

## Towards a More Safe Environment: (6) Monitoring the Recovery of Boron Adsorbed by Some Clay Sediments in Egypt by FTIR Spectroscopy

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**Abstract:** The increasing environmental pollution concerns render the clay sediments to play an important role as natural adsorbents to immobilize different pollutants and nuclear metals contaminants including boron. Boron is used in manufacturing the control rods of the nuclear reactions due to its ability to adsorb thermal neutrons and to produce only soft gamma rays. For the present study, the clay samples were collected from either clay exploitation localities or from nearby radioactive mineralizations in Egypt. Obtained results were found to fit of Langmuir equation isotherms. The amount of boron adsorbed increases with the increase of B concentration and pH till 6 for El Hafafit vermiculite and till 8 for both Kalabsha kaolinite and Abu Tartur bentonite. Adsorption maxima (B) for boron were high for vermiculite followed by kaolinite and were the least for bentonite. However, the binding energy (b) that affects the adsorption process can be arranged in the opposite direction. Recovery of B from the loaded clay sediments was possible to different extents depending upon the adsorbed form by clay type and recovering agent. Trigonal boron, pyroborate, tetrahedral boron and orthoborate may be the most adsorbed boron forms by clay sediments used in the study. Trigonal boron adsorbed form recovers only from kalabsha kaolinite by both acid and alkaline treatments, while did not recover from other clay sediments by any leaching treatments. Pyroborate adsorbed form by Abu Tartur bentonite was recovered only by alkaline treatment while resistant to recover by any other leaching treatment from El-Hafafit vermiculite. orthoborate recovered by acid and alkaline treatments from El-Hafafit vermiculite.

**Key words:** Adsorption – Recovery –Clay sediments – Boron –Spectroscopy

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### INTRODUCTION

From the nuclear material view, boron is one of the important controlling elements in the nuclear chemical reactions. Boron has two isotopes B<sup>10</sup>, B<sup>11</sup> which are characterized by their ability to adsorb neutrons. B<sup>10</sup> has a great importance in controlling chemical reactions in the nuclear reactors as well as in shielding the nuclear radiations. On the other hand, B<sup>11</sup> can be used in the nuclear applications that require low neutron absorption. From the agriculture view, boron is an essential micronutrient for plants, but high B levels in soils are often responsible for toxicity effects in plants. The range between these extremes is quite narrow. Excess soil solution B concentrations can lead to marked yield decrement in crop plants resulting in economic losses. From the industrial view, boric acid and boron compounds have extensive industrial use in the manufacture of glasses and porcelain, in wire drawing, the production of leather, carpets, cosmetics, photographic chemicals, for fireproofing fabrics, certain fertilizers and others, Sahin (2002). Clays are the main components of the mineral fraction of soils Seyhan *et al.* (2006). Goldberg *et al.* (1996) mentioned that the important source of boron adsorbing surfaces is clay minerals. The boron adsorption on clay minerals is fast but fixation is slow. Up to now, many different materials such as modified or unmodified clay minerals, were used for the removal of boron and /or other pollutants from water and wastewaters by adsorption technique, Abdallah (2004 and 2006). Certain clays having mostly SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> such as modified bentonite, Karahan *et al.*(2006),siral samples, Yurdakoc *et al.*(2005), siral-30 and pural, Seki *et al.*(2006) and fly ash,Ozturk and Kavak (2005) have been used in the application of boron sorption.

Most of research of boron chemistry has provided information about the sorption of boron on soils, clay minerals and oxides. Researchers have indicated that the mineralogy of the sorbent has large role on both the extent and mechanism of boron adsorption. But few spectroscopic studies of boron interaction with different sorbents have been attempted, Peak *et al.*(2003) and Su and Suarez (1997). The majority of boron infrared studies concentrate on distinguishing boric acid from borate at the mineral surface. On the other hand, studies related to boron recovery by different sorbing agents and its monitoring by I.R spectroscopy may be rare in

the literatures. For this reason, careful quantification of boron recovery forms is needed. The FTIR technique has many clear advantages for investigating chemical processes in natural microenvironments as exists in soils and their components.

The aim of the current study is to monitor the different forms of boron adsorption and recovery by some clay sediments in Egypt by using FTIR spectroscopy.

## MATERIALS AND METHODS

### Materials:

Three natural clay sediments differ in their mineralogical composition were selected from Egypt. Full characterization of these sediments including locations, radiometric analysis, X-ray diffraction analysis, Infrared spectroscopic analysis, Differential Thermal Analysis, full chemical analysis (major oxide and trace elements) by X-ray fluorescence and cation and anion exchange capacities were carried out in separate study by Abdallah *et al.* (2007). The collected samples were grinded in a porcelain ball mill, washed with distilled water to remove soluble impurities and wet sieved through 350 mesh sieve (45  $\mu\text{m}$ ), homogenized and < 45  $\mu\text{m}$  fraction was collected. Boric acid ( $\text{H}_3\text{BO}_3$ ) ADWIC with assay 99.5 % was used to prepare the gradient boron concentrations.

### Methods:

#### 1-Adsorption Method:

The adsorption experiments were conducted upon 0.2 gm of the clay samples, mixed with 20 ml of the adsorbent (solid/liquid ration of 1:100) and having the gradient boron concentration ranged between 0.5 - 10.15 mmol/L. The suspensions were equilibrated for 3 hours using a mechanical shaker of 175 rpm at room temperature, three replicats of each experiment were take place.

#### 2 – Recovery Method:

Boron recovery experiments were conducted on the 0.2gm of loaded clay samples with initial B concentration of 5.07 mmol/L were equilibrated with 20 ml aliquots of three leaching solutions tap water, 0.1M HCl and 0.1M NaOH separately. The experiments were carried out as the procedures mentioned in Abdallah *et al.* (2005).

It is worthy to mention that the amount of the adsorbed element was calculated from the difference between the initial B concentration and its concentration at equilibrium. Recovery percentage was calculated from the B concentration in the desorbing solution divided on the loaded B  $\times$  100. The analysis of the B element was performed by flame atomic absorption spectrometry (FAAS).

## RESULTS AND DISCUSSION

The Langmuir equation isotherm was first used to describe P adsorption by Olsen and Watanabe in 1957 and later has been widely used, Abdallah *et al.* (2005) and Shafiq *et al.* (2008). The main advantage of this equation is that allows the adsorption maximum and binding energy for the element sorption to be calculated, Hussain *et al.* (2006).

Boron adsorption isotherms for clay sediments was drawn as the amount of boron adsorbed as a function of equilibrium boron concentration and shown in table (1). The obtained results revealed that the bentonite sample could adsorb greater amounts of B than the other two sediments. While kaolinite sample adsorb more B than the vermiculite sample. This may be related to their A.E.C. which reached 11.66, 9.58 and 4.96 for bentonite, kaolinite and vermiculite, respectively, as mentioned in previous study of characterization of these sediments by Abdallah *et al.* (2007).

**Table 1:** Equilibrium B concentration (C) and adsorbed amount (X/M) on clay sediments by Langmuir equation isotherm

Initial conc.	Equilibrium conc. (C) m mol/l			Adsorbed amount X/M, c mol/kg			C/X/M		
	Kaolinite Kalabsha	Bentonite Abu Tarture	El Hafafit Vermic-ulite	Kaolinite Kalabsha	Bentonite Abu Tarture	El Hafafit Vermic-ulite	Kaolinite Kalabsha	Bentonite Abu Tarture	El Hafafit Vermic-ulite
0.51	0.26	0.10	0.28	2.42	4.06	2.20	0.10	0.024	0.12
1.01	0.55	0.17	0.61	4.62	8.38	4.00	0.11	0.020	0.15
1.52	0.85	0.23	0.95	6.68	12.91	5.70	0.12	0.017	0.16
2.53	1.47	0.45	1.52	10.71	20.80	10.10	0.13	0.022	0.15
3.55	2.14	0.62	2.18	14.19	29.30	13.70	0.15	0.021	0.16
5.07	3.14	1.78	3.38	19.42	32.90	16.90	0.16	0.054	0.20
7.61	4.83	4.07	5.12	28.00	35.40	24.90	0.17	0.110	0.21
10.15	6.87	5.99	7.13	33.09	41.60	30.20	0.20	0.140	0.23

Fig. (1) describing the sorption data plotted according to linear form of Langmuir adsorption isotherm i.e.  $C/x/m$  vs.  $C$ . The mentioned equations expressed the same B adsorption features represented before. Table (2) demonstrates the Langmuir constants and linear equations for B adsorption by the studied clay samples. It is evident that the B maximum capacities can be arranged in the order: El Hafafit vermiculite > Kalabsha Kaolinite > Abu Tartur bentonite. In fact, this is opposite to their AEC arrangement.

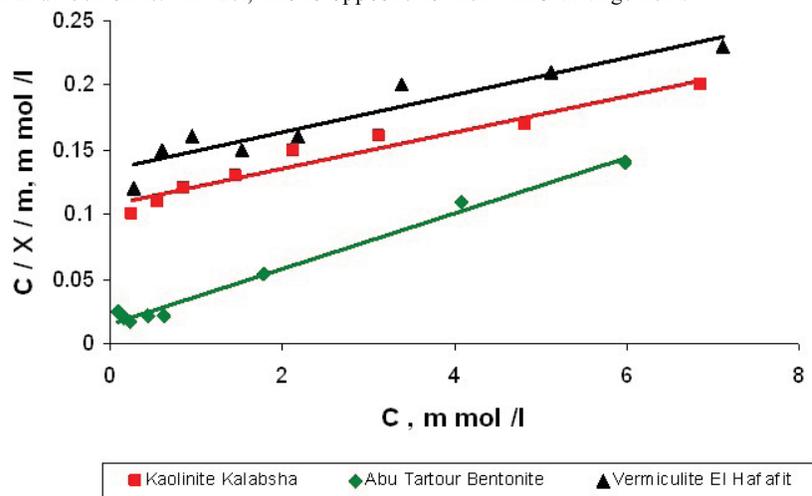


Fig. 1: Langmuir adsorption isotherms of B on different adsorbents.

Table 2: The constants of Langmuir equation isotherm and  $R^2$  of B adsorption in various adsorbents.

Sample	Adsorption Maxima (B)	Binding energy (b)	Equation	$R^2$
Kaolinite	66.7	0.15	$Y = 0.0151 X + 0.107$	0.94
Bentonite	47.6	1.50	$Y = 0.0216 X + 0.0148$	0.98
Vermiculite	71.4	0.10	$Y = 0.0145 X + 0.1341$	0.90

$R^2$  values in Langmuir equation isotherm were significant in all clay sediments studied. In this context, the binding energy (b) calculated from Langmuir equation shows opposite trends relative to the adsorption maxima (B). In the other words, El-Hafafit vermiculite has the highest adsorption maxima (71.4 c mol/kg) but with the lowest binding energy (0.1). While the lowest adsorption maxima noticed in Abu-tartur bentonite (47.6 c mol/kg) has the highest binding energy (1.5). Kalabsha kaolinite appears in between.

**pH:**

The adsorption of boron was studied over the pH range from 2 to 12 Fig. (2). In general, increasing pH lead to increasing of the B adsorption efficiency. The maximum adsorption efficiency of boron takes place at pH 6 for vermiculite and pH 8 for kaolinite and bentonite. Goldberg *et al.* (1993), Goldberg (1999) and Karahan *et al.* (2006) recorded the same trend. These increases can be attributed to the ionization of boric acid to tetrahydroxyborate anion. It can be reached that a competition can occur between hydroxyl ion and tetrahydroxyborate anion for the increasing of negative charge on the clay edges due to ionization, as the pH of solution increased. In agreement with this idea, after adsorption maximum was reached, decreasing of the amount of adsorbed boron with the increasing of solution pH was observed as in Fig, (2).

Above pH=6-8, the increase in the pH was accompanied by a decrease in the B adsorption efficiency. Mattigod *et al.*, (1985), Goldberg and Glaubig (1986) and Goldberg *et al.*, (1993) previously recorded the same result. The latters stated that B adsorption increased in all tested materials including gibbsite, kaolinite and montmorillonite from pH=3 to 7 and exhibited a peak at pH=7.5 to 10 then decreased from pH=10.5 to 12. Thus, it could be said that the B adsorption by Kalabsha kaolinite, Abu Tartur bentonite and El Hafafit vermiculite is a pH dependent.

**Boron Recovery from Loaded Clay Sediments:**

The obtained boron recovery results were presented as cumulative curves of the released B percentage relative to the initial adsorbed amounts (Fig. 3). From the obtained data, it is clear that about 63.12, 43.43 and 72.46 % from the initial adsorbed, B were recovered by four successive  $H_2O$  leaching from Kalabsha

kaolinite, Abu Tartur bentonite and El Hafafit vermiculite respectively. When applying 0.1 M HCl as leaching solution, the recovered B percentage was increased to reach 78.22, 50.00 and 82.62 % respectively. Moreover, the recovered B percentages were still increased to be 81.50, 70.79 and 81.90 % when using an alkaline leaching solution 0.1 M Na OH. These results indicated that B is weakly bonded to the clay samples and thus it is easily exchanged. However, B was slightly more bonded to Abu Tartur bentonite.

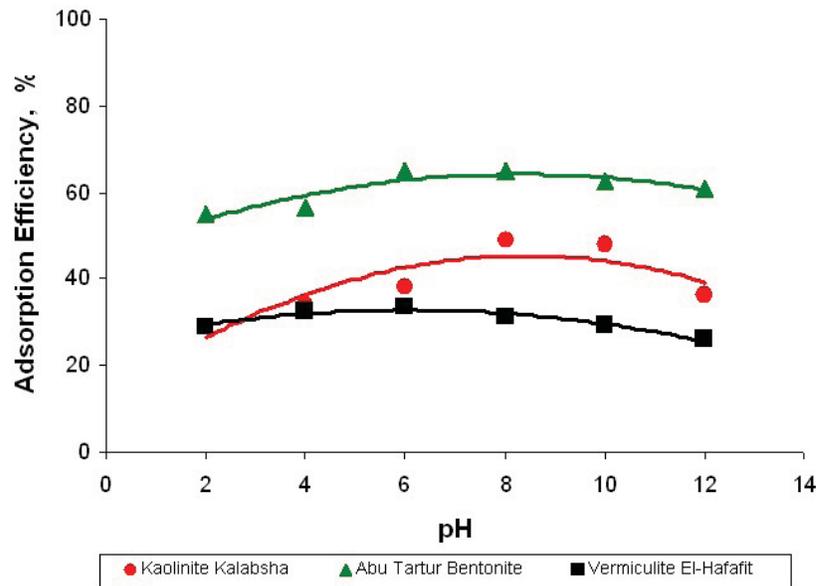


Fig. 2: Effect of pH on B adsorption percentage.

On the other hand, it is noticed that washing the loaded clay samples by four successive water leaching, resulted in a considerable amounts of B recovered. This may be due to the existence of some B droplets between the clay particles. These droplets are easily washable by water.

From the obtained B recovery data, it is clear that B recovering from vermiculite was easier than from kaolinite followed by bentonite. Comparing this notice with the calculated binding energy (b), which is arranged as  $1.5 > 0.15 > 0.1$  for bentonite, kaolinite and vermiculite respectively one can see the positive correlation between them.

**FTIR Spectroscopic Studies on Boron Adsorption - Recovery:**

To elucidate the changes occurred in the kaolintie, bentonite and vermiculite samples after B adsorption and recovery, these samples were subjected to FTIR analysis. The obtained IR spectra are represented in Fig. (4), while the additional reported vibrational frequencies obtained from the IR analysis are tabulated in Table (3). On the other hand, there may be found two modes of B vibrational frequencies as follows:

- 1 - a-  $(BO_3)^{-3}$ ,    b-  $(B_2O_5)^{-4}$ pyroborate    c-  $(BO)_2^{-1}$  metaborate
- d-  $(B_3O_6)^{-3}$  ring metaborated    e -  $B(OH)_3$     f-  $B_3O_3(OH)_3$
- 2 - a-  $(BO_4)^{-5}$                     b-  $B(OH)_4$     c-  $B(Ox, OH_{5-x})-(x+1)$

The majority of boron infrared studies concentrate on distinguishing boric acid from borate at the mineral surface. This is reasonably straightforward, as there is ample infrared spectral data for minerals containing trigonal  $(BO_3)^{-3}$  and  $B(OH)_3$  and tetrahedral B  $(BO_4)^{-5}$  and  $B(OH)_4^-$  boron groups. From the variation of mineral spectra with structure, it is possible to get a good grasp of what vibrational bands are accessible in the midinfrared region and how interpret them. This fact makes conclusive peak assignment in samples with mixtures of trigonal and tetrahedral boron quite problematic. This is especially difficult when attempting to assign peaks for tetrahedral boron , as peaks from B – O - H bending , trigonal B – O stretching and tetrahedral B – O stretching all occur in the 700 -1000  $cm^{-1}$ region. None of the previous boron mineral

adsorption studies thoroughly discuss the relationship between infrared spectra and the structure of boric acid on the surface of minerals peak *et al.* (2003). This is likely due to the fact that the relationship between molecular symmetry and infrared spectra of boron containing compounds has not been specifically discussed in the infrared literature, as is case for phosphate and sulfate. This means that the symmetry rules must be worked out for the bands that are accessible for midinfrared spectroscopic studies in aqueous suspensions. Experimental constraints mean that the region from 800 to 1600  $\text{cm}^{-1}$  is available for study. It is convenient to consider the O – H ligand as a single entity for purpose of determining symmetry rules. This is reasonable since the center of mass for B – O – H is not greatly shifted from the position of B – O molecules.

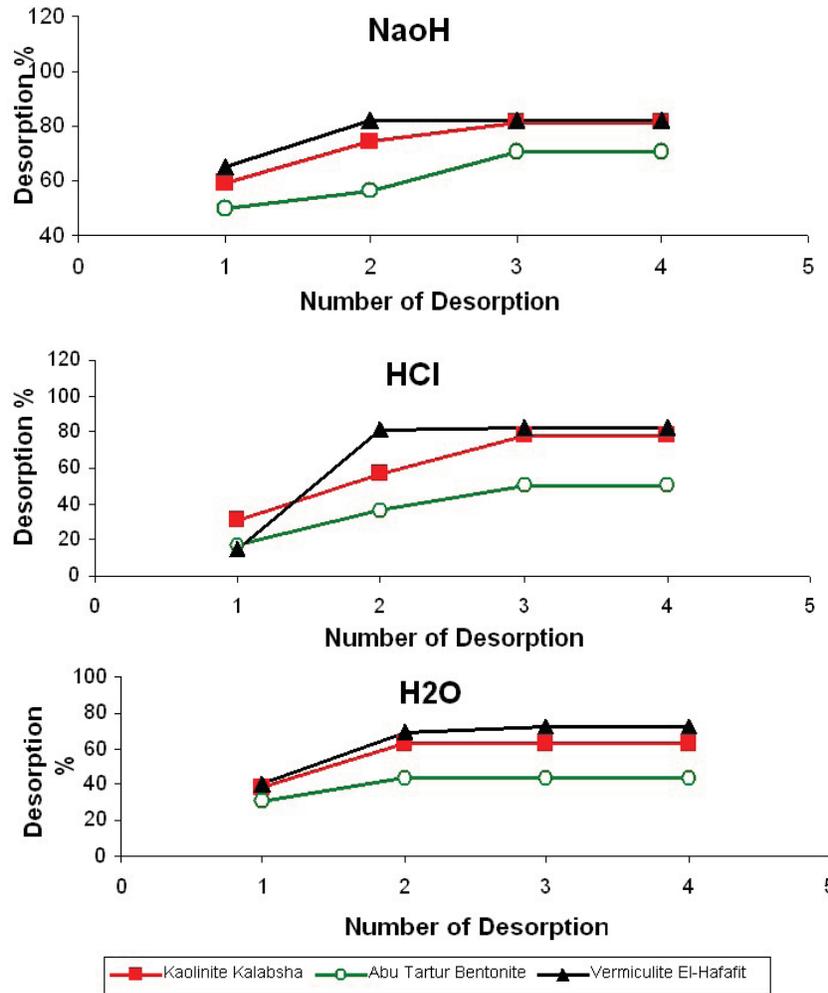


Fig. 3: Recovery data of B loaded clay samples using different leaching agents.

**Kalabsha Kaolinite:**

After B adsorption by the studied clay samples, Kalabsha kaolinite exhibited four vibration frequencies at 3467, 2856, 1829 and 1544  $\text{cm}^{-1}$ . The first vibration frequency may be attributed to the bonded O-H group investigated by Farmer (1974) in the boron mineral hambergite (anhydrous borate). While the second vibration frequency attributed to the clay hydrolysis by the aqueous B adsorption solution (H<sub>2</sub>O stretching and O-H group). The third vibration frequency could be attributed to the Co-OOH group (Farmer, 1974). The fourth refers to asymmetric stretching modes of trigonal boron peak *et al.*(2003) that consider the form of adsorbed boron by kalabsha kaolinite.

**Table 3:** Additional reported IR spectra interpretation of kaolinite, bentonite and vermiculite after boron adsorption and desorption experiments.

Adsorption	Kalabsha Kaolinite			Adsorption	Abu Tartur bentonite			Adsorption	El Hafafit vermiculite		
	Desorption				Desorption				Desorption		
	H <sub>2</sub> O	HCl	NaOH		H <sub>2</sub> O	HCl	NaOH		H <sub>2</sub> O	HCl	NaOH
-	-	-	-	-	3904	-	-	-	3904	3903	
-	-	-	-	-	3838	-	-	-	3838	3838	
-	-	-	-	-	3802	3803	3803	3803	3802	3802	
-	-	-	-	3694	-	-	-	3694	-	-	
-	-	-	-	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	3616	-	-	
3467	-	3469	3446	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	-	2960	-	
*	-	-	-	2928	2926	2927	-	-	2928	2926	
2856	2856	2856	-	-	2855	2855	-	-	-	-	
-	-	-	-	2340	2340	2340	2340	2340	2340	2340	
1829	1829	1930	-	-	-	-	-	-	-	-	
-	-	1817	-	-	-	-	-	-	-	-	
-	-	1780	-	-	-	-	-	-	-	-	
-	-	1750	-	-	-	-	-	-	-	-	
-	-	1705	-	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	-	-	1563	
1544	1544	-	-	-	1543	-	1544	1544	1544	1544	
-	-	-	-	1460	1460	1460	-	-	1459	-	
*	1113	1115	-	-	-	-	-	-	-	-	
*	1007	1008	-	-	-	-	-	-	-	-	
-	-	-	-	915	915	915	-	-	-	-	
-	-	-	-	-	-	-	-	-	796	-	
-	-	-	-	-	-	-	756	758	-	-	
-	-	-	-	693	693	693	693	687	686	690	
-	-	-	-	-	-	-	-	-	-	677	
-	-	-	-	-	-	-	-	533	-	-	
-	-	-	-	-	-	-	-	465	460	465	

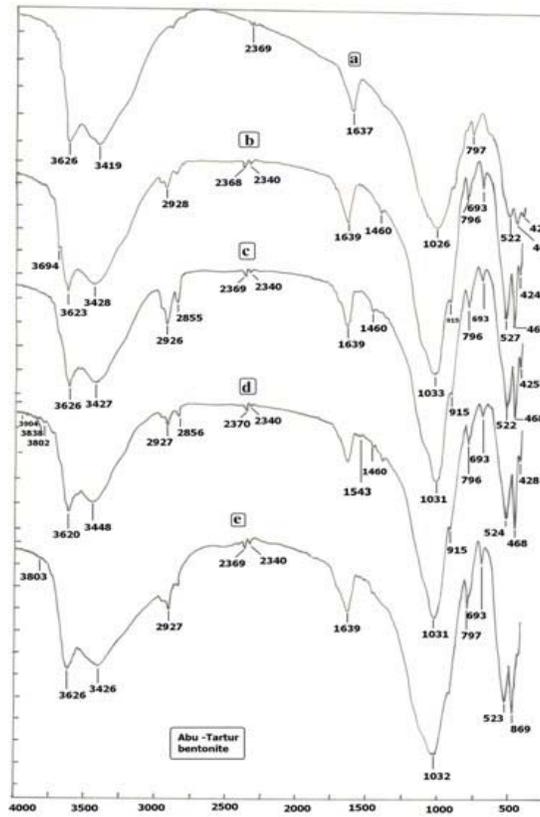
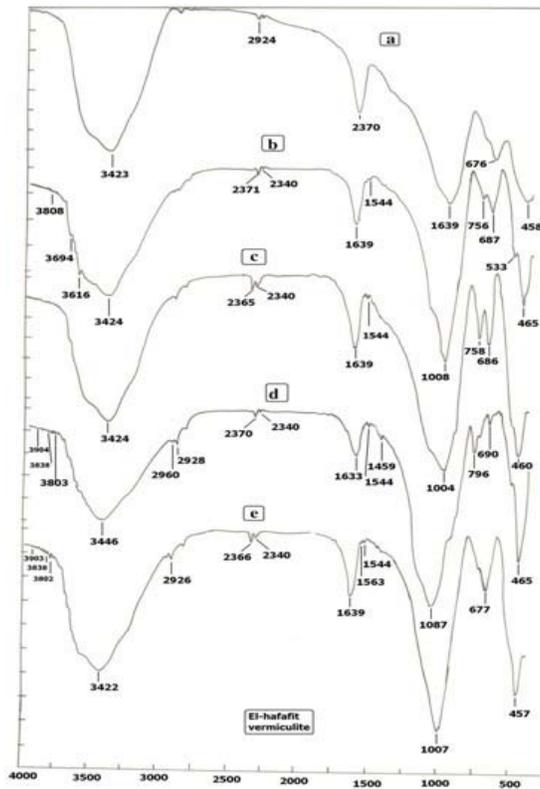
\* Present in the original sample.

After performing the recovery experiment with H<sub>2</sub>O the vibration frequency at 3467 cm<sup>-1</sup> was disappeared; this may be due to B easily wash. However, the vibration frequencies at 2856, 1829 and 1544 cm<sup>-1</sup> still existed indicating that adsorbed trigonal boron form did not recover by water. Two new vibration frequencies have appeared at 1113 and 1007 cm<sup>-1</sup>. These vibration frequencies although they reappeared again, they are fundamental vibration frequencies of Kalabsha kaolinite. Their reappearance may be attributed to the regeneration of the kaolinite by the water washings.

After conducting the kaolinite desorption by 0.1 M HCl, the vibration frequency at 1544 cm<sup>-1</sup> was disappeared. It means that adsorbed trigonal boron form was recovered by acid leaching. Four vibration frequencies still existed at 2856, 1930, 1115 and 1008 cm<sup>-1</sup>. The vibration frequency at 3469 cm<sup>-1</sup> reappeared while five new vibration frequencies has appeared at 3909, 1817, 1780, 1750 and 1705 cm<sup>-1</sup>. It is proposed that the vibration frequency at 3909 cm<sup>-1</sup> is due to water held in the structure as OH group. The boron recovery due to the stretching occurs at 3909 cm<sup>-1</sup> and overtones and combination are seen at 1817, 1780, 1750 and 1705 cm<sup>-1</sup>. The OH group replaced oxygen according to the scheme: (Farmer, 1974)



After performing the recovery by 0.1 M NaOH upon the B loaded Kalabsha kaolinite, only one vibration frequency at 3446 cm<sup>-1</sup> reappeared which is corresponding to the bonded OH group (Farmer, 1974). All the other vibration frequencies are the same as those in the original kaolinite sample before performing the adsorption and recovery experiments. It means that NaOH consider the strongest leaching solution (desorbing agent) and remove the trigonal boron adsorbed by kalabsha kaolinite. From the above discussion, trigonal boron consider the boron adsorbed form by kalabsha kaolinite and this form was stable in water but recovered by both acid and alkaline agents.



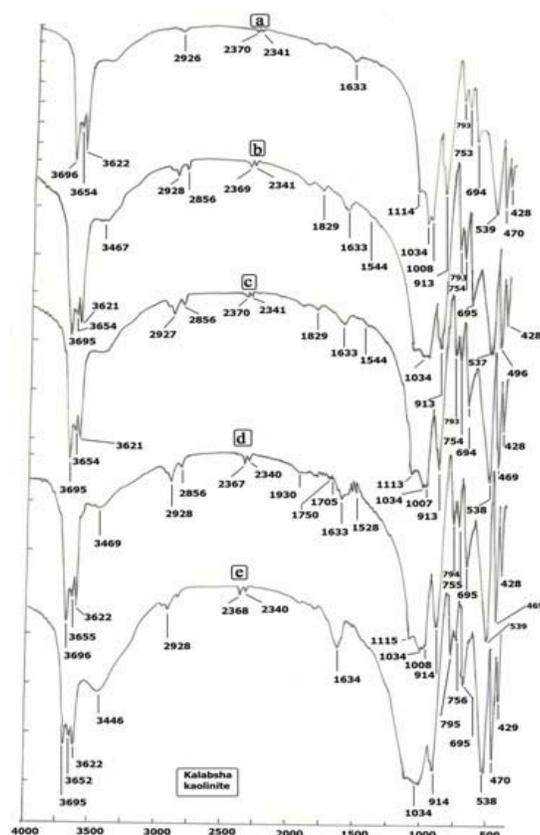


Fig. 4: I.R spectra of Boron adsorption and recovery by studied clay sediments : (a) before adsorption (b) after adsorption (c) after recovery by H<sub>2</sub>O (d) after recovery by HCl (e) after recovery by NaOH.

**Abu Tartur Bentonite:**

After B adsorption by Abu Tartur bentonite, six additional vibration frequencies have been appeared at 3694, 2928, 2340, 1460, 915 and 693 cm<sup>-1</sup>. These frequencies are actually characterizing the kaolintic clays in the abu Tartur bentonite sediment used in this study. The appearance of these vibration frequencies may propose that the boric acid absorbent initiate the surfaces of the kaolinite mineral in the bentonite sample or else B has been adsorbed on the surfaces exchanging sites of the kaolinite in the bentonitic sample.

The presence of band at 1460 and 915 cm<sup>-1</sup> refer to asymmetric stretching and symmetric stretching modes of tetrahedral pyroborate, respectively. In this respect, Peak *et al.* (2003) mentioned that for the trigonal planar boric acid, one peak at 1400 cm<sup>-1</sup> caused by asymmetric B – O stretching as well as the in plane B – O – H bending at 1150 cm<sup>-1</sup>. Also appearance of band at 693 cm<sup>-1</sup> attributed to bending modes of trigonal boron liao *et al.*(2007). Presence of bands at 1460, 915 and 693cm<sup>-1</sup> indicated that both pyroborate and trigonal boron were the forms of boron adsorbed by Abu Tartur bentonite.

After desorbing the benonite sample with water, the vibration frequency at 2855 cm<sup>-1</sup> characterizing the koalinites has appeared in addition to the preexisting five vibration frequencies at 2926, 2340, 1460 ,915 and 693 cm<sup>-1</sup>.It means that both boron forms (trigonal boron and pyroborate) adsorbed by Abu Tartur bentonite resistance to recover by water. However the existed one at 3694 cm<sup>-1</sup> has disappeared.

When desorbing Abu Tartur bentonite by 0.1 M HCl, six vibration frequencies were still existed at 2927, 2856, 2340, 1460, 915 and 693 cm<sup>-1</sup> the first two bands are fundamentals characteristics of kaolinites. The others indicated that both pyroborate and trigonal boron adsorbed forms were resistant to recover by the acid treatment. Three additional vibration frequencies at 3904, 3838, and 3802 cm<sup>-1</sup> have appeared. These could be explained on the basis of the water held in the structure as OH group. The adsorption of the IR spectra which may be due to the stretching occurred at 3904 cm<sup>-1</sup> and overtones and combinations seen at 3838 and 3802 cm<sup>-1</sup>.

After treating Abu Tartur bentonite sample with 0.1 M Na OH leaching solution, the vibration frequencies at 3904, 3838, 2856, 1543, 1460 and 915  $\text{cm}^{-1}$  have disappeared. Disappearing of these vibration frequencies was indicated that the NaOH was the strongest desorbing agent for boron from clay sediments and pyroborate form was recovered by alkaline agent. However the vibration frequencies at 3803, 2340 and 693  $\text{cm}^{-1}$  were still existed. These frequencies are fundamental characteristics of kaolinite and the latter indicated that trigonal boron form was still resistant to recover by alkaline agent.

From the previous discussion, two forms of boron were adsorbed by Abo Tartur bentonite, pyroborate and trigonal boron. All recovering solutions did not recover the trigonal boron form adsorbed by Abu Tartur bentonite. While , pyroborate adsorbed form recovered only by alkaline treatment and recovery resistance by water and acid treatment.

#### ***El Hafafit Vermiculite:***

The B adsorption upon El Hafafit vermiculite sample has been expressed in the appearance of the additional recorded frequencies at 3803, 3694, 3616, 2340, 1544, 756, 687, 533 and 465  $\text{cm}^{-1}$ . The interpretation of the vibration frequency appearance at 3803, 3694, 2340, 1544 and 687  $\text{cm}^{-1}$  was discussed before. The latter two bands refer to the trigonal boron form as stretching and bending modes. On the other hand, the vibration frequencies appeared at 3616, 756, 533 and 465  $\text{cm}^{-1}$  may be attributed to different forms of B adsorption. Considering the vibration frequency at 3616  $\text{cm}^{-1}$ , Farmer (1974) mentioned that the vibration frequency at the region 3500-3000  $\text{cm}^{-1}$  is attributed to OH stretching or free  $\text{H}_2\text{O}$ . The vibration frequency at 3695  $\text{cm}^{-1}$  may be referred to possible free O-H. When considering the vibration frequency at 756  $\text{cm}^{-1}$ , Farmer (1974) interpreted the vibration frequency at the range from 705 to 760  $\text{cm}^{-1}$  to either the meta borate fundamentals or to out- of - plane bend of orthoborates. The vibration frequencies at 533 and 465  $\text{cm}^{-1}$  can be correlated to those 530 and 465  $\text{cm}^{-1}$  reported for the possible B-O stretching. Farmer (1974) considered that the vibration frequency region from 700 and 400  $\text{cm}^{-1}$  could be attributed to the bending modes of trigonal and tetrahedral boron or to the pyroborate respectively.

From the above discussion, trigonal boron, metaborate, orthoborate, and pyroborate may be the different forms of boron adsorbed by El - Hafafit vermiculite.

When conducting the B recovery of El Hafafit vermiculite by tap water, the vibration frequencies at 3803, 3694, 3616 and 533  $\text{cm}^{-1}$  have disappeared. This may be attributed to the release of the easily washable B solution captured between El Hafafit vermiculite particles. However, vibration frequencies at 2340, 1544, 758, 686 and 460  $\text{cm}^{-1}$  were still existed indicating the adsorbed different forms of B ions did not recover by water. They may be referring to out of plane of orthoborate, pyroborate, and stretching and bending modes of trigonal boron which recovery resistant adsorbed form by water.

After performing the B recovery from El Hafafit vermiculite by 0.1 M HCl, five vibration frequencies at 3904, 2340, 1544, 690 and 465 $\text{cm}^{-1}$  were still existed it is may be referring to resistance of trigonal boron and pyroborate adsorbed forms to recover by Hcl. Four vibration frequencies at 3694, 3616, 756 and 533  $\text{cm}^{-1}$  have disappeared may be referred to orthoborate adsorbed form recovered by acid treatment. By recovering the adsorbed B by 0.1M HCl, the exchangeable sites on the clay mineral became free due to performing the desorption experiment and replacing B upon the same of the exchanging sites by (OH) group. The water held in the structure as OH group began to appear and the adsorption due to the stretching has occurred at 3904, 3838 and 3802  $\text{cm}^{-1}$ . In the same time four vibration frequencies at 2960, 2928, 1459 and 796  $\text{cm}^{-1}$  have newly appeared. The first one is characterizing the  $\text{H}_2\text{O}$  stretching of El Hafafit vermiculite that newly appeared might be due the regeneration of the vermiculite sample by 0.1 M HCl. The second vibration frequency at 2928  $\text{cm}^{-1}$  may be attributed to the OH stretching of the disordered vermiculite sample after the treatment with HCl. However, the third and the fourth vibration frequencies, at 1459 and 796  $\text{cm}^{-1}$  were attributed to non- recovered trigonal boron form. It is worthy to mention that the vibration frequencies at 1459  $\text{cm}^{-1}$  were previously attributed to either asymmetric stretching of tetrahedral boron. On the other hand, the vibration frequency at 796  $\text{cm}^{-1}$  could be attributed to possibly vibration spectra at (700 – 400 $\text{cm}^{-1}$ ) of the tetrahedral borate. Liao *et al.*(2007) reported that the vibration frequency region at 850-700  $\text{cm}^{-1}$  is attributed to symmetric stretching of the tetrahedral boron (OH out of plane bending). Also, the vibration frequency of the borate minerals at 795  $\text{cm}^{-1}$  could be related to out of plane bending of some orthoborates. In general, the vibration frequencies at the region from 705-760  $\text{cm}^{-1}$  could be considered as borate fundamentals. Acid treatment recovers orthoborate but did not recover trigonal and pyroborate adsorbed forms.

On performing the B desorption by 0.1 M Na OH form El Hafafit vermiculite sample, eight vibration frequencies at 3903, 3838, 3802, 2926, 2340,1544, 690 and 457  $\text{cm}^{-1}$  are still present for trigonal boron and pyroborate adsorbed forms. Three vibration frequencies at 2960 (OH stretching), 796 and 756  $\text{cm}^{-1}$  have been

disappeared may be attributed to orthoborate which recovered by alkaline treatment. It is well known that the alkaline agent was stronger than the acidic one under this study. So, it leads to the recover more of the adsorbed boron. Two vibration frequencies at 1563 and 677  $\text{cm}^{-1}$  are newly appeared. It could be attributed to the still resistant adsorbed B or to the (BO) group, which may cause a vibration frequency at 670  $\text{cm}^{-1}$  or else, the vibration frequency at 676  $\text{cm}^{-1}$  could be revealed to the presence of trigonal boron Liao *et al.* (2007). From the above discussion, orthoborate adsorbed form recovered by both acid and alkaline agents. Trigonal boron and pyroborate were resistant to recover by all leaching agents used under the study.

#### **Conclusions:**

In this study, kalabsha kaolinite, Abu Tartur bentonite and El Hafafit vermiculite can be used as safe disposal of boron from aqueous media. The amount of adsorbed boron increases with the increase of B concentration and pH till 6 for vermiculite and till 8 for both kaolinite and bentonite. Obtained results indicated that B adsorption by studied clay sediments were pH dependent.

Recovery of boron by 0.1 M HCl, 0.1 M NaOH and tap water show clearly the ability of the different sediments to release boron. This was a function of leaching solution and binding energy. Spectroscopic studies represent that trigonal, pyroborate, tetrahedral and orthoborate may be the most adsorbed boron forms by clay sediments used. Alkaline leaching treatment recovered adsorbed trigonal boron from kalabsh kaolinite, pyroborate from Abu Tartur bentonite and orthoborate from El-Hafafit vermiculite. Acid leaching treatment recovered adsorbed trigonal boron from Kalabsh and orthoborate from El-Hafafit.

This study is useful for extracting boron from its ores. Knowing boron form may put suitable leaching solution to get a lot amount of boron from its ores.

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