particles. It was observed that the adsorption capacity reaches an equilibrium value, beyond which, there was a negligible change in the residual boron concentration. For initial concentration of 5mg/l, the uptake of boron reaches about 82%, 42.5%, and 37% for magnesium, aluminum and iron oxide respectively (Figures 4, 5 and 6) at adsorbent dose of 10g/l and stirring time of 1h.

5.3 Effect of Stirring Time

The importance of stirring lies in the fact that it maintains the adsorbent in suspension, offering the maximum surface and enough time to boron adsorption.

As can be observed in Figures (7- 9) for magnesium, aluminum and iron oxide the concentration of boron in solution decreases as the

stirring time increasing, this is due to more boron in solution was adsorbed these curves show that an initial portion with high slope and after that, the solute diffusion towards the sorbent is slower due to a decrease in its concentration.

The amount of boron adsorbed increases with increasing stirring time and attains equilibrium at about (180, 60 and 90) min for magnesium, aluminum and iron oxide respectively. For initial concentration of 5mg/l, the uptake of boron reaches about 90%, 42.5%, and 41.5% for magnesium, aluminum and iron oxide respectively (Figures 7, 8 and 9) at adsorbent dose of 10 g / l and pH 9.5 for magnesium oxide and pH 8 for aluminum and iron oxide.

5. CONCLUSION

-Maximum removal of boron was achieved at pH 8 for aluminum and iron oxide and 9.5 for magnesium oxide.

-The adsorption rate of magnesium, aluminum and iron oxide increased with increasing adsorbent dose and stirring time and batch results showed that the equilibrium time was 60, 90 and 240 minute for aluminum, iron and magnesium oxide respectively.

-For a given conditions the sorption capacity and efficiency of magnesium oxide was higher than those of alumina and iron oxide. Magnesium oxide is more favorable for boron removal than alumina and iron oxide because it has high ability to remove boron. In addition to that, maximum allowable percentage of magnesium ion in water is 100 mg/l while for aluminum and iron are 0.2 and 0.3 mg/l respectively [Iraqi guidelines for drinkingWater,2009].

-The percentage adsorption of boron onto magnesium, aluminum and iron oxide reaches up to 90, 42.5 and 41.5% respectively under appropriate conditions; so boron percentage in the effluent water after adsorption onto magnesium oxide reaches to the allowable percentage according to WHO and Iraqi drinking water guidelines it will be 0.5 mg/l, while for aluminum and iron oxide concentration of boron in the effluent water reaches to more than allowable guidelines, it will be 2.85 and 2.9 mg/l respectively, so magnesium oxide is more suitable as adsorbent for boron from water, it has high adsorbent capacity and high removal ability for boron compared with aluminum and iron oxide.

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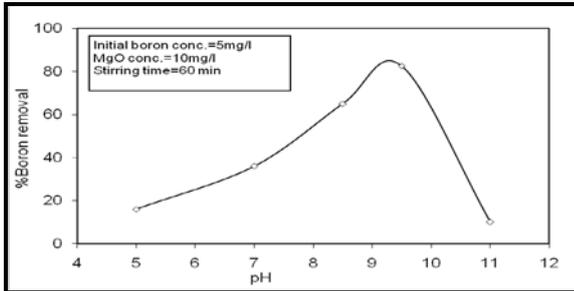


Fig. 1: Effect of pH on percentage of boron removal by adsorption onto magnesium oxide

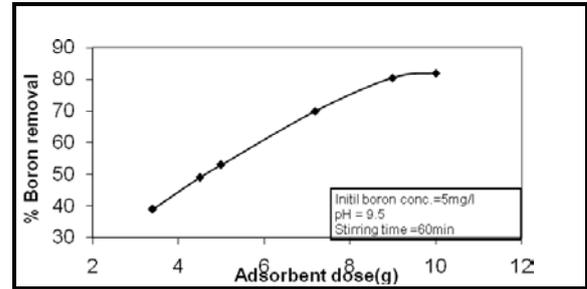


Fig. 4: Effect of magnesium oxide concentration on percentage boron removal

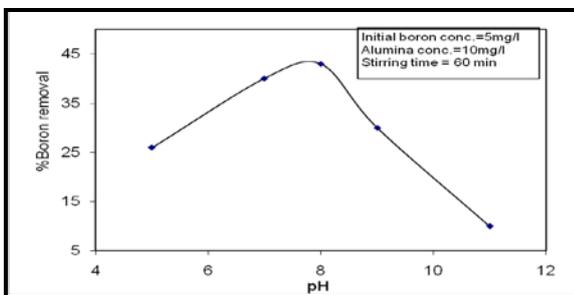


Fig. 2: Effect of pH on percentage of boron removal by adsorption onto alumina

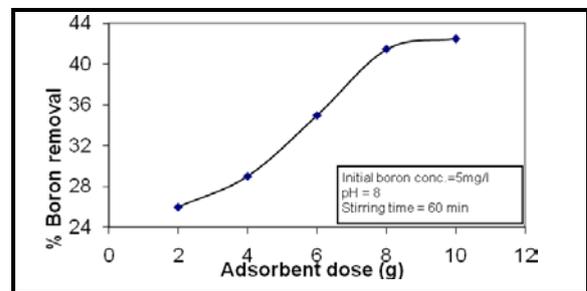


Fig. 5: Effect of aluminum oxide concentration on percentage boron removal

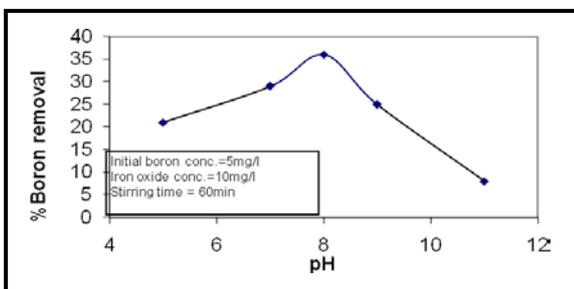


Fig. 3: Effect of pH on percentage of boron removal by adsorption onto iron oxide

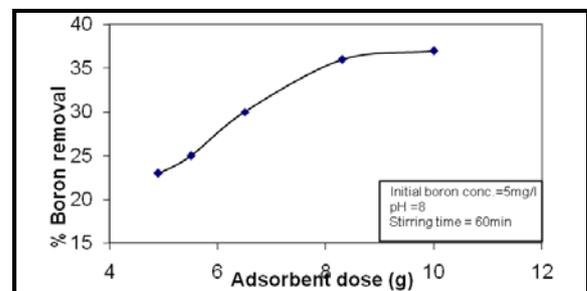


Fig. 6: Effect of iron oxide concentration on percentage of boron removal

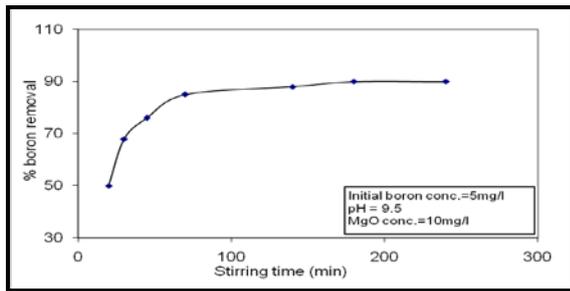


Fig.7: Effect of stirring time on percentage of boron removal by adsorption onto magnesium oxide

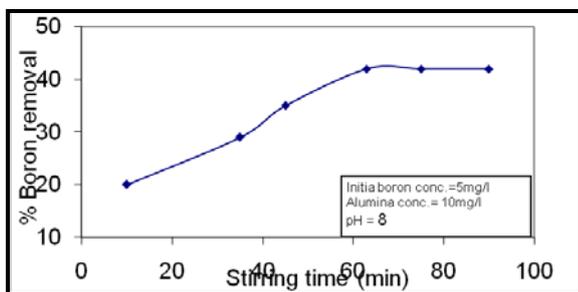


Fig.8: Effect of stirring time on percentage of boron removal by adsorption onto aluminum oxide

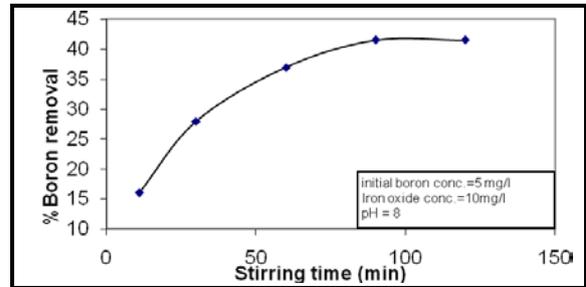


Figure 9: Effect of stirring time on percentage of boron removal by adsorption onto iron oxide