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Boron adsorption by composite magnetic particles

Haining Liu [a,b], Binju Qing [a,b], Xiushen Ye [a,b], Quan Li [a],
Kangtaek Lee [c,*], Zhijian Wu [a,d,**]

[a] Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[c] Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Republic of Korea
[d] The Key Laboratory for Functional Materials of Fujian Higher Education, College of Materials Science and Engineering, Huaqiao University, Quanzhou 362021, China

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ABSTRACT

We prepared Fe_3O_4 particles and two types of composite magnetic particles derived from Fe_3O_4 and bis(trimethoxysilylpropyl)amine (TSPA), and from Fe_3O_4 and a flocculating agent 1010f (a copolymer of acrylamide, sodium acrylate, and [2-(acryloyloxy)ethyl]trimethylammonium chloride). Using these particles, boron adsorption in aqueous solution was comprehensively investigated. The adsorption was found to occur rapidly in the first 2 h and the particle composition did not have a significant effect on the equilibrium time. We found that Fe_3O_4–TSPA particles presented the highest adsorption capacity, whereas the pure Fe_3O_4 particles showed the lowest capacity. For all particles, amount of boron adsorption decreased with the initial pH in the order of $6.0 > 2.2 > 11.7$. In general, the adsorption amount appeared to decrease with the increase in ionic strength. We propose that boron is adsorbed in the form of both H_3BO_3 and $B(OH)_4^-$ through the interactions of hydrogen bonding, electrostatic and hydrophobic attractions. The information gained in this study would be helpful for both understanding the adsorption mechanism and designing low-cost and easily available adsorbents for boron.

1. Introduction

Boron is one of the minor elements dissolved in natural water and 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. Boron is also an important micronutrient for animals and human beings [1], but the range between deficiency and excess is very narrow. The World Health Organization defines boron level of 0.3 mg/l as the non-observed effect level (NOEL) for drinking water. High boron levels in drinking water can be toxic to human beings [2,3].

There is no easy method available for the removal of boron from water and wastewater. One or more methods may be applied according to boron concentration in the 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, and (6) adsorption (including ion exchange adsorption) [4,5]. Among these methods, adsorption is a very useful and economical technique at low boron concentration [4,6]. 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 boric acid and low selectivity of the adsorbents. The most promising boron adsorbents are hydroxyl-containing boron-selective adsorbents, such as Amberlite XE 243 and Amberlite IRA 743 [4], polyol and *N*-methylglucamine grafted mesoporous SBA-15 and MCM-41 [3,7]. Selective adsorption of boron by these adsorbents is caused by complexation. It was reported that coexisting salts did not significantly interfere with the adsorption when boron is adsorbed through complexation.

Although the above-mentioned boron-selective adsorbents are effective for the removal of boron, they are usually difficult to prepare and are also expensive, which limits their application in practical boron removal processes. Magnetic assisted adsorption separation is a promising technology employed in water treatment [8]. Magnetic adsorbents can be used to adsorb contaminants from aqueous effluents. After adsorption the adsorbents can be separated from the medium by a simple magnetic process [9–11]. Magnetic adsorbents are usually prepared by the functionalization of magnetic particles through organic vapor condensation, polymer coating, surfactant adsorption, and direct silanation with silane-coupling agents [12–14]. Functionalized magnetic particles have been used in the fields of magnetic assisted separation [15–18],

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[*] Corresponding author. Tel.: +82 2 2123 2760; fax: +82 2 312 6401.
[**] Corresponding author at: Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 18 Xinning Rd., Xining 810008, China. Tel.: +86 971 6307871; fax: +86 971 6307871.
E-mail addresses: ktlee@yonsei.ac.kr (K. Lee), zjw6512@hotmail.com (Z. Wu).

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magnetic resonance image (MRI) [19,20], magnetic hyperthermia [21,22], drug delivery [18,23], magnetic biosensing [15], immunoassay [23], tissue repair [19], etc.

In this study, we prepared pure Fe_3O_4 particles and two types of composite magnetic particles derived from Fe_3O_4 and bis(trimethoxysilylpropyl)amine (TSPA), and from Fe_3O_4 and a flocculating agent 1010f (copolymer of acrylamide, sodium acrylate, and [2-(acryloyloxy)ethyl]trimethylammonium chloride). All these particles were used to adsorb boron in water, which enables us not only to understand the adsorption mechanisms, but to design inexpensive and easily available adsorbents for boron.

2. Experimental

2.1. Preparation of pure Fe_3O_4 particles and the composite magnetic particles

Pure Fe_3O_4 particles were prepared by co-precipitating Fe(II) and Fe(III) ions in aqueous solution with ammonia according to the method reported in Refs. [24,25]. For the preparation of TSPA-functionalized Fe_3O_4 composite particles, 5.0 g of the wet Fe_3O_4 particles were dispersed in 150 ml water with stirring. 2.5 ml of TSPA (Gelest) was added to this mixture under gentle stirring. The reaction mixture was stirred for 30 min. Then, the TSPA-functionalized particles were recovered from the reaction mixture using a permanent magnet, and then washed with pure water until the pH of the water after washing was around 7. For the preparation of 1010f–Fe_3O_4 composite particles, 5.0 g of the wet Fe_3O_4 particles were dispersed in 150 ml of water with stirring. 2.5 ml of 0.5 g/l 1010f (Zibo Zhisheng Industrial Co., Ltd., PR China) aqueous solution was added to this mixture under gentle stirring until the floccules appeared. Then, the 1010f–Fe_3O_4 composite particles were recovered from the reaction mixture using a permanent magnet.

A SONY DSC-T50 digital camera was used to take photos of the particles in water. Water content of the particles was determined by the weight change before and after drying the particles at 25 °C. Point of zero charge (PZC) of the composite particles was determined by the method described by Mustafa et al. [26] and Wu et al. [24,25]. A PB-10 (Sartorius) pH meter was used to record solution pH.

2.2. Boron adsorption

Wet particles were used in the adsorption experiments. 3.0 g of the wet particles were dispersed in 50 ml solution at the desired initial boron concentration, pH, and ionic strength. All the adsorption experiments were carried out using a SHA-C shaking water bath (Changzhou Guohua Co., Ltd., PR China) with a shaking speed of 80 rpm at 22 °C. Solution pH was adjusted with dilute HCl and NaOH solutions. Ionic strength was controlled with $MgCl_2$ solution. Except for the adsorption kinetic experiments, time for the adsorption experiment was set to 2 d.

After adsorption, the mixture was separated with a permanent magnet and the supernatant was used to determine the concentration of boron by a UV–vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd, China) at 412 nm with azomethine-H as a colorimetric reagent according to the method described in Refs. [27,28]. The amount of boron adsorbed onto the particles (q, in millimoles per kilogram of the dried particles) was calculated by a mass balance relationship:

$$q = \frac{V(C_0 - C)}{W} \quad (1)$$

where C_0 and C are the boron concentrations in the solutions before and after adsorption (mmol/l), V is the volume of the solutions (l), and W is the dry weight of the particles used (kg). The adsorption amount was calculated based on the dry weight of the particles.

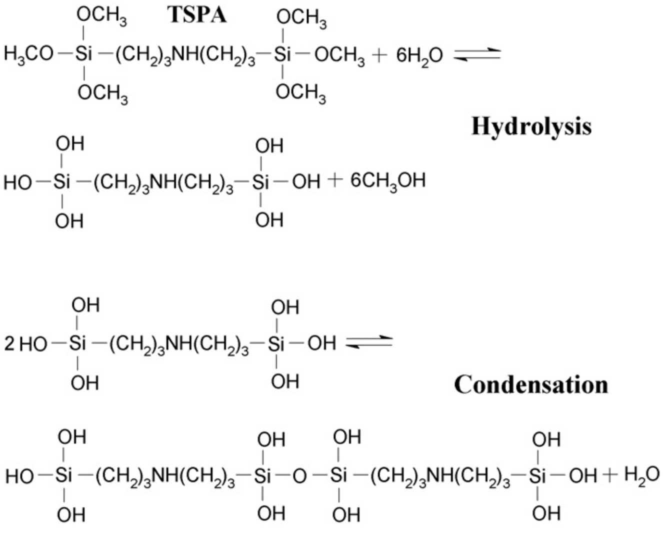


Fig. 1. Hydrolysis and condensation reactions of TSPA.

3. Results and discussion

3.1. Preparation and characterization of the particles

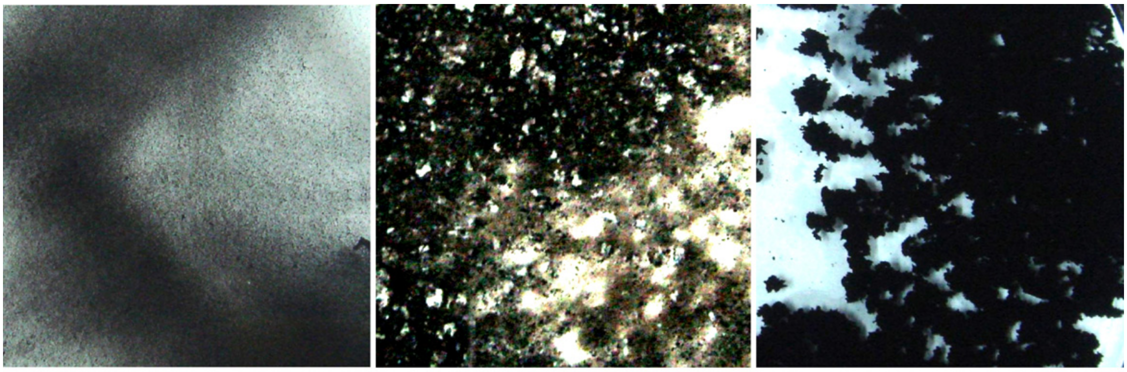
After the addition of TSPA to the suspension of Fe_3O_4 particles, TSPA undergoes hydrolysis and condensation reactions as shown in Fig. 1. Since there are six methoxy groups in TSPA monomer and the hydrolysis and condensation reactions occur simultaneously, there are many kinds of hydrolysis and condensation products. The hydrolysis products of TSPA condense not only with themselves but also with the surface hydroxyl groups of the Fe_3O_4 particles, forming the Fe_3O_4–TSPA composite particles. In the preparation of the Fe_3O_4–1010f composite particles, the 1010f, a flocculating agent, physically associates with Fe_3O_4 particles, forming the floccules of the Fe_3O_4–1010f composite particles. The photographs of the pure Fe_3O_4 and the composite particles are shown in Fig. 2. It is clear from Fig. 2 that both composite particles show the flocculated structure compared to pure Fe_3O_4 particles.

Water content of the Fe_3O_4, Fe_3O_4–TSPA, and Fe_3O_4–1010f particles was found to be 84.4, 92.4, and 86.8%, respectively, which is consistent with the fact that after drying the volume of the particles decreases dramatically.

For the determination of the PZC of the composite particles, the relationship between pH change and the initial pH of the solutions was measured as shown in Fig. 3. The pH change is the difference between the final and initial pH values of the solutions after acid–base equilibrium between the composite particles and the solutions. The initial pH at which the pH change is zero is the PZC of the composite particles, which was found to be 7.5 and 8.5 for the Fe_3O_4–1010f and Fe_3O_4–TSPA composite particles, respectively. The PZC of the pure Fe_3O_4 particles was reported to be 6.5 [29]. The particles functionalized with TSPA have the highest PZC because of the presence of basic –NH– groups in TSPA.

3.2. Adsorption kinetic curves

Fig. 4 shows the amount of adsorbed boron as a function of time. As shown in Fig. 4, adsorption occurs rapidly in the first 2 h, after which the adsorption amount changes slowly. The particle composition does not have a significant effect on the equilibrium time. The variation in the extent of the adsorption may be because initially all



Fe_3O_4 Fe_3O_4-TSPA Fe_3O_4-1010f

Fig. 2. Digital photographs of the particles.

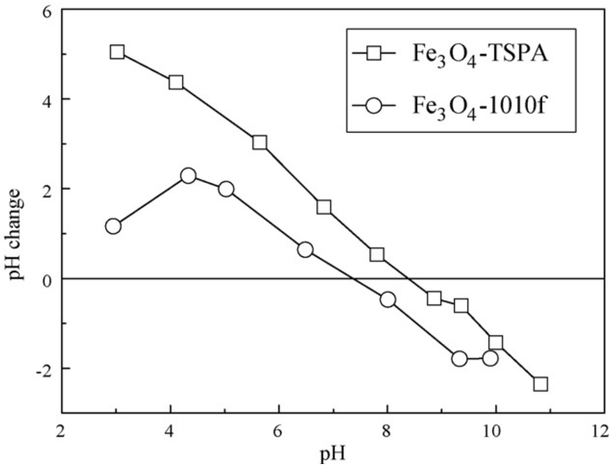


Fig. 3. PZC determination of the composite particles.

sites on the surfaces of the particles were vacant and the boron concentration gradient was relatively high. Consequently, the extent of each ion uptake decreases significantly with the increase of contact time, caused by the decrease in the number of vacant sites on the surface of the particles. According to the adsorption kinetic results, the adsorption time was fixed at 2 d in the following experiments to make sure that the equilibrium was reached.

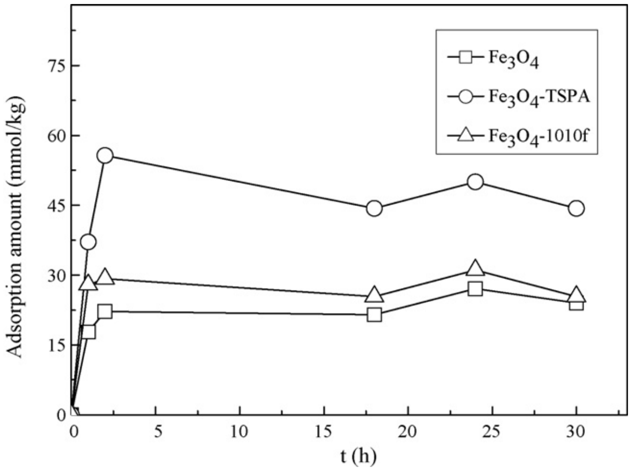


Fig. 4. Adsorption kinetic curves. Initial boron and $MgCl_2$ concentrations were 2.0 and 0.0 M, respectively. Initial solution pH was 6.0.

3.3. *Effect of initial solution pH on the adsorption*

Boron adsorption in aqueous solutions with three different initial pH values is compared in Fig. 5. All three particles showed the same trends with pH change: the amount of boron adsorption decreased with the initial pH in the order of 6.0 > 2.2 > 11.7. At the same solution composition, amount of boron adsorption decreased in the order of Fe_3O_4–TSPA > Fe_3O_4–1010f > pure Fe_3O_4 particles.

3.4. *Effect of ionic strength on the adsorption*

The effect of ionic strength on the adsorption is shown in Fig. 6. In general, the adsorption is found to decrease with the increase in ionic strength. For the adsorption of boron from aqueous solutions using fly ash, adsorption was also found to decrease in the presence of two salts [4]. However, for the adsorption of boron by polymer supported iminodipropylene glycol, the presence of Ca^{2+} or Mg^{2+} ions does not bring any significant interference on boron adsorption [30].

3.5. *Adsorption mechanisms*

It is reasonable to expect that the adsorption difference is caused by the interactions between boric acid/borate and the particles. The effect of ionic strength on adsorption can be used

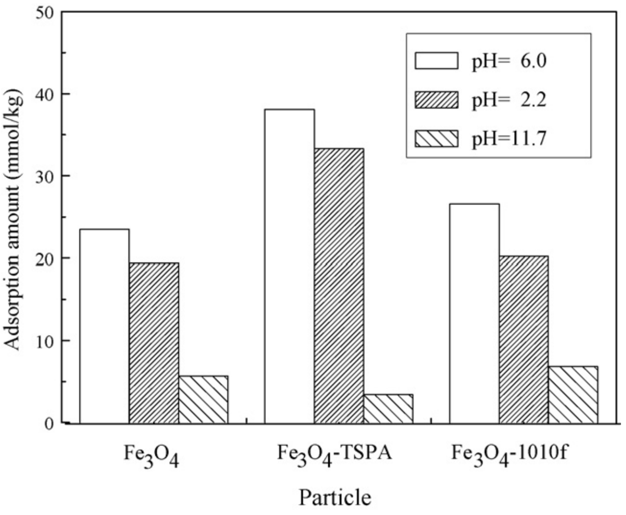


Fig. 5. Effect of initial solution pH on the adsorption. Initial boron and $MgCl_2$ concentrations were 2.0 and 0.0 M, respectively.

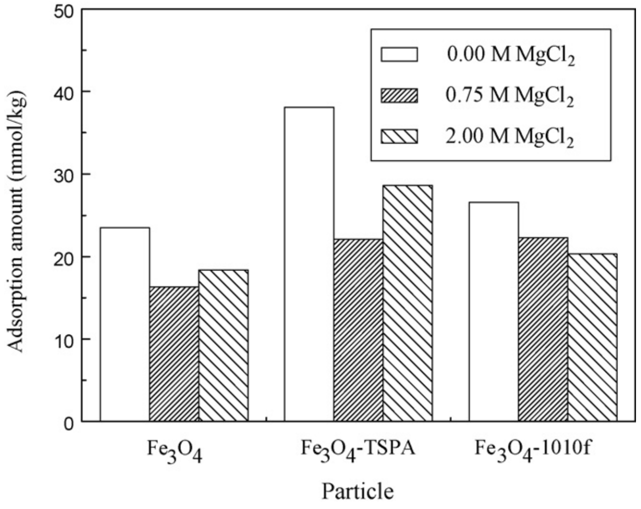


Fig. 6. Effect of solution ionic strength on the adsorption. Initial boron concentration was 2.0 mM. Initial solution pH was 6.0.

to distinguish the inner-sphere surface complexation from the outer-sphere one in adsorption, and hence, to give some useful information about the interactions between the adsorbents and the adsorbates [27]. In inner-sphere surface complexes the adsorbed molecules or ions and the surface functional groups establish covalent bonds. Inner-sphere complexes contain no water molecules between the adsorbed molecules or ions and the surface functional groups, whereas, in outer sphere surface complexes, water molecules remain between the adsorbed molecules or ions and the surface functional groups [31]. In this case, no covalent bonds form between the adsorbents and the adsorbates. Thus, other interactions, such as electrostatic attraction, hydrogen bonding, or hydrophobic attraction are responsible for the adsorption.

Insensitivity to ionic strength has been taken as an indication for inner-sphere surface complexation. Decrease of adsorption with increasing ionic strength has been interpreted as outer-sphere surface complexation [31]. Adsorbed boron can form both inner-sphere and outer-sphere surface complexes with different adsorbents [27,32]. For the adsorption of boron by hydroxyl-containing boron-selective adsorbents, the adsorption is usually independent of solution ionic strength [32], indicating that inner-sphere surface complexes form and boron is covalently bonded onto the adsorbents. In this study, however, adsorption of boron generally decreased with the increase in ionic strength. This means that the interactions between boric acid/borate and the particles are not specific. That is, complexation may not be responsible for adsorption.

In natural aqueous environments where boron content is low, boron is present mainly as boric acid and partially as $B(OH)_4^-$ according to the dissociation reaction ($pK_a = 9.1$). When solution $pH < 9.1$, boron exists mainly as H_3BO_3, whereas, when solution $pH > 9.1$, boron exists mainly as $B(OH)_4^-$. 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 mM), but at higher concentrations many poly-borate polymers are known to form [33,34]. In this study, initial boric acid concentration in all the solutions is lower than 5 mM, so boron exists mainly as $B(OH)_3$ and $B(OH)_4^-$.

For pure Fe_3O_4 and the composite particles, at solution pH < PZC, the particle surface is positively charged, whereas at solution pH > PZC, the particle surface is negatively charged. Therefore there should be different electrostatic interactions between borate and the particles under different adsorption conditions. The experimental results show that boron adsorption in the solution at pH 11.7 is much lower than that at pH 2.2 or 6.0 because of the electrostatic repulsion between borate and the particle surface (Fig. 5), confirming the importance of the electrostatic interactions in boron adsorption.

Fig. 6 demonstrates that adsorption generally decreases with the increase in ionic strength. When $MgCl_2$ concentration changes from 0 to 2.0 M, however, the adsorption amount does not decrease to a very low value, indicating that electrostatic interaction is only partly responsible for the adsorption.

From the physicochemical natures of boric acid, borate, and the particle surfaces, it could be deduced that hydrogen bonding and hydrophobic interactions may play roles in the adsorption. All the particles have the suitable functional groups and atoms on their surfaces for the formation of hydrogen bonds with boric acid or borate (including ionic hydrogen bonds [35]), which can promote the adsorption.

Hydrophobic interactions represent a tendency of nonpolar groups to associate in aqueous solutions. They commonly occur in aqueous solutions of low-molecular weight organic substances as well as of biological macromolecules [36]. In this study, in solutions with a pH value lower than 9.1, boron exists mainly as non-poplar boric acid which can present some hydrophobic attractions with the hydrophobic carbon chains of the composite particles. So it is expected that hydrophobic attractions should play a role in boric acid adsorption by the composite particles. It was reported

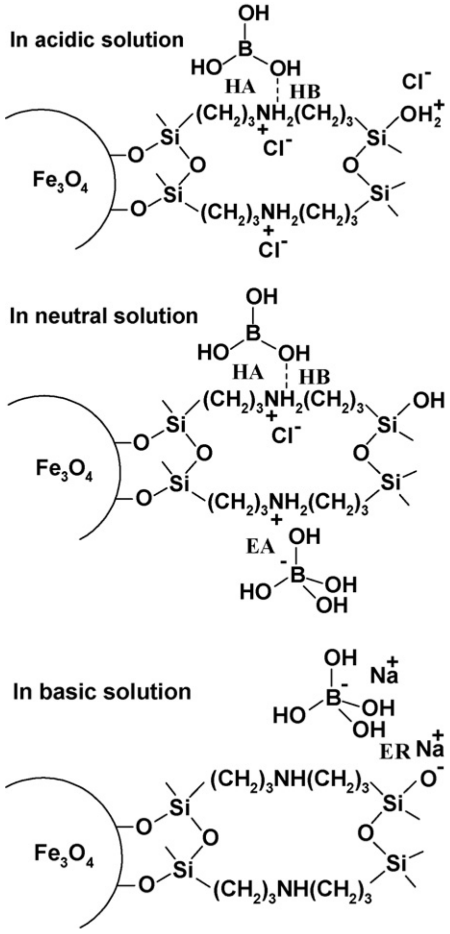


Fig. 7. Schematic diagrams for the interaction between boric acid/borate and the Fe_3O_4–TSPA composite particles. HA, hydrophobic attraction; HB, hydrogen bonding; EA, electrostatic attraction; ER, electrostatic repulsion.

that based on the relative adsorption capacity values, adsorption of boron onto clays (bentonite and sepiolite) was enhanced by changing the clay surface from hydrophilic to hydrophobic with nonylammonium chloride [37], confirming the importance of the hydrophobic attractions.

Based on the above analysis, the interactions between boric acid/borate and the Fe_3O_4–TSPA composite particles are schematically demonstrated in Fig. 7. There are three types of interactions: (1) electrostatic interaction; (2) hydrogen bonding; (3) hydrophobic interaction.

In neutral solution the adsorption of boron is enhanced by hydrogen bonding, electrostatic and hydrophobic attractions (hydrophobic attraction only for the composite particles). In basic solution, however, the adsorption is suppressed by electrostatic repulsion. In acidic solution the adsorption amount of boron is smaller than that in neutral solution probably because of the lack of electrostatic attraction.

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 [28,38]. 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 [33,39]. Ligand exchange with surface hydroxyl groups has been invoked as the mechanism of boron adsorption on Al and Fe oxide minerals [39] and clay minerals. 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.

4. Conclusion

Pure Fe_3O_4 particles and two kinds of composite Fe_3O_4 particles were used to adsorb boron from aqueous solution. Boron adsorption occurred rapidly in the first 2 h and the effect of particle composition was negligible for the equilibrium time. We found that boron adsorption decreased with the initial pH in the order of $6.0 > 2.2 > 11.7$ for all particles, and that at the same solution composition it decreased in the order of Fe_3O_4–TSPA > Fe_3O_4–1010f > Fe_3O_4 particles. In general, the adsorption amount decreased with the increase in ionic strength. It was suggested that boron is adsorbed in both forms of H_3BO_3 and $B(OH)_4^-$. Thus, for all the particles the amount of boron adsorption is highest in neutral solution probably due to the hydrogen bonding, electrostatic and hydrophobic attractions, but lowest in basic solution because of the electrostatic repulsion.

Acknowledgments

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References

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

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

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

[4] N. Öztürk, D. Kavak, Adsorption of boron from aqueous solutions using fly ash: batch and column studies, J. Hazard. Mater. 127 (2005) 81–88.

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

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

[7] O. Kaftan, M. Acikel, A.E. Eroglu, T. Shahwan, L. Artok, 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.

[8] X. Peng, Z. Luan, H. Zhang, Montmorillonite–Cu(II)/Fe(III) oxides magnetic material as adsorbent for removal of humic acid and its thermal regeneration, Chemosphere 63 (2006) 300–306.

[9] L.C.A. Oliveira, D.I. Petkowicz, A. Smaniotto, S.B.C. Pergher, Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water, Water Res. 38 (2004) 3699–3704.

[10] L.C.R. Machado, F.W.J. Lima, R. Paniago, J.D. Ardisson, K. Sapag, R.M. Lago, Polymer coated vermiculite–iron composites: novel floatable magnetic adsorbents for water spilled contaminants, Appl. Clay Sci. 31 (2006) 207–215.

[11] L.C.A. Oliveira, R.V.R.A. Rios, J.D. Fabris, V. Garg, K. Sapag, R.M. Lago, Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water, Carbon 40 (2002) 2177–2183.

[12] M. Takafuji, S. Ide, H. Ihara, Z. Xu, Preparation of poly(1-vinylimidazole)-grafted magnetic nanoparticles and their application for removal of metal ions, Chem. Mater. 16 (2004) 1977–1983.

[13] Z. Wu, J. Wu, H. Xiang, M.-S. Chun, K. Lee, Organosilane-functionalized Fe_3O_4 composite particles as effective magnetic assisted adsorbents, Colloids Surf. A 279 (2006) 167–174.

[14] W. Wu, Q. He, C. Jiang, Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies, Nanoscale Res. Lett. 3 (2008) 397–415.

[15] S.A. Corr, Y.P. Rakovich, Y.K. Gun'ko, Multifunctional magnetic-fluorescent nanocomposites for biomedical applications, Nanoscale Res. Lett. 3 (2008) 87–104.

[16] J. Wang, J. You, Z. Li, P. Yang, X. Jing, M. Zhang, Preparation and characteraction of new magnetic Co–Al HTLc/Fe_3O_4 solid base, Nanoscale Res. Lett. 3 (2008) 338–342.

[17] K. Babu, R. Dhamodharan, Grafting of poly(methyl methacrylate) brushes from magnetite nanoparticles using a phosphonic acid based initiator by ambient temperature atom transfer radical polymerization (ATATRP), Nanoscale Res. Lett. 3 (2008) 109–117.

[18] S. Wang, Y. Zhou, W. Guan, B. Ding, Preparation and characterization of stimuli-responsive magnetic nanoparticles, Nanoscale Res. Lett. 3 (2008) 289–294.

[19] Y. Ge, Y. Zhang, S. He, F. Nie, G. Teng, N. Gu, Fluorescence modified chitosan-coated magnetic nanoparticles for high-efficient cellular imaging, Nanoscale Res. Lett. 4 (2009) 287–295.

[20] K.T. Thurn, E.M.B. Brown, A. Wu, S. Vogt, B. Lai, J. Maser, T. Paunesku, G.E. Woloschak, Nanoparticles for applications in cellular imaging, Nanoscale Res. Lett. 2 (2007) 430–441.

[21] Z.P. Chen, R.Z. Xu, Y. Zhang, N. Gu, Effects of proteins from culture medium on surface property of silanes-functionalized magnetic nanoparticles, Nanoscale Res. Lett. 4 (2009) 204–209.

[22] S. Zhang, X. Chen, C. Gu, Y. Zhang, J. Xu, Z. Bian, D. Yang, N. Gu, The effect of iron oxide magnetic nanoparticles on smooth muscle cells, Nanoscale Res. Lett. 4 (2009) 70–77.

[23] D.K. Bora, P. Deb, Fatty acid binding domain mediated conjugation of ultrafine magnetic nanoparticles with albumin protein, Nanoscale Res. Lett. 4 (2009) 138–143.

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

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

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

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

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

[29] X. Lai, J. Bi, D. Gao, J. Wang, Preparation of Fe_3O_4 magnetic fluid, J. Magn. Mater. Devices 31 (2000) 15–18.

[30] B.F. Senkal, N. Bicak, Polymer supported iminodipropylene glycol functions for removal of boron, React. Funct. Polym. 55 (2003) 27–33.

[31] J. Lützenkirchen, Ionic strength effects on cation sorption to oxides: macroscopic observations and their significance in microscopic interpretation, J. Colloids Interf. Sci. 195 (1997) 149–155.

[32] C. Jacob, Seawater desalination: boron removal by ion exchange technology, Desalination 205 (2007) 47–52.

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

[34] G. Yuan, D. Xue, Crystal chemistry of borates: the classification and algebraic description by topological type of fundamental building blocks, Acta Crystallogr. B 63 (2007) 353–362.
[35] M. Meot-Ner (Mautner), The ionic hydrogen bond, Chem. Rev. 105 (2005) 213–284.
[36] K. Muller-Dethlefs, P. Hobza, Noncovalent interactions: a challenge for experiment and theory, Chem. Rev. 100 (2000) 143–167.
[37] S. Karahan, M. Yurdakoc, Y. Seki, K. Yurdakoc, Removal of boron from aqueous solution by clays and modified clays, J. Colloids Interf. Sci. 293 (2006) 36–42.
[38] O.P. Ferreira, S.G. de Moraes, N. Duran, L. Cornejo, O.L. Alves, Evaluation of boron removal from water by hydrotalcite-like compounds, Chemosphere 62 (2006) 80–88.
[39] C. Su, D.L. Suarez, Coordination of adsorbed boron: a FTIR spectroscopic study, Environ. Sci. Technol. 29 (1995) 302–311.