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Boron removal from seawater using adsorption and Ion exchange techniques

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ABSTRACT

Boron is found in the environment at low concentrations as boric acid or borate salts. Boron is a micronutrient required for most plants and animals; however, the range between lower limit and higher limit is not wide. In an industrial sector, the removal of boron from water, such as in the treatment of magnesium brines or in the ultrapurewater production for the semi-conductor industry is essential. In other industrial sectors, a boronselective resin can be applied to remove and or to eliminate boron from discharge water reject. Boron occurrence in most natural fresh waters is at less than 1.0 mg/L and in seawater at 5.0 mg/L levels. The high concentrations of boron are often reported as anindicator of pollution from sources such as laundry detergents, boiler blow down water, or mining zones, which may require treatment prior to discharge to the main streams. In the present investigation, different material were employed to remove boron ions from its solution such as fly ash, zeolite, and dematerialized lignite and also Boron Selective Resin (BSR) (Dow's XUS43594.00). The isotherm, removal capacity, kinetics of process were studied for batch process. Results showed boron removal by employing fly ash is 92.6% and 89.6% boron removed using BSR. pH of the solution seems important variable in boron removal process and maximum removal occurred at pH 11.

Key words*: Boron, Seawater, Removal, Adsorption and Ion exchange techniques.*

Introduction

It is necessary to first understand from where drinking water comes, to understand drinking water pollution. For most cities, depend on municipal water systems, drinking water comes from two main sources: underground and surface waters. Seawater is not accepted as drinking water in literature. Because of the sources of drinking water is decreasing, seawater is used as- drinking water and irrigation water after desalination process in most countries (Glueckstern and Priel, 2003; Hilal *et al.*, 2011).

Boron is existing in the environment, occurring naturally or due to anthropogenic activities, mainly in the form of boric acid or borate salts. Boron is found in the earth's crust at concentration of about 10 mg/L. The most important commercial borate products and minerals are borax pentahydrate, borax, sodium perborate, bone acid, colemanite and ulexite (Koseoglu *et al.*, 2008; Güler *et al.*, 2011).

Boron is essential element for the most of fruits and vegetables. It will be toxic to human in high concentration. (Huertas *et al.*, 2008; Tu *et al.*, 2011).

Conserving drinking water resources is a pressing issue worldwide. Due to increasing water demand, both for drinking and irrigation uses, coupled with a decrease in fit water sources, Drinking and irrigating water resources become important issue in the world , this is because of the highly requirement of water, therefore searching another resource become possible. Water treatment of sea water or waste water by desalination by different techniques which still water contains soluble salts boron ions which considered a toxic matter but its mechanism is still not obvious. Depending on the present model (Oo and Ong, 2012) , the high concentration of boron causes a diffuse of the ions inside the tissue cell as boric acid converts to borate due to higher internal acidity, then establish acomplex with legends inside of the cells . However at low boron concentration there is no such effect in the cell especially at concentration level less than 0.4 gm/l.

By water treatment boron ions can be eliminated by using different methods such as adsorption by using different such material have a selectivity towards removing of boron ion from water or using ion exchanged method or other permissible methods.

Boron exists in the soil, rocks, and water. The boron concentration is from seawater and the act of evaporation that considered the major contributor in nature (Jacob,2007).Boron content in seawater is about 4-5 mg/L, and other contribution comes from other activities such as coke burning and power plant that uses the steam and other chemical plants. Since the low volatility of boron,therefore it would not exist significantly in the atmosphere (Jacob,2007). Also boron may exist in the food therefore the exposure of human consumer can be faced. The location is important variable that plays a major role in the magnitude of the concentration of boron the food. However the high content of boron is due to sedimentation in the land covered with water previously and content is ranged from very low not detected to 26 μg/g. However it can be concluded that the dose of boron taken a day through food, drink for human is about 5-6 mg/day (Nadav, 1999). Different activity ranged from human activities and products such as detergent, fertilizer, medicine, food and cosmetics considered as a source of boron. Exposure to boron by swallowing water, and food is much higher than exposure to it through the skin therefore there is no dermatology effect reported and therefore considered negligible (Nadav, 1999).

Boron contribute in very important way in the growth of different plants as well as it is very necessary in a minor amount for cell function and some other nutrient (Oo and Ong, 2012). However there is study done on people working with boron compound mines and other working without it was concluded that boron effected on reproductive system by delaying of pregnancy with people work with boron as well as it found there is carcinogenicity on human because of boron (Simonnot *et al.,* 2000).

Boron compound is very toxic therefore employed in insecticide production. Plants needs a small amount of boron for its growth, therefore it is one of component of fertilizers which effect the growth of plants (Simonnot *et al.,* 2000). High amount of boron effects on leaves of plants and reduction in fruit yield. Low consumption of boron by animal will cause the cell a failure to function in a normal manner. Therefore boron content should be in the range of 0.3 mg/L to 0.5 mg/L (Simonnot *et al.,* 2000; Bachelier *et al.,* 1996).

Predominatingly boron exists with compound include oxygen found in compounds with oxygen (Power and Woods, 1997). According to the concentration of boron in aqueous, the dissolved boron exists at different kind of species, at low concentration (d”216 mg/L), it is mainly observed as the mononuclear, $B(OH)_3^-$ and $B(OH)_4$. At higher concentration it exist as, polynuclear. The existences of polynuclear boron ions are not important at lower concentrations less than 290 mg/L. Since boron concentration in seawater is about 4.8 mg/L, in seawater boron exist as mononuclear because it is about 4.8 mg/L (Bachelier *et al* .,1996 ; Power and Woods, 1997). While boron exist as boric acid in natural water and it is Lewis acid (Waggott, 1969)

$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ pKa= 9.2$

Boric acid in seawater is dependent upon pH, for pH equal to7 the percentage of H_3BO_3 is 99.5% and in pH equal to8 the percentage is 93.6% of total boron. Elimination of boric acid is in the range of 82-92% when using SWR membranes and is 25-78% for

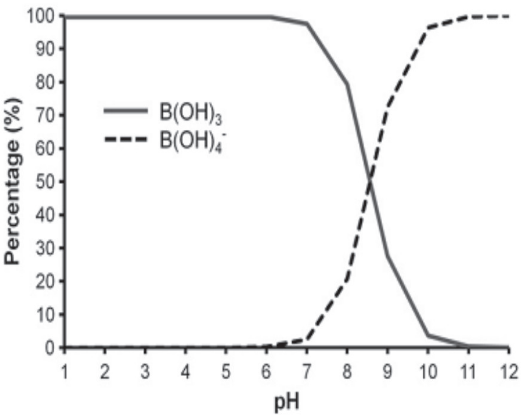

Fig. 1. Effect of pH on boric acid and borate distribution in seawater

BWRO membrane (Power and Woods, 1997).

At pH equal to 10.5 boron reject is more than about 98%. However all boron is in the form of borate ions. The effects of pH on both boric acid and boron exist in seawater are shown in Figure 1. The main reason of boric acid low reject is the transportation of boric acid across the pores of membranes (Huertas *et al*., 2008). However the reason is the radius of boric acid molecules (2.1A) is twice of radius of water molecules and this makes a strong ability to make hydrogen bond with active groups of polymeric membranes (Tu *et al.*, 2011) as shown in Figure (1) all dissolved ions (Oo and Ong, 2012). The radius of boron crystal is large about 0.244-0.261 nm (Jacob, 2007). The hydrated boric acid have small radius, this is because is very poor hydrated (Jacob, 2007). To allowing for boron ions to pass through the polymeric membrane depend upon the diffusivity, therefore rejection of boron ion is like rejection other ions dissolved in water suchsuch as chloride and sulfate (Oo and Ong, 2012)

Cellulose acetate (CA) frequently used as reverse osmosis membrane for water softening for drinking and treatment of sea water (Glueckstern and Priel, 2003; Hilal *et al*., 2011). This is because it is flexible and simple and have high efficiency in rejection the dissolved ions. The main industrial criteria is low operating pressure, low fouling, low pore plugging and low total dissolved solid (TDS) in RO permeate. These criteria is needed for water softening for drinking purpose and it is necessary to reduce of boron ions to minimum allowable level like other trace element down to 0.5 mg/L (Kunin and Preuss, 1964). Therefore, boron level set is set to about 0.5 mg/L according to WHO regulation for water drinking water.

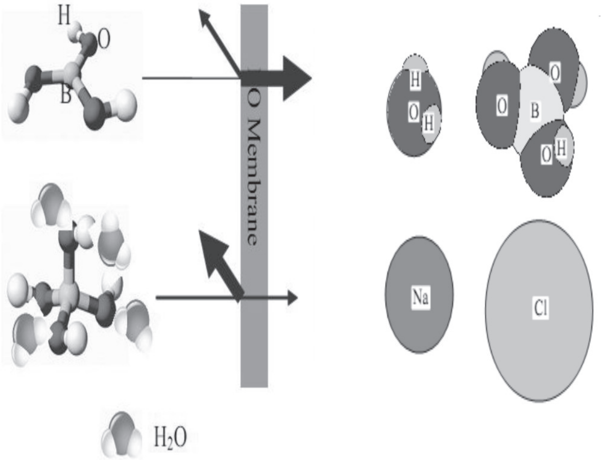

Fig. 2. Water, boric acid, borate, sodium ion, and chloride ionmolecules

Membrane Processes

Membrane technologies have been established as very effective and commercially attractive options for separation and purification processes (Kunin and Preuss, 1964; Su and Suarez, 1995). Membrane considered as barrier woks according to selectivity in separation of two phases by diffusion of one phase through it whether it is polar or not polar depending upon concentration gradient or other parameter work toward establishing of the gradient. However the membrane thickness about 100 micron and less (Kunin and Preuss, 1964; Su and Suarez, 1995).

Membrane Separation

This process is driven by pressure and very simple employed to separate two phases by using membrane made of poly condensate polymers such as poly amide or made of ceramic or metal and contains very small pores. The process utilize the mechanism of diffusion through the membrane, this process needs high pressure, and used in water softening for drinking water by separate of boron ions or other of trace element ions from water depending on selectivity. Therefore, the membrane should be thin, having small pores, polymeric type, does not dissolve, and does not disintegrate (Glueckstern and Priel, 2003; Hilal *et al*., 2011).

Boron Removal By Reverse Osmosis (RO)

The process of boron removal in a single pass by using membranesfor sea water are not enough to produce drinking water according to WHO standards with boron content (less than 0.5 mg/L). Sea water contains high level of boron about 5 mg/L. While new technique industry reported the removal range of boron 90 - 94% comparing with the conventional technique the removal level of boron is about 35 - 55% (Hilal *et al*., 2011; Koseoglu *et al*., 2008). Therefore boron removal is the challenge facing the industry to prepare water drink in accordance to criteria set by WHO. Practically single pass RO is not enough to produce water according to standard, besides membrane get consumed during operation of removing great amount of salt, therefore need to maintenance and pre treatment of water in order to use RO individual or companied with other techniques (Oo and Ong, 2012; Jacob, 2007).

The feasibility of boron removal from wastewater by EC using iron and aluminum electrodes was studied by others. In the present investigation this study Al and Fe were employed cathode and anode electrode. The experimental results showed that Al electrode which provide enhancement in removing efficiency However efficient removal should be above 95% (Koseoglu *et al*., 2008; Güler *et al*., 2011).

In this study, the cost reduction effect of recently developed high boron rejecting SWRO membrane in an advanced seawater desalination system was evaluated.

Materials and Methods

Boron chemistry

Boron is comprised of a mixture of ^{10}B (19.78%) and ^{11}B (80.22%) isotopes. In water, boron mainly exists as undissociated boric acid, H_3BO_3. Boric acid is a very weak acid, with a pKa of 9.2, and, therefore, at neutral pH, $[B(OH)_3]$ is the predominant form of boric acid. At a pH greater than 11, the borate anion $Ba(OH)_4^-$ becomes the main species in solution. Between these two pH values, boric acid de-protonates into a hydrogen cation and a mono-borate anion, as shown below (Data and Bahadoria, 1999; Keren *et al*., 1994; Peak *et al*., 2003).

$$H_3BO_3 \leftrightarrow H^+ + H_2BO_3^- \qquad \text{pKa } 9.2$$

$$H_2BO_3^- \leftrightarrow H^+ + HBO_3^{2-} \qquad \text{pKa } 12.7$$

$$HBO_3^{2-} \leftrightarrow H^+ + BO_3^{3-} \qquad \text{pKa } 13.8$$

In addition to mono-borate anions, a variety of poly-nuclear boron species like $B_2O(OH)_6^{-2}$ or those incorporating B_3O_3rings such as $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, and $[B_5O_6(OH)_4]^-$ are also formed (Matsumoto, 1977).

According to Ristic *et al.*, (1996), those poly-nuclear anions are negligible at concentrations below 290 mg/L. Given that the boron concentration in seawater ranges from non detectable to approximately 7 mg/L, dissolved boron is mainly found as the mono-nuclear boron species, $B(OH)_3$and $Ba(OH)_4^-$. The total boron (tB) in water is, therefore, a sum of all boron species expressed as the molecular weight of boron atom:

$$tB \leftrightarrow (H_3BO_3) + (H_2BO_3^-) + (HBO_3^{2-}) + (BO_3^{3-}) \text{ as mg B/L}$$

The pKa values of boric acid depend on ionic strength, pressure, and temperature. Elevating the temperature from 285 K to 320 K decreased the pKa value from 9.4 to 9.1. Furthermore, increasing the hydrostatic pressure from 0 to 6 kbars increased the pKa value from 9.2 to 11. The latter observation, however, is of little relevance for boron removal technologies, given that it is uncommon to operate at extremely high pressures. The effect of salinity on B retention was found to be membrane dependent, when temperature increases boric acid dissociates.

Table 1. Different type of technique of boron removing process (Nadav,1999; Simonnot *et al.,* 2000).

Process	Applications	Boron level	Advantages	Disadvantages
Reverse osmosis	Desalination, and reclamation.	1-35 mg/L	Flexible to nm. Good removal at high pH.	Need high pH for good removal. Risk of short membrane life.
Ion exchange	Desalination, reclamation, and ultra-pure water.	2–500 mg/L	>99% removal. Selectively remove boron.	Need chemicals for regeneration and disposal of chemical.
Adsorption	Wastewater	100 mg/L	Low initial cost Can handle high concentration	Long contact time, and unable to attain low level of boron in product water.
Precipitation	Wastewater	5 mg/L	Low initial cost. Can handle high concentration	Long contact time, and unable to attain low level of boron in product water
Electrodialysis	Pure water	4.5 mg/L	>99% removal.	Require high energy input.
Hybrid membrane	SWRO permeate	5 mg/L	>99% removal.	Need chemicals. Resin abrasion.

This is perhaps at higher ionic strength the value of zeta potential is positive then a repulsion takes place (Data and Bahadoria,1999; Peak *et al*., 2003).

Absorbent

Fly ash and zeolite were obtained from the local market, Iraq. The fly ash had basic pH that varied in the range of 11-12. The main component of the fly ash is CaO (45.7%), and CaO was the component that gave its basic property to fly ash. The type of mineral in zeolite was clinoptilolite (95 w%), rich of K and Ca.

Boron concentrations

Boron concentrations of the solutions were measured with a Varian, Vista-Pro CCD simultaneous inductively coupled plasma ICP-OES spectrophotometer. Samples before and after adsorption experiments were analyzed for boron.

Batch System for Removal of Boron

In the batch system, the resin and solution are mixed in a batch tank, the exchange is allowed to come to equilibrium, and then the resin is separated from solution. This study was conducted to define the equilibrium time and sorption capacity required for sorption of boron in boric acidsolution using Amberlite IRA 743 ion exchange resin. Sample solutions with concentration of 100mL, and flasks of 250 mL were used as batch systems. The initial concentrations of sample solutions were obtained through dilution of the 1000 mg B/L stock solution. Desired amount ofresins weighted and used in each batch system. In case, pH adjustment was required, diluted solutions of hydrochloric acid or sodium hydroxide (0.1 N) were added to the solution in order to adjust the pH values. All agitation processes were employed with an orbital agitator the speed of which was fitted to 140 rpm.

Results and Discussion

Effect of Initial Concentration of Boron on Boron Removal

All experiment carried out for a certain time of 2 hrs at constant temperature 30 °C to study this parameter in order to know this effect on concentration of boron ion in its solution. Different set of concentration are used 10, 20, 30, 40, 50 and 60 mg/L at constant temperature of 30 °C, pH value kept invariant equal to (8.2). However the results are showed in Fig. 3.

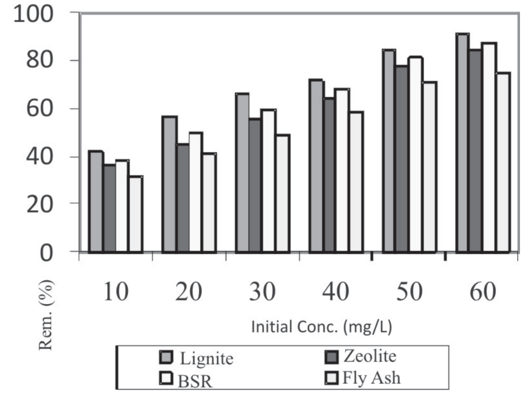

Fig. 3. Effect of initial concentration on the removal % of B

The decline in removal efficiency in the presence of background electrolyte can be explained as a competition of perchlorate anions (ClO_4^-) with borate anions on active sites of magnesia and shows there are no more local active sites are present, where boron is adsorbed preferentially. Furthermore, a strong effect of the ionic strength indicate an electrostatic interaction between boron ions and magnesia active local surface. Further increase of the initial boron concentration results in the decline of the relative amount of adsorbed boron, particularly in 0.1 M $NaClO_4$ solution, emphasizes there are no more boron ions can be adsorbed on locally on surface. This means saturation on surface was reached, this means local allowable sites present and boron ions moles are similar in magnitude (Bachelier *et al*., 1996; Su and Suarez, 1995).

Effect of pH on Boron Removal

Experiments were carried out and conducted for 120 min at a constant operating temperature of 30 °C to study the effect of pH on boron reduction from aqueous solutions for pH of 5, 6, 7, 8, 9, 10 and 11 mg/L. B concentration was 2.0 mg/L. The results obtained are explained in Figure 2. Both boron hydroxide $B(OH)_3$ and $B(OH)_4$ are controlled by adjusting pH. Boron hydroxide and boron ions competes for the adsorption on the local surface resin. Depending on some investigation $B(OH)_4$ ions become mainions in its solution at pH 8.8-10.2 for boron concentrations below 2,000 mg B/L. zeolite Amberlite IRA743 type has a good selectivity for the boron removal at high pH (Data and Bahadoria, 1999; Matsumoto, 1977).

Effect of Temperature on Boron Removal

Batch experiments were conducted for 120 min at pH 8.1 to study the effects of temperature on the process of boron ion adsorption from aqueous solutions are 15, 20, 30, 35 and 40 °C. The boron ion concentration was 2.0 mg/L. The results obtained are illustrated in Figure 3. The value of ΔG^o is negative indicate that the adsorption of boron on magnesia is a spontaneous, and the value of ΔH^o is positive, this means the adsorption process is endothermic and the adsorption takes place at entropy negative value. The thermodynamic data indicate also an electrostatically interacted process, since a complex occurs by adsorption of the ions (Peak *et al.,* 2003; Simonnot, 1999; Matsumoto, 1977; Ristic and Rajakovik, 1996; Goldberg *et al.,* 1996; Yilmazlpek, 2007; Simonnot, 1999).

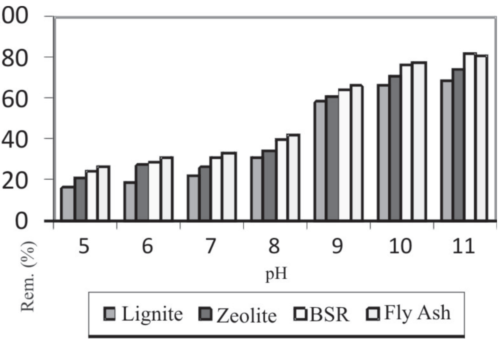

Fig. 4. Effect of pH on the removal % of B

Effect of Adsorbent Dose on Boron Removal

Batch experiments were conducted for 120 min at pH 8.1 to evaluate the effects of adsorbent doseon boron removal from aqueous solutions. The effect of adsorbent doses level were studied in order to estimate the removal level of boron ion in the solution for different levels namely 5, 10, 20, 25, and 30 g/L. The B concentration was 2.0 mg/L. The results obtained are illustrated in Figure 4. However when using higher level of doses of the adsorbents that leads to increase the site of adsorption, therefore the efficiency will increase through out of the process of adsorption of the ions of boron from its solution.

Adsorption Isotherms

The removal process of the boron ions from its solution were conducted by batch type operation. However the isotherms of adsorption are depicted in Figure 5 and 6. Meanwhile Figure 7 shows the isotherm as type I, that's mean the rate of adsorption increases until it become steady, this is because the different sites on surface of adsorbent become saturated and the isotherm leads as Langmuir behavior

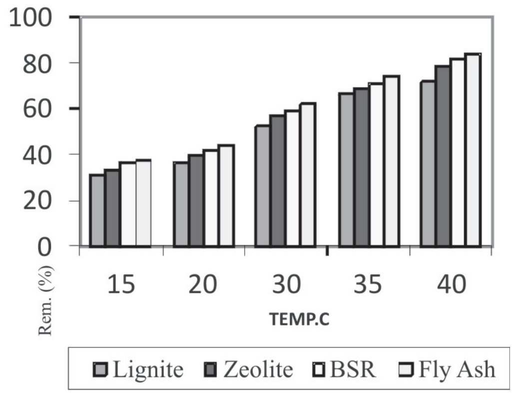

Fig. 5. Effect of Temperature on the removal % of B

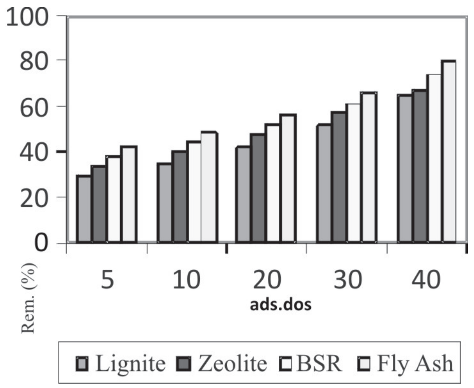

Fig. 6. Effect of Adsorbent Dose on the removal % of B

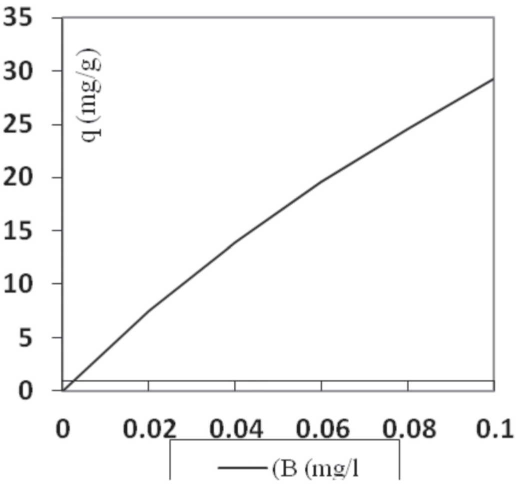

Fig. 7. *Langmuir* adsorption isotherm of Boron using fly ash as adsorbent

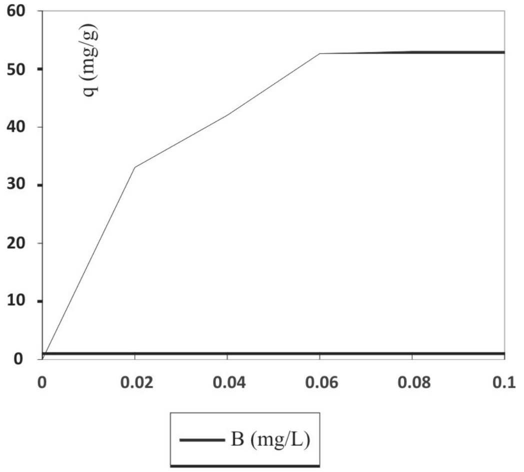

Fig. 8. *Freundlich* adsorption isotherm of Boron using fly ash as adsorbent

(mono layer adsorption) established on the surface of adsorbent and no more adsorption takes place. The isotherm is chemisorptions type were molecules adsorbed by active site until it covered by the ions and eventually become saturated, and no more adsorption occurs. Type I isotherm behavior is the Langmuir isotherm type, and monolayer adsorption occurs. This means the active sites are distributed homogeneously on the surface and each have similar capacity availability towards adsorption of the ions from its solution. Comparable with Figure 8 that shows *Freundlich* adsorption isotherm.

Conclusion

The present wok investigated the adsorption process on boron ion from its solution. Parameter studied are pH of solution, amount of adsorbent by employing different types of materials of adsorbents namely zeolite, deminerilsed lignite, and fly ash. However the fly ash is most effective material in the removal process which removed more than 90% of the ions from solution, while the others are not effective. The study showed the adsorption effected by pH of solution were maximum removal occurred at 10-11 for all adsorbents, and when increasing the amount of adsorbent, consequently capacity of removal increases as well. Results showed fly ash gave higher adsorption capacity. The isotherm of adsorption follows Langmuir and Freundlich behavior with pseudo second order kinetics controlled by intra particle diffusion kinetics.

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