Desalination and Water Treatment 2 (2009) 185–194
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Comparison of boric acid adsorption by hybrid gels

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Received 27 June 2007; Accepted 24 October 2008

ABSTRACT

Mannitol doped and un-doped hybrid gels derived from bis(trimethoxysilylpropyl)amine (TSPA), or the mixture of TSPA with tetraethoxysilane (TEOS), or the mixture of 3-aminopropyltriethoxysilane (APTES) with TEOS were prepared. Textual properties and point of zero charges were determined to characterize the gels. The adsorption of boron from its water solutions by the acidified and un-acidified gels in solutions at three different initial pH values were compared comprehensively. In general the gels derived from APTES and TEOS have the highest adsorption amount among all the gels. The gels doped with mannitol and the gels without doping show similar adsorption amount, that is, the addition of mannitol does not promote the adsorption. After acidification the adsorption amount of the gels increases. In general, the adsorption decreases with the increase in solution pH. It was found that boron is adsorbed in both H_3BO_3 and $B(OH)_4^-$ forms through the interactions of hydrogen bonding, electrostatic and hydrophobic attractions. The information gained in this study is helpful for the understanding of the adsorption mechanisms, designing and preparing some low cost and easily available adsorbents for boron.

Keywords: Boric acid; Hybrid gel; Adsorption mechanism; Hydrogen bonding; Electrostatic interaction; Hydrophobic interaction

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1. Introduction

Boron is one of the elements dissolved in natural water. The dominant form of inorganic boron in natural aqueous systems is un-dissociated boric acid. Since boric acid is very weak, borate ions have a strong affinity for protons. Although borate salt solutions contain several ionic species, tetrahedral $B(OH)_4^-$ ions usually predominate [1]. Boron usually appears in a concentration lower than 1 $mg{\cdot}L^{-1}$ and rarely exceeds the concentration existing in seawater, estimated between 4.4 and 4.6 $mg{\cdot}L^{-1}$. The main sources of boron that account for its presence in surface water are urban wastewater containing detergents and cleaning products, industrial effluents of a great number of industrial activities, and the diverse chemical products used in agriculture [2].

The World Health Organization defines a boron level of 0.3 $mg{\cdot}L^{-1}$ as the non-observed effect level (NOEL) for drinking water. High boron levels in drinking water can be toxic to humans [3]. Boron is one of the seven essential micronutrient elements required for the normal growth of most plants. It has a marked effect on plants in terms of both nutrition and toxicity. Its over-dose or under-dose may cause toxicity or deficiency symptoms, respectively. There is a relatively narrow range of soil boron concentrations between the level required for growth and its toxic level [4]. A very low boron content is required in irrigation water for certain metabolic activities, but if its concentration is only slightly higher, plant growth will exhibit effects of boron poisoning, which are yellowish

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spots on the leaves and fruits, accelerated decay and ultimately plant expiration. Safe concentrations of boron in irrigation water are 0.3 mg·L^{-1} for sensitive plants, 1–2 mg·L^{-1} for semi-tolerant plants, and 2–4 mg·L^{-1} for tolerant plants [5,6]. Therefore, the removal of boron from boron-contaminated natural aqueous systems is of great importance.

There is no easy method for the removal of boron from waters and wastewaters. One or more methods may be applied according to boron concentration in medium. For boron removal, main processes that have been studied are: (1) precipitation-coagulation, (2) reverse osmosis, (3) electrodialysis, (4) solvent extraction, (5) membrane filtration, (6) adsorption (including ion exchange adsorption) [6,7]. Among these methods, adsorption is a more useful and economical technique at low boron concentration [5,6]. In this method, conventional ion exchange adsorption, or adsorption using common adsorbents, such as oxides, clays, and activated carbons, is not so effective due to a poor ionization of boron acid and low selectivity of adsorbents. The most promising boron adsorbents are hydroxyl-containing boron-selective adsorbents, such as Amberlite XE 243 and Amberlite IRA 743 [6], polyol and *N*-methylglucamine grafted mesoporous SBA-15 and MCM-41 [8,9]. Selective adsorption of boron by these adsorbents is caused by the complexation. It is reported that coexisted salts do not significantly interfere with the adsorption [1].

Although the above-mentioned boron-selective adsorbents are effective for the removal of boron, they are usually difficult to prepare and expensive, therefore, are not so applicable for some practical boron removal processes. In this study, mannitol immobilized hybrid gels and the corresponding hybrid gels without mannitol were prepared. Mannitol is an effective complexing reagent for boric acid [10]. Mannitol was chosen as the dopant due to its high complexation equilibrium constant and its compatibility with drinking water. The complexation reaction occurs at neutral pH and produces a negatively charged di-borate ester [11]. The doped and un-doped gels were used to adsorb boric acid from its water solutions with the purpose of getting some useful information for understanding the adsorption mechanisms, designing and preparing some low cost and easily available adsorbents for boron.

2. Experimental

2.1. Preparation of the gels

The gels were prepared through a one-step sol-gel process catalyzed by the -NH- groups of TSPA (Gelest) or the -NH_2 groups of APTES (Hubei Wuhan University Silicone New Material, China). TSPA, or the mixture of TSPA with TEOS (Tianjin No. 3 Chemical Reagent Factory, China), or the mixture of APTES with TEOS, 0.1 mol·L^{-1} mannitol solution (for mannitol doped gels), H_2O (for the gels without mannitol added) were quickly mixed to get uniform sols in 50 mL beakers. The sol composition is listed in Table 1. The prepared sols were placed without stirring for gelation. The obtained gels were dried at 25°C for 4 days. The dried gels were grinded and sieved. The gels with a particle size between 20 and 40 meshes (830–380 μm) were selected for the adsorption experiments. For the gels doped with mannitol (Gels 2, 4, and 6), the gel particles were washed five times with pure water, and then dried at 25°C before they were used for the adsorption experiments.

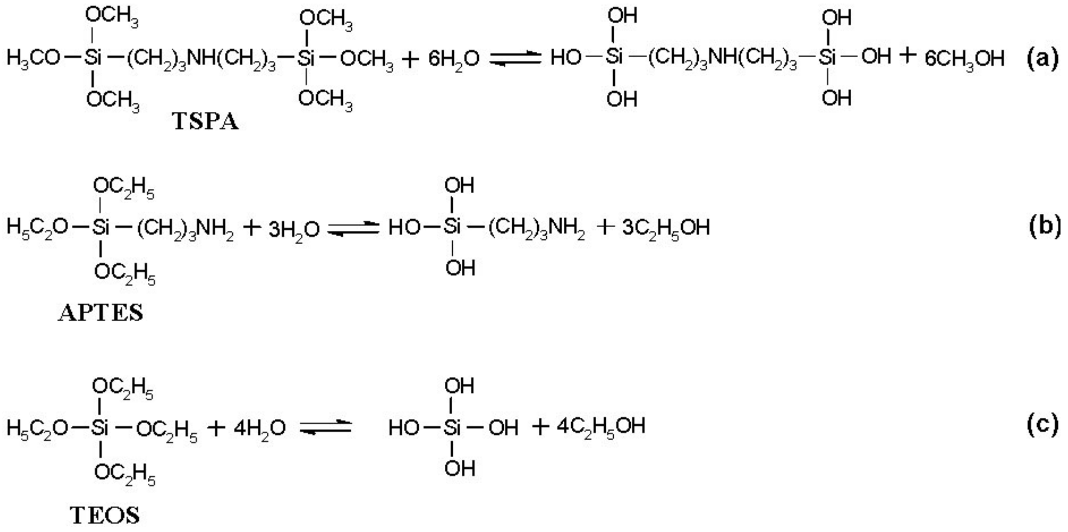
For the acidification of the gels, Gels 1–4 were immersed in 0.5 mol·L^{-1} HCl for 24 h and Gels 5 and 6 were immersed in 0.02 mol·L^{-1} HCl for 36 h. After that all the gels were washed several times with pure water until the pH of the water after washing was around ~7. Finally the gels were dried at 25°C.

2.2. Determination of the textural properties and PZC of the gels

Textural properties of the gels were estimated using nitrogen sorption experiments. The desorption isotherms of nitrogen at 77 K were measured with a JW-K apparatus (JWGB Science & Technology, PR China). Prior to the measurements, the gels were degassed at 105°C for 2 h. The specific surface area was calculated from the BET equation and the pore volume and pore size was

Table 1
Sol composition and gel time

No.	TSPA (mol)	APTES (mol)	TEOS (mol)	H_2O (mol)	Mannitol (mol)	Gel time (s)
1	0.061			1.11		8
2	0.061			1.11	0.002	7
3	0.030		0.045	1.11		12
4	0.030		0.045	1.11	0.002	11
5		0.043	0.045	1.11		288
6		0.043	0.045	1.11	0.002	310



$$(H_3CO)_3Si-(CH_2)_3NH(CH_2)_3-Si(OCH_3)_3 + 6H_2O \rightleftharpoons (HO)_3Si-(CH_2)_3NH(CH_2)_3-Si(OH)_3 + 6CH_3OH \quad (a)$$

$$(H_5C_2O)_3Si-(CH_2)_3NH_2 + 3H_2O \rightleftharpoons (HO)_3Si-(CH_2)_3NH_2 + 3C_2H_5OH \quad (b)$$

$$(H_5C_2O)_3Si-OC_2H_5 + 4H_2O \rightleftharpoons HO-Si(OH)_2-OH + 4C_2H_5OH \quad (c)$$

Fig. 1. Hydrolysis reactions of the precursors.

calculated by the BJH method based on the desorption isotherms.

Point of zero charge (PZC) of the gels was determined by the method described by Mustafa et al. [12] and Wu et al. [13,14]. A PB-10 pH meter (Sartorius) was used to record solution pH.

2.3. Boric acid adsorption by the gels

Both the un-acidified and acidified gels were used for the adsorption experiments. Samples of 0.5 g of the gels were equilibrated with 60 mL solutions containing 2.0 $mmol\cdot L^{-1}$ boric acid at initial solution pH of 2.12, 6.02, and 11.6. Solution pH was adjusted with HCl or NaOH solutions. The adsorption experiments were carried out at 25°C for 3 days.

Boric acid concentrations in the solutions after adsorption were determined by a TU-1810 UV-visible spectrophotometer (Beijing Purkinje General Instrument, China) with azomethine-H as a colorimetric reagent according to the method described in refs. [15,16].

The amount of boric acid adsorbed onto the gels (q, in micromoles per kilogram of gel) was calculated by a mass balance relationship:

$$q = \frac{V\left(C_0 - C\right)}{W} \qquad (1)$$

where C_0 and C are the boric acid concentrations in the solutions before and after adsorption ($mmol\cdot L^{-1}$), V is the volume of the solutions (L), and W is the weight of the gels used (kg).

The fraction of boric acid adsorbed F was calculated by the following equation:

$$F = \frac{C_0 - C}{C_0} \qquad (2)$$

3. Results and discussion

3.1. Preparation and characterization of the gels

In the preparation of the gels, if only TSPA is used without the addition of any TEOS, it is quite easy to get the corresponding gel. However, if only APTES is used, it is difficult to get the gel. In order to get the gel using APTES as a precursor, TEOS must be added. TSPA, APTES, and TEOS hydrolyze according to Reactions (a), (b), and (c) in Fig. 1, respectively. Their corresponding hydrolysis products condensate according to Reactions (d)–(h) in Fig. 2, depending on the compositions of the sols. The organic group of TSPA is a bridged group, which does not terminate the condensation reaction according to Reaction (d). However, the organic group of APTES is a terminal group, which can terminate or suppress the condensation reaction according to Reaction (f). So if only APTES is used without the addition of any TEOS, it is difficult to get the gel because the -$(CH_2)_3NH_2$ group of APTES cannot hydrolyze, and therefore can terminate the condensation reaction, and hinder the condensation reaction of the three Si-OH groups of the APTES hydrolysis products due to steric hindrance.

The N_2 desorption isotherms of the gels are presented in Fig. 3. The pore size distribution of the gels based on the N_2 desorption isotherms is presented in Fig. 4. The textual properties of the gels are listed in Table 2. The gels derived from APTES and TEOS (Gels 5 and 6) have the smallest surface areas, pore volumes and pore sizes. While the gels derived from TSPA and TEOS (Gels 3 and 4) have the largest surface areas, pore volumes and pore sizes.

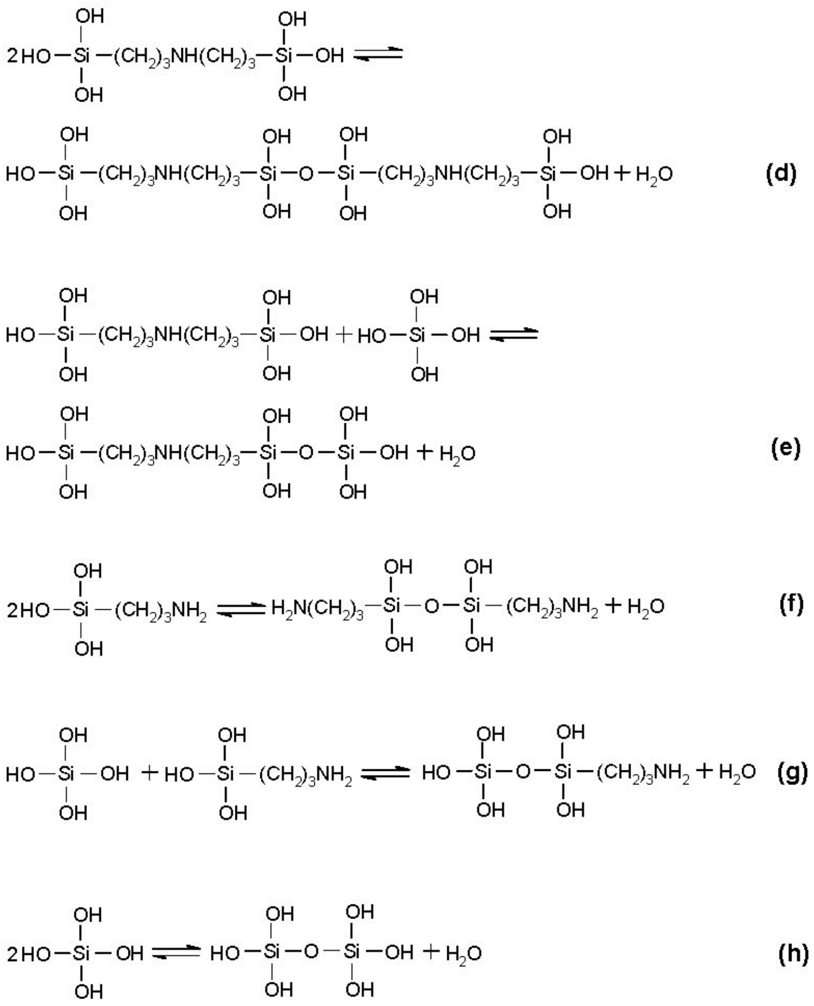


Fig. 2. Condensation reactions.

Table 2
Textual properties and PZC of the gels

No	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size (nm)	PZC
1	66.3	0.256	<2	7.90
2	31.6	0.265	<2	8.20
3	316	1.690	<4	7.92
4	256	0.854	<3	7.99
5	12.1	0.090	<2	9.96
6	21.9	0.175	<2	9.82

For the determination of the point of zero charge (PZC) of the gels, the relationship between pH change and initial pH of the solutions is demonstrated in Fig. 5. pH change is the difference between the final and initial pH values of the solutions after acid-base equilibrium between the gels and the solutions. The initial pH where the pH change is zero is the PZC of the gels, which is listed in Table 2. All the gels have a PZC above 7, which is consistent with the fact that both -NH- and $-NH_2$ groups are basic in nature. The gels derived from APTES and TEOS (Gels 5 and 6) have higher PZCs than the other gels.

3.2. Boric acid adsorption comparison

Boric acid adsorption comparison is presented in Fig. 6. In general, the comparative results can be summarized as: (1) the gels derived from APTES and TEOS (Gels 5 and 6) have the highest adsorption amount among all the gels; (2) the gels doped with mannitol and the gels without doping show similar adsorption amount, that is, the addition of mannitol does not promote the adsorption; (3) after acidification the adsorption amount of the gels increases; (4) the adsorption decreases with the increase in solution pH. This trend is clearer for the un-acidified gels. For the acidified gels this trend is not so clear because of the acidification of the gels, which can interfere with the solution pH.

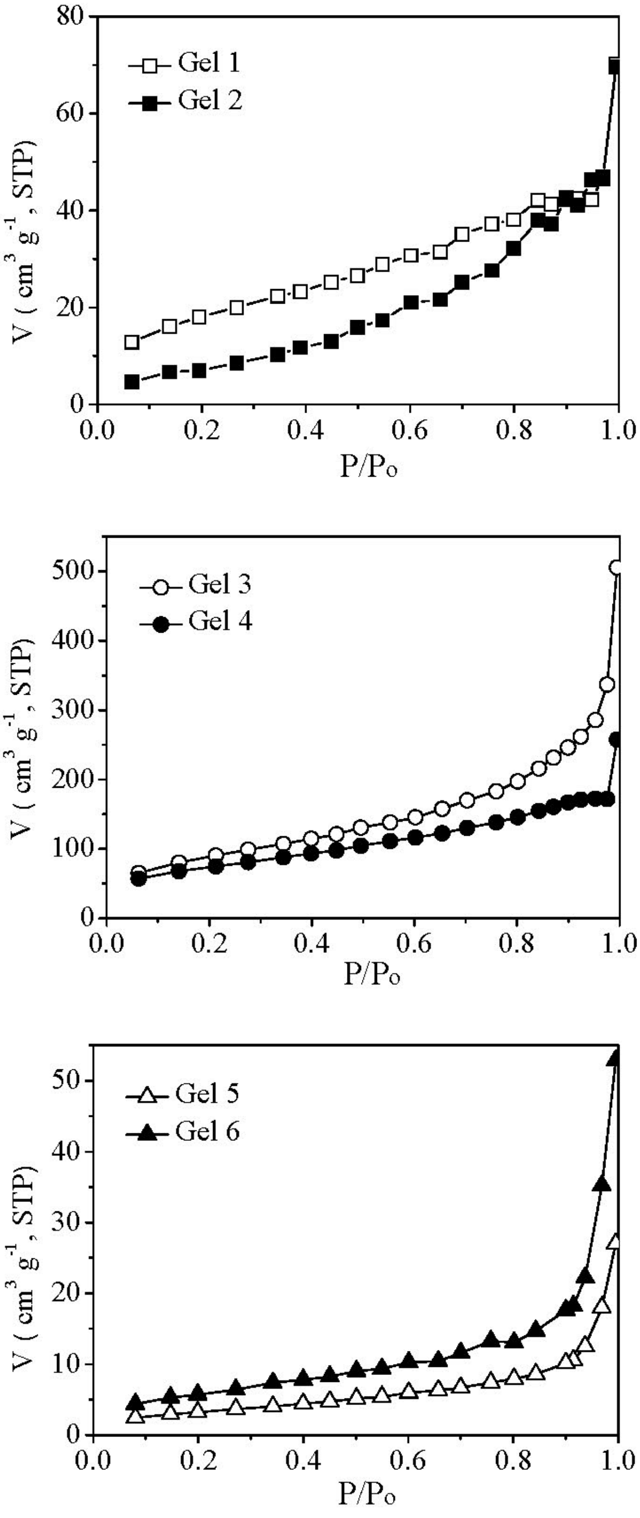


Fig. 3. N_2 desorption isotherms of the gels.

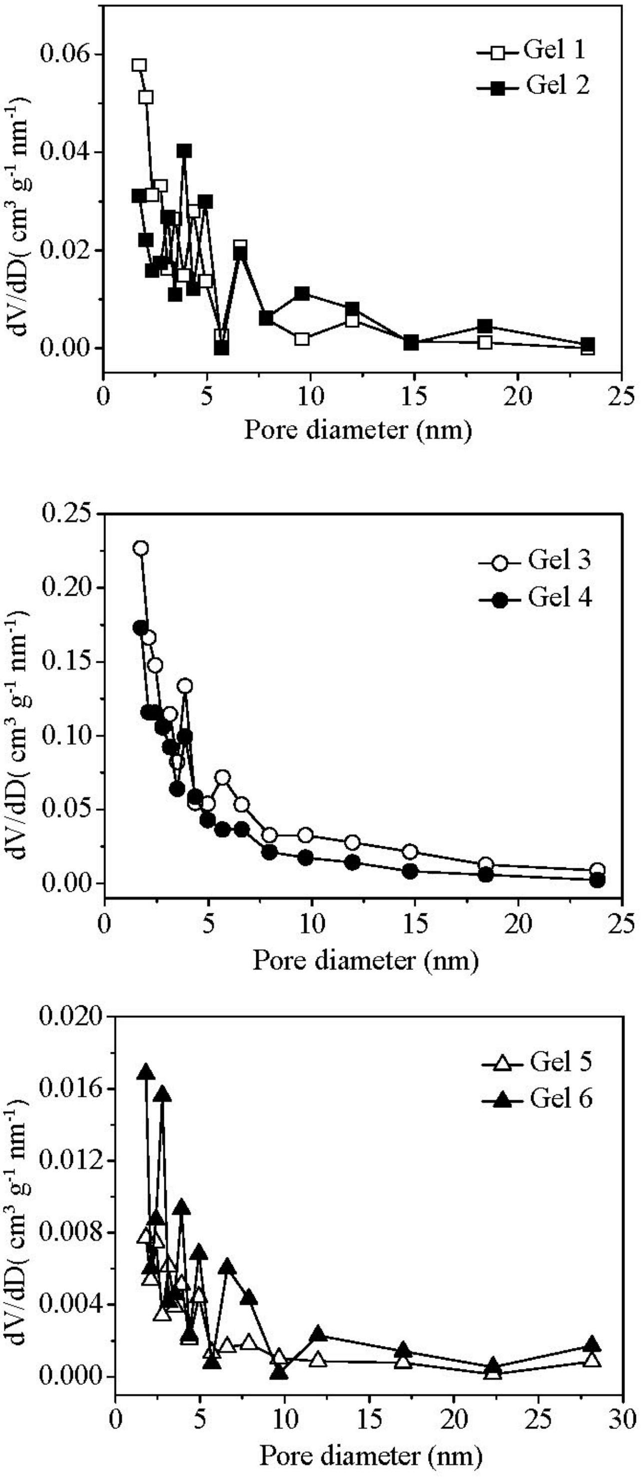


Fig. 4. Pore size distribution of the gels based on the N_2 desorption isotherms.

The adsorption differences are mainly caused by the textural properties of the gels and the interactions between boric acid/borate and the gel surfaces. Generally speaking, an adsorbent with a larger surface area and pore volume should have a higher adsorption amount. In this study, Gels 5 and 6 have lower surface area and pore volume than the other gels (Table 2), however, their adsorption amount is much higher than that of Gels 1 and

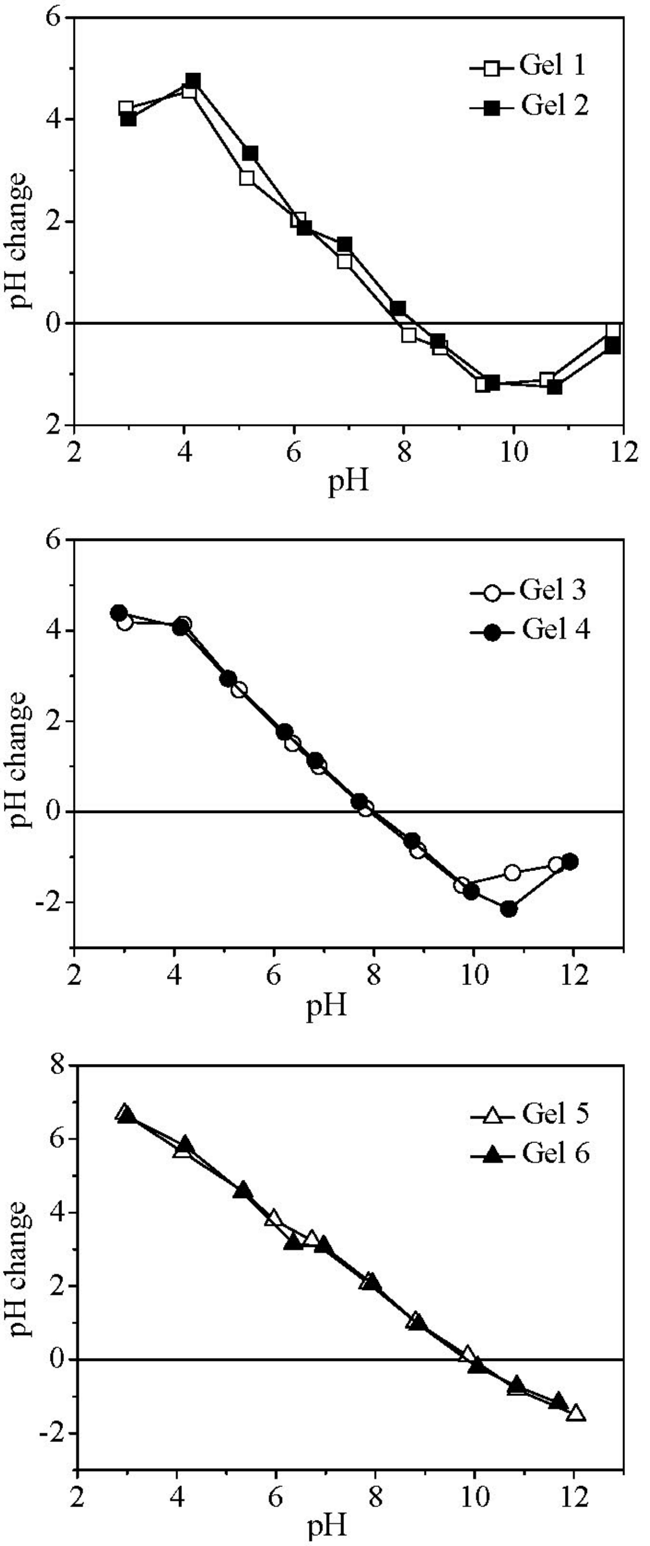


Fig. 5. PZC determination of the gels.

2 (Fig. 6). Therefore, we may suspect that, in this study, the effect of the interactions between boric acid/borate and the gel surfaces may be more important for the adsorption.

The interactions between boric acid/borate and the gel surfaces are based on the chemical species of boron in solution and the surface properties (especially the surface charge) of the gels. In solutions of different pH, boron species and gel surfaces with different properties have different interactions. As an example, the interactions between boric acid/borate and the surface of Gel 5 are summarized and schematically demonstrated in Fig. 7. There can be three types of interactions: (1) hydrogen bonding; (2) electrostatic interaction; and (3) hydrophobic interaction.

Based on the molecular structure of H_3BO_3, it could be deduced that H_3BO_3 can form hydrogen bonds (including ionic hydrogen bonds [17]) with the -OH, $-NH_2$, and $-NH_3^+$ groups on the surface of Gel 5. The formation of the hydrogen bonds can promote the adsorption.

In natural aqueous environments where boron content is low, boron is mainly present as boric acid and partially as $B(OH)_4^-$ according to the dissociation reaction (pK_a = 9.1). Boric acid $B(OH)_3$ and its anion borate $B(OH)_4^-$ have solution chemistry that is quite different from most other oxyanions. Borate forms by the addition of a hydroxyl group to the trigonal planar boric acid molecule, forming a tetrahedral anion. Boric acid and borate both typically exist as monomers in solution at low concentrations (below 25 $mmol \cdot L^{-1}$), but at higher concentrations many polyborate polymers are known to form [18]. In this study, initial boric acid concentration in solution is about 2.0 $mmol \cdot L^{-1}$. So boron exists mainly as $B(OH)_3$ and $B(OH)_4^-$. According to the H_3BO_3 and $B(OH)_4^-$ acid–base equilibration reaction, and the pK_a value of 9.1, when solution pH <9.1, boron exists mainly as H_3BO_3, whereas when solution pH >9.1, boron exists mainly as $B(OH)_4^-$ [18].

Silica or composite silica gel surface has deferent charges in solutions of deferent pH due to the acid-base equilibrium of the functional groups on the gel surface [19]. When an oxide or composite oxide is placed in a solution, the surface charge of the oxide is determined by the PZC of the oxide and the solution pH. The particular pH at which the negative and positive charges are balanced, and therefore, there is no net charge on the oxide surface is called the PZC. At pH <PZC, the oxide surface is positively charged, whereas at pH >PZC, the oxide surface is negatively charged [20]. In aqueous solutions, -OH and $-NH_2$ groups on the surface of Gel 5 can be protonated or deprotonated depending on solution pH, which results in the corresponding changes of the surface charge of the gel. The PZC of Gel 5 is 9.96, so at pH <9.96, the gel surface is positively charged, whereas at pH >9.96, the gel surface is negatively charged.

Based on the above considerations, in solutions of different pH, there should be different electrostatic interactions between boron and the surface of Gel 5. Under the

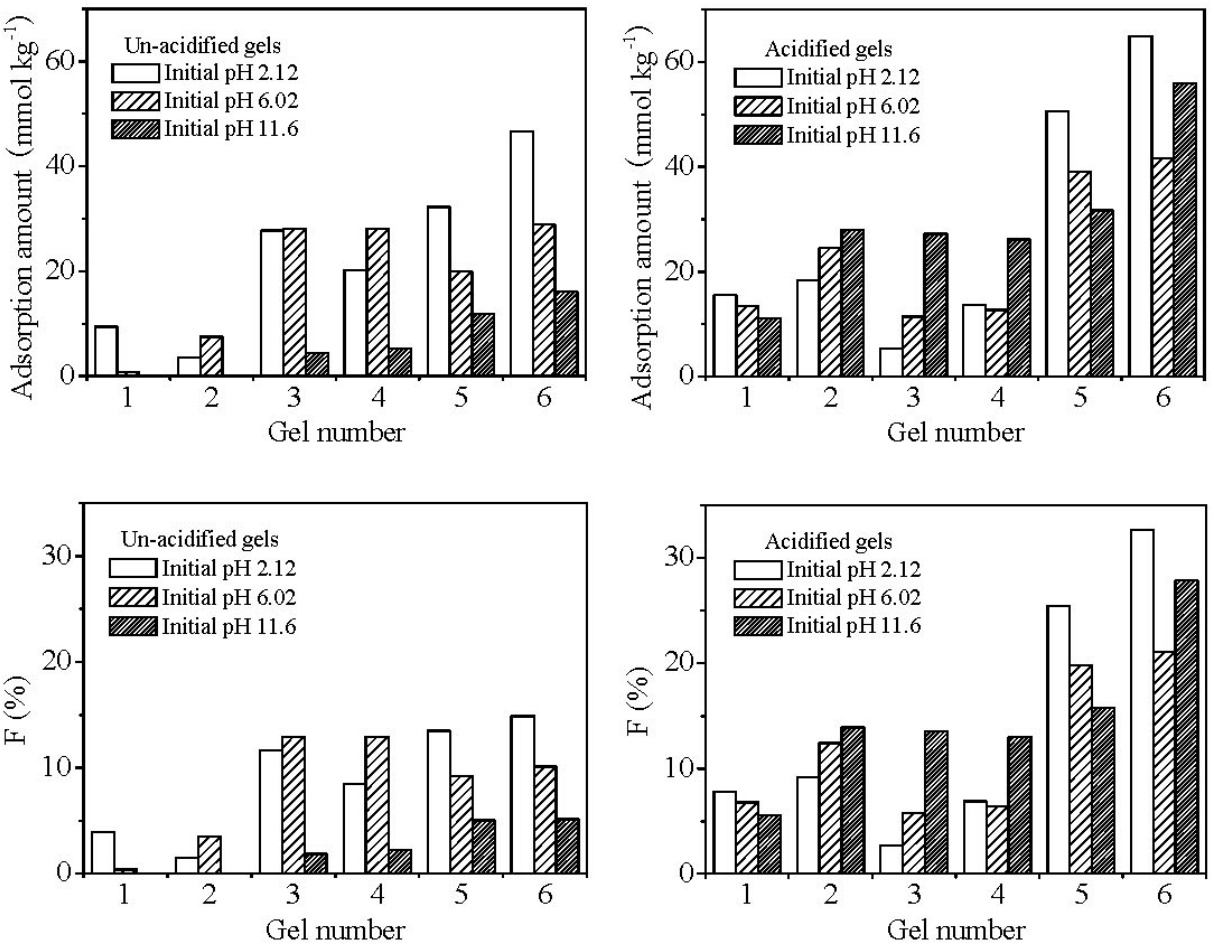


Fig. 6. Comparison of boric acid adsorption by the gels after adsorption for 3 days.

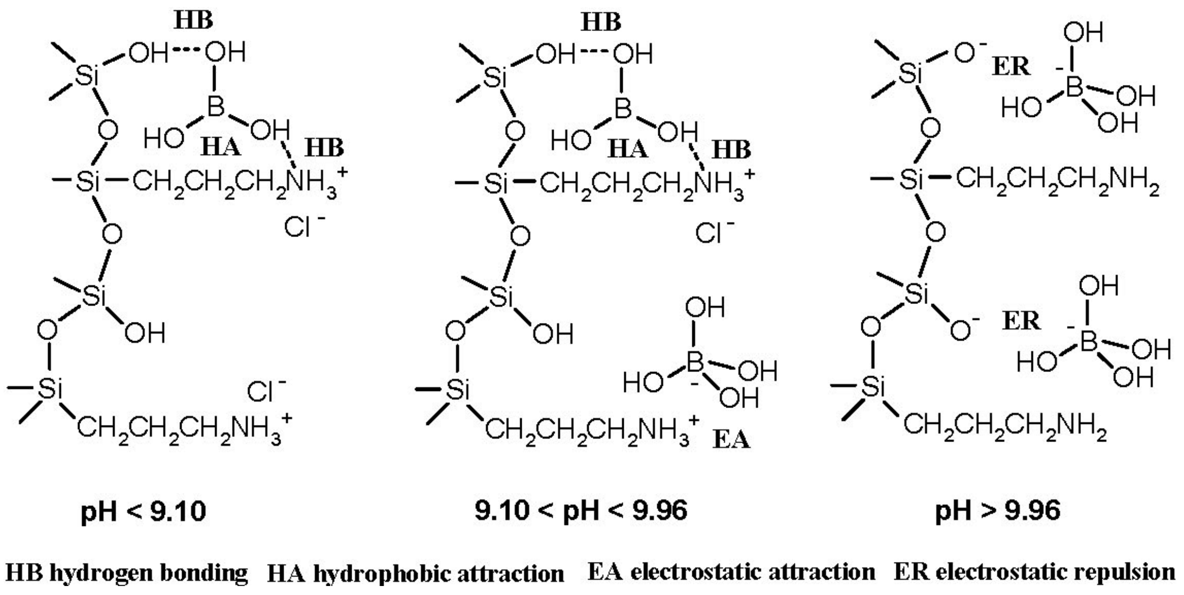


Fig. 7. Schematic diagrams for the interactions between boric acid/borate and the surface of the gel derived from APTES and TEOS (Gel 5).

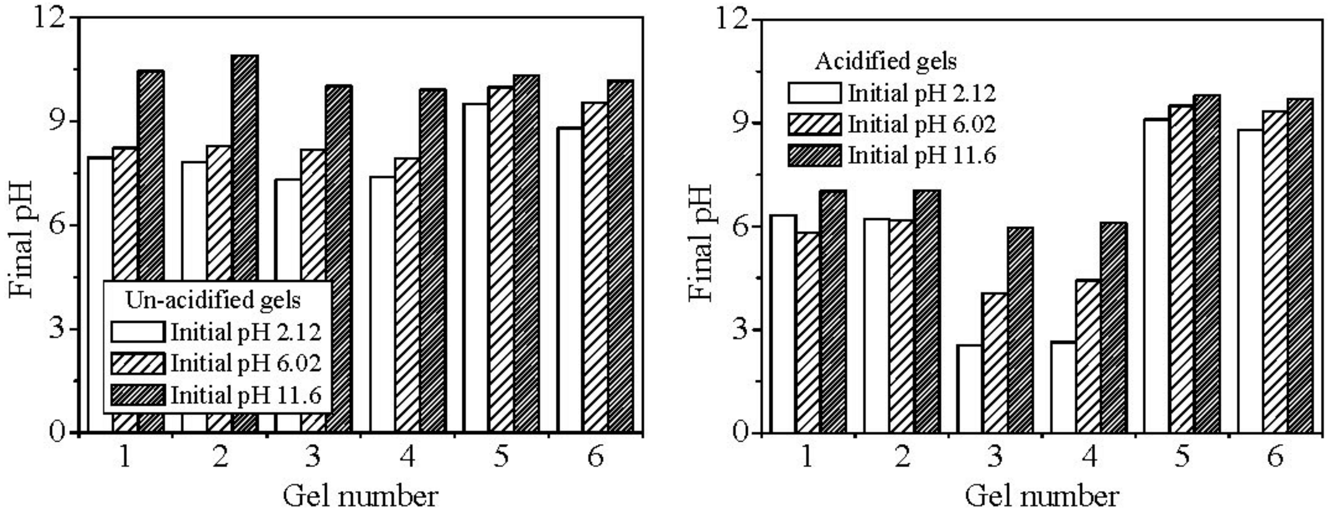


Fig. 8. Solution pH after adsorption for 3 days.

condition of 9.10 <pH <9.96, boron exists mainly as $B(OH)_4^-$. The surface of Gel 5 is positively charged. So there is electrostatic attraction between $B(OH)_4^-$ and the gel surface, promoting the adsorption. Whereas when solution pH is higher than 9.96, the surface of Gel 5 is negatively charged, and boron also exists mainly as $B(OH)_4^-$. In this case, there is electrostatic repulsion between $B(OH)_4^-$ and the gel surface, suppressing the adsorption (Fig. 7).

In this study, during the experiments it was found that all the gels present a "buffer" effect for HCl, because both -NH- and $-NH_2$ groups can neutralize HCl as shown in Fig. 8. For the un-acidified gels, when initial solution pH is 2.12 or 6.02, after adsorption for 3 days, for all the un-acidified gels the solution pH is near the PZC of the corresponding gels. In this case, the gel surfaces are neutrally charged, or slightly positively or negatively charged. Whereas, when initial solution pH is 11.6, for all the un-acidified gels, after adsorption for 3 days, all the solution pH is larger than the PZC of the corresponding gels. The gel surfaces are negatively charged. For the acidified gels, no matter what initial solution pH is, after adsorption for 3 days, all the solution pH is smaller than the PZC of the corresponding gels, so all the gel surfaces are positively charged. In this case, there are electrostatic attractions between $B(OH)_4^-$ and all the gels.

For the removal of boron from aqueous solutions by layered double hydroxides (LDHs), experimental results indicated that anion exchange was an important mechanism for the adsorption [15,21]. Since the chemical nature of anion exchange is electrostatic interaction, $B(OH)_4^-$ is one of the boron species to be adsorbed. Direct experimental evidence for the presence of both trigonal and tetrahedral B on the surface of amorphous Fe oxide was provided by attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectroscopy [18,22]. Ligand exchange with surface hydroxyl groups has been invoked as the mechanism of B adsorption on Al and Fe oxide minerals [22,23] and clay minerals [24]. Ligand exchange is a mechanism whereby anions become specifically adsorbed onto mineral surfaces [16]. These reported results and our experimental results show that boron can be adsorbed in both H_3BO_3 and $B(OH)_4^-$ forms as demonstrated in Fig. 7.

Hydrophobic interactions which represent a tendency of nonpolar groups to associate in aqueous solutions commonly occur in aqueous solutions of low-molecular organic substances as well as of biological macromolecules [25]. In this study, in solutions with a pH value smaller than 9.1, boron exists mainly as non-poplar boric acid, which can presents some hydrophobic interactions with the hydrophobic carbon chains of the gels. So it is expected that hydrophobic attractions should play a role in the adsorption. It was reported that based on relative adsorption capacity values, adsorption of boron onto clays (bentonite and sepiolite) was enhanced by changing the clay surface from hydrophilic to hydrophobic by modifying with nonylammonium chloride [26], confirming the importance of the hydrophobic attractions in boron adsorption.

Below we offer an explanation of the general experimental results. The gels derived from APTES and TEOS (Gels 5 and 6) have the highest adsorption amount among all the gels. Gels 5 and 6 have terminal $-(CH_2)_3NH_2$ groups, which are flexible for the interactions with boric acid or borate. Among all the gels, Gels 5 and 6 have the largest PZC, allowing them adsorb boron at higher solution pH.

The gels doped with mannitol and the gels without doping show similar adsorption amount. That is, the doping of mannitol does not enhance the adsorption. This is not the result we expected. We wanted to enhance the

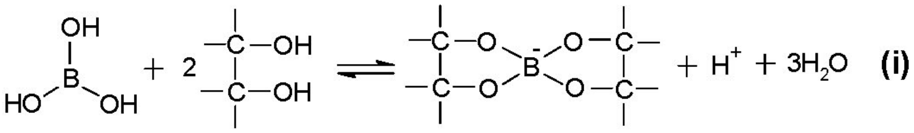


Fig. 9. Schematic diagram for the complexation reaction of boric acid with a polyol such as mannitol.

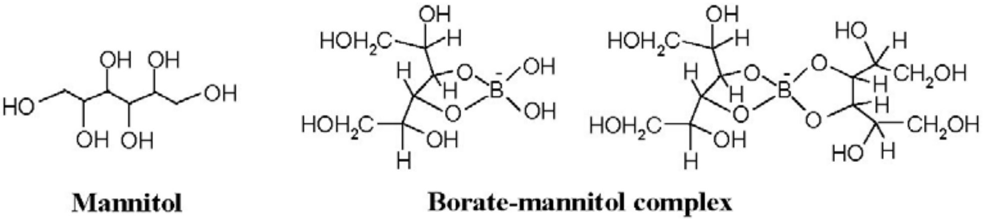


Fig. 10. Molecular structures of mannitol and its complexes with borate.

adsorption by taking advantage of the complexation reaction. Boric acid/borate reacts with carbohydrates or polyols, such as mannitol, generating anionic complexes [27], according to the equation shown in Fig. 9.

With carbohydrates and most polyols possessing 1,2-diol systems, the borate ion forms anionic mono (1:1) and bis (1:2) diol-monoborate species [28]. The stability of the borate complex formed is strongly dependent on the type of diol, namely 1,2 or 1,3-diols. If the diol involves the -OH groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated boron, a strong complex will be formed [11,29].

The molecular structures of mannitol and its complexes with boric acid/borate are shown in Fig. 10. Our experimental results show that the gels doped with mannitol and the gels without doping show a similar adsorption amount, which means that mannitol doped in the gels does not complex with boric acid/borate effectively. This is probably caused by two reasons: (1) during gel preparation, mannitol takes part in the gelation reactions with its -OH groups. (2) The -OH groups of mannitol are "fixed" in the gels. Their orientation does not match the structural parameters required by tetrahedrally coordinated boron. Therefore, there is no effective complexation.

After acidification the adsorption amount of the gels increases. All the gels are basic because of the presence of -NH- or -NH_2 groups. Acidification partly neutralizes the basicity of the gels. Therefore, reduces the solution pH after adsorption. In general, the adsorption is promoted by hydrogen bonding and electrostatic and hydrophobic attractions in solutions of lower pH, whereas it is suppressed by electrostatic repulsions in solutions of higher pH. For the adsorption of boron from aqueous solutions using fly ash and the neutralized red mud, the maximum uptake of boron takes place at pH 2 [6], and in a pH range of 2–7 [30], respectively.

The adsorption decreases with the increase in solution pH. This trend is clearer for the un-acidified gels. For the acidified gels this trend is not so clear because of the acidification of the gels, which can interfere with the solution pH. In solutions with a pH value <PZC, the adsorption is promoted by hydrogen bonding, electrostatic and hydrophobic attractions, whereas in solutions with a pH value >PZC, the adsorption is suppressed by the electrostatic repulsion. Such results are consistent with the adsorption of boron by Al_2O_3 and Fe_2O_3 where the adsorption maximum was found to be between pH 6.0 and 7.0 for Al_2O_3, and between pH 8.0 and 9.0 for Fe_2O_3. At higher pH the adsorption decreased [31].

4. Conclusions

Mannitol doped and un-doped hybrid gels derived from TSPA, or TSPA/TEOS, or APTES/TEOS were prepared. Textual properties and point of zero charges (PZCs) were determined to characterize the gels. The adsorption of boron from its water solutions by the acidified and un-acidified gels in solutions at three deferent initial pH values were compared comprehensively.

The gels derived from APTES and TEOS (Gels 5 and 6) have the smallest surface areas, pore volumes and pore sizes. While the gels derived from TSPA and TEOS (Gels 3 and 4) have the largest surface areas, pore volumes and pore sizes. The gels derived from APTES and TEOS (Gels 5 and 6) have higher PZCs than the other gels.

In general, the gels derived from APTES and TEOS (Gels 5 and 6) have the highest adsorption amount among all the gels, probably because of their terminal -$(CH_2)_3NH_2$ groups and the largest PZC. The terminal -$(CH_2)_3NH_2$ groups are flexible for the interactions with boric acid or borate. Higher PZC allows these gels adsorb boron at higher solution pH.

The gels doped with mannitol and the gels without doping show similar adsorption amount, that is, the addition of mannitol does not promote the adsorption. This is probably caused by two reasons: (1) during gel preparation, mannitol takes part in the gelation reactions with its -OH groups. (2) The -OH groups of mannitol are "fixed" in the gels. Their orientation does not match the structural parameters required by tetrahedrally coordinated boron. Therefore, there is no effective complexation.

After acidification the adsorption amount of the gels increases. In general, the adsorption decreases with the increase in solution pH. All the gels are basic because of the presence of -NH- or $-NH_2$ groups. Acidification partly neutralizes the basicity of the gels. Therefore, reduces the solution pH after adsorption. In general, the adsorption is promoted by hydrogen bonding and electrostatic and hydrophobic attractions in solutions of lower pH, whereas it is suppressed by electrostatic repulsions in solutions of higher pH.

Acknowledgments

This work was financially supported by the Foundation of Knowledge Innovation Program of the Chinese Academy of Sciences (kzcx2-yw-115), Hundred Talent Program of Chinese Academy of Sciences (0660011106), and National Natural Science Foundation of China (40673022).

References

[1] S. Şahin, A mathematical relationship for the explanation of ion exchange for boron adsorption, Desalination, 143 (2002) 35–43.

[2] M.M. García-Soto and E.M. Camacho, Boron removal by processes of chemosorption, Solvent Extr. Ion Exc., 23 (2005) 741–757.

[3] H. Polat, A. Vengosh, I. Pankratov and M. Polat, A new methodology for removal of boron from water by coal and fly ash, Desalination, 164 (2004) 173–188.

[4] Y. Fujita, T. Hata, M. Nakamaru, T. Iyo, T. Yoshino and T. Shimamura, A study of boron adsorption onto activated sludge, Bioresource Technol., 96 (2005) 1350–1356.

[5] İ. Yilmaz, N. Kabay, M. Brjyak, M. Yüksel, J. Wolska and A. Koltuniewicz, A submerged membrane-ion-exchange hybrid process for boron removal, Desalination, 198 (2006) 310–315.

[6] N. Öztürk and D. Kavak, Adsorption of boron from aqueous solutions using fly ash: Batch and column studies, J. Hazard. Mater., B127 (2005) 81–88.

[7] Z. Yazicigil and Y. Oztekin, Boron removal by electrodialysis with anion-exchange membranes, Desalination, 190 (2006) 71–78.

[8] L. Wang, T. Qi and Y. Zhang, Novel organic-inorganic hybrid mesoporous materials for boron adsorption, Colloids Surf. A, 275 (2006) 73–78.

[9] Ö. Kaftan, M. Açıkel, A. E. Eroğlu, T. Shahwan, L. Artok and C. Ni, Synthesis, characterization and application of a novel sorbent, glucamine-modified MCM-41, for the removal/preconcentration of boron from waters, Anal. Chim. Acta, 547 (2005) 31–41.

[10] T. Ishikawa and E. Nakamura, Suppression of boron volatilization from a hydrofluoric acid solution using a boron-mannitol complex, Anal. Chem., 62 (1990) 2612–2616.

[11] N. Geffen, R. Semiat, M.S. Eisen, Y. Balazs, I. Katz and C.G. Dosoretz, Boron removal from water by complexation to polyol compounds, J. Membr. Sci., 286 (2006) 45–51.

[12] S. Mustafa, B. Dilara, K. Nargis, A. Naeem and P. Shahida, Surface properties of the mixed oxides of iron and silica, Colloids Surf. A, 205 (2002) 273–282.

[13] Z. Wu, I.S. Ahn, C.H. Lee, J.H. Kim, Y.G. Shul and K. Lee, Enhancing the organic dye adsorption on porous xerogels, Colloids Surf. A, 240 (2004) 157–164.

[14] Z. Wu, L. You, H. Xiang and Y. Jiang, Comparison of dye adsorption by mesoporous hybrid gels: Understanding the interactions between dyes and gel surfaces, J. Colloid Interf. Sci., 303 (2006) 346–352.

[15] A.N. Ay, B. Zümreoglu-Karan and A. Temel, Boron removal by hydrotalcite-like, carbonate-free Mg-Al-NO_3-LDH and a rationale on the mechanism, Micropor. Mesopor. Mat., 98 (2007) 1–5.

[16] S. Goldberg, Inconsistency in the triple layer model description of ionic strength dependent boron adsorption, J. Colloid Interf. Sci., 285 (2005) 509–517.

[17] M. Meot-Ner (Mautner), The ionic hydrogen bond, Chem. Rev., 105 (2005) 213–284.

[18] D. Peak, G.W. Luther and D.L. Sparks, ATR–FTIR spectroscopic studies of boric acid adsorption on hydrous ferric oxide, Geochim. Cosmochim. Acta, 67 (2003) 2551–2560.

[19] R. Atkin, V.S.J. Craig, E.J. Wanless and S. Biggs, Mechanism of cationic surfactant adsorption at the solid-aqueous interface, Adv. Colloid Interface Sci., 103 (2003) 219–304.

[20] C.J. Brinker and G.W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press, Boston, 1990.

[21] O.P. Ferreira, S.G. Moraes, N.D.L. Cornejo and O.L. Alves, Evaluation of boron removal from water by hydrotalcite-like compounds, Chemosphere, 62 (2006) 80–88.

[22] C. Su and D.L. Suarez, Coordination of adsorbed boron: A FTIR spectroscopic study, Environ. Sci. Technol., 29 (1995) 302–311.

[23] M. McPhail, A.L. Page and F.T. Bingham, Adsorption interactions of monosilicic and boric acid on hydrous oxides of iron and aluminum, Soil Sci. Soc. Am. J., 36 (1972) 510–514.

[24] R. Keren and H. Talpaz, Boron adsorption by montmorillonite as affected by particle size, Soil Sci. Soc. Am. J., 48 (1984) 555–559.

[25] K. Muller-Dethlefs and P. Hobza, Noncovalent interactions: A challenge for experiment and theory, Chem. Rev., 100 (2000) 143–167.

[26] S. Karahan, M. Yurdakoç, Y. Seki and K. Yurdakoç, Removal of boron from aqueous solution by clays and modified clays, J. Colloid Interf. Sci., 293 (2006) 36–42.

[27] R. Belcher, G.W. Tully and G. Svehla, A comparative study of various complexing agents (polyols) used in the titration of boric acid, Anal. Chim. Acta, 50 (1970) 261–267.

[28] S. Chapelle, J.-F. Stella and J.F. Verchere, A ^{11}B and ^{13}C NMR determination of the structures of borate complexes of pentoses and related sugars, Tetrahedron, 44 (1988) 4469–4482.

[29] P.P. Power and W.G. Woods, The chemistry of boron and its speciation in plants, Plant Soil, 193 (1997) 1–13.

[30] Y. Cengeloglu, A. Tor, G. Arslan, M. Ersoz and S. Gezgin, Removal of boron from aqueous solution by using neutralized red mud, J. Hazard. Mater., 142 (2007) 412–417.

[31] M.M.F. García-Soto and E.M.Camacho, Boron removal by means of adsorption with magnesium oxide, Sep. Purif. Technol., 48 (2006) 36–44.