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Effect of pH, ionic strength, foreign ions, humic acid and temperature on Zn(II) sorption onto γ-Al_2O_3

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Abstract−The sorption of Zn(II) on γ-alumina was investigated as a function of contact time, pH, ionic strength, foreign ions, solid amount, humic acid (HA) and temperature by using batch technique. The results indicated that the sorption of Zn(II) onto γ-alumina was strongly dependent on pH and ionic strength. The sorption of Zn(II) increased slowly with increasing pH at pH 2-5, then increased sharply with pH increasing from 5 to 8.5, and at last maintained a maximum value at pH>8.5. A positive effect of HA on Zn(II) sorption was found at pH<7, whereas a negative effect was observed at pH>7. The thermodynamic data (ΔG^0, ΔS^0, ΔH^0) were calculated from the temperature-dependent sorption isotherms, and the results suggested that the sorption of Zn(II) on γ-alumina was endothermic and spontaneous. The sorption results revealed that the γ-alumina can be as a cost-effective sorbent for pre-concentration of Zn(II) from large volumes of aqueous solutions in environmental pollution cleanup.

Keywords: Zn(II), γ-Alumina, Sorption, pH, Humic Acid, Thermodynamic Data

INTRODUCTION

The removal of toxic heavy metal ions and radionuclides from aqueous streams is of great concern due to the potential threat to human health, living resources and ecological systems. Zn(II) is one of the most serious contaminants in the wastewaters continuously discharged from industrial production processes such as electroplating, alloy processing, battery manufacturing, plating, ammunition, oil-based paint pigments and pesticides [1-6]. The concentration of Zn(II) from polluted aqueous streams can continuously accumulate in soil and water environment, which can lead to harmful effects on aquatic creatures, plants and human beings through the transmission of food chain. Human intake of too much Zn(II) may cause paralysis, respiratory incapacitation, mutagenesis, carcinogenesis and decrease in oxygen uptake efficiency [7]. For the sake of ecosystem stability and human health, it is necessary to evaluate the isolation, migration, bioavailability and ecotoxicity of Zn(II) in environmental mediums [8]. Currently, various methods have been introduced for the removal of metal ions such as oxidation/reduction, precipitation, co-precipitation, oxidation, membrane filtration, ion-exchange and sorption. Each method has its advantages and disadvantages. But sorption offers the most effective method of producing the highest quality treated water [9].

So far, various inorganic oxides such as TiO_2 [10-12], ZnO [13], SiO_2 [14], iron oxide [15] and Al_2O_3 [16] have been found to be effective materials for the disposal of wastewater and retention of nuclear waste due to the property of crystal defect, which can lead to certain bonding capabilities inside and outside of the crystal [17, 18]. Alumina is a kind of ubiquitous oxide mineral in the geological environment that has been widely used as a sorbent in the sorption of metal ions. Al is present in both the tetrahedral as well as octahedral sites of the close-packed arrangement of oxygen atoms in alumina [14]. The aluminol site (≡AlOH) in alumina is attached either to an octahedron or a tetrahedron, which leads to a significant change in the surface reactivity of alumina towards the sorption of metal ions. The sorption of heavy metal ions and radionuclides onto γ-alumina has been reported in recent years, and many sorption processes have been postulated, such as ion exchange, precipitation, diffusion into particle micropores, inner-sphere and outer-sphere surface complexation [19-22]. Compared to the other metal oxides, we selected γ-alumina as a promising sorbent for the removal of Zn(II) from wastewater in this study because of its high specific surface area, high cation exchange capacity (CEC), low cost and easy regeneration [23,24]. What's more, to the best of our knowledge, the study of Zn(II) on γ-Al_2O_3, especially the thermodynamic data of Zn(II) sorption on γ-Al_2O_3 and the influence of humic acid on Zn(II) sorption is still not available. Hence, it is of significance to investigate the sequestration mechanisms of radionuclides and heavy metal ions at γ-Al_2O_3/water interfaces.

Humic acid (HA) is considered as a natural organic matter present in surface soil and waters. It is a chemically heterogeneous compound with various functional groups with different configurations and proportions. HA contains carboxyl (-COOH), hydroxyl (-OH), amine ($-NH_2$), and phenol (Ar-OH) functional groups, and has negative charges in weakly acidic-to-basic media due to deprotonation reactions [25]. The acidity constants pKa of HL_1 (carboxyl groups), HL_2 (hydroxyl groups) and HL_3 (phenol groups) are optimized to be 5.23, 7.24 and 9.57, respectively [26].

The nature of organic functional groups of HA is very important in the process of determining the stability of metal ion complexes. HA may enhance or reduce metal ion sorption, depending on the relative stabilities of metal–HA binary and metal-HA-γ-Al_2O_3 sur-

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face ternary complexes as a function of pH [19]. Among the vast literature on HA, only a few have dealt with HA sorption onto γ-Al_2O_3 and metal-HA-γ-Al_2O_3 ternary surface complexation. Therefore, it is necessary to study the sorption of radionuclides on HA-mineral hybrids for the safety assessment of nuclear waste repository.

We investigated the sorption of Zn(II) onto γ-alumina by varying experimental conditions: contact time, solid amount, pH, ionic strength, foreign ions, the presence and absence of humic acid and temperature. The kinetic sorption of Zn(II) onto γ-alumina was simulated by pseudo-second-order model, intraparticle diffusion model and liquid film diffusion model, respectively. The mechanisms of the kinetics sorption are discussed in detail according to the results. The Langmuir and Freundlich isotherm models were adopted to simulate the sorption isotherms at three different temperatures, and the sorption mechanisms of Zn(II) onto γ-alumina was discussed.

EXPERIMENTAL SECTION

1. Chemicals

A stock solution of Zn(II) (120 mg/L) was prepared in Milli-Q water with $ZnCl_2$. It was then diluted to prepare solutions of the desired concentrations. Radioactive Zn-65 was used as radiotracer. The γ-alumina sample was first washed with 0.1 M HNO_3, then with 0.1 M NaOH up to pH 10 and finally rinsed with Milli-Q water until the conductivity of the washing solution reached that of water, and the point of zero charge (pH_{pzc}) of the sample was measured to be 9.2±0.1 [16]. Humic acid was extracted from the soil samples of Hua-jia county of Gansu province (China) near 35 °N and 105 °E, which is very near to the site of nuclear weapon tests [27,28].

All other chemicals used in the experiments were purchased as analytical purity. Milli-Q water was used in all experiments.

2. Experimental Procedure

All sorption experiments were carried out by using batch technique in 10 mL sealed polyethylene centrifuge tubes under ambient conditions. The stock suspension of γ-alumina and $NaClO_4$ was pre-equilibrated for 24 h and then the Zn(II) stock solution was added to achieve the desired concentrations of different components. In addition, negligible volumes of 0.1 or 0.01 M $HClO_4$ or NaOH were added to the prepared suspensions in order to adjust the initial pH to desired values before the sorption experiments. The suspensions were gently oscillated for 24 h to achieve sorption equilibrium, and then the solid was separated from liquid phases by centrifugation at 8,000 rpm for 10 min. The concentration of Zn(II) was analyzed by liquid scintillation counting using a Packard 3100 TR/AB Liquid Scintillation Analyzer (Perkin Elmer). The scintillation cocktail was ULTIMA GOLD AB™ (Packard). The amount of Zn(II) adsorbed onto γ-alumina was calculated from the difference between the initial concentration (C_0) and the equilibrium concentration (C_e). All experimental data were the averages of duplicate determinations. The relative errors of the data were about 5%.

RESULTS AND DISCUSSION

1. Kinetic Sorption

The sorption of Zn(II) on γ-alumina as a function of contact time is shown in Fig. 1(a). As can be seen, the removal of Zn(II) increased fast in the first 3 h, and then increased slowly until the sorption process maintained a high level with increasing time. The result indicates that the sorption of Zn(II) onto γ-alumina mainly contributes to the chemical sorption rather than physical sorption [29,30]. The high initial uptake rate may be attributed to the rapid diffusion of Zn(II) from the solution to the external surfaces of γ-alumina. As the sites were filled up gradually, the uptake became slow and the mechanism of kinetics became more dependent on the rate at which the sequestrated Zn(II) was transported from the bulk phase to the actual binding sites (i.e., inner-sphere pores of γ-alumina) [31,32]. The pseudo-second-order model, intraparticle diffusion model and liquid film diffusion model were applied to simulate the kinetic sorption data. The pseudo-second-order model can be expressed by the following equation [33]:

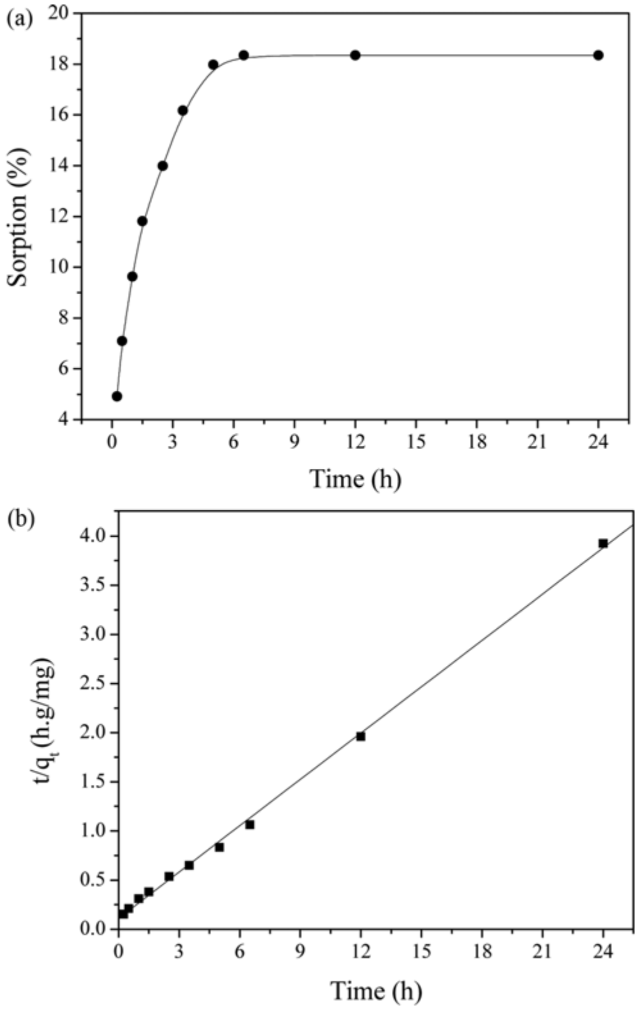

Fig. 1. Effect of contact time on the sorption of Zn(II) onto γ-alumina. (a) Plot of q_t vs. t for Zn(II) sorption. (B) Plot of t/q_t vs. t for the pseudo-second-order model. T=293.15 K, pH=6.0±0.1, $C_{(Zn)initial}$=1.527×10^{-4} mol/L, m/V=0.3 g/L, I=0.01 M $NaClO_4$.

$$\frac{t}{q_t}=\frac{1}{2K'q_e^2}+\frac{1}{q_e}t \qquad (1)$$

where q_t (mg/g) is the amount of Zn(II) adsorbed on γ-alumina at time t (h), q_e (mg/g) is the amount of Zn(II) adsorbed on γ-alumina at equilibrium and K′ (g/(mg·h)) is the rate constant of pseudo-second-order kinetics. The linear plot of t/q_t versus t is shown in Fig. 1(b). The K' and q_e values calculated from the slope and intercept of the straight line are 0.116 g/(mg·h) and 6.25 mg/g, respectively. The correlation factor (R^2) of the pseudo-second-order rate equation for the linear plot is 0.999, indicating that the kinetic sorption process of Zn(II) on γ-alumina can be described by the pseudo-second-order rate equation well.

The sorption process of Zn(II) onto γ-alumina may comply with the following steps. The first step can be attributed to the diffusion of solute molecules from the aqueous to the external surface of the absorbent. The second step is particle diffusion, which describes the diffusion of absorbent surface to the intraparticle active sites, and the third step is attributed to the very low sorbate concentration left and the retention on the active sites via sorption, complexation or intraparticle precipitation processes. The former two steps may be the slowest steps to be regarded as the rate-limiting step, while the last step is so rapid that it can be considered negligible. The first and second steps can be modeled by the liquid film diffusion model and intraparticle diffusion model, respectively [34,35]. The intraparticle diffusion model is expressed as [36]:

$$q_t=K_i(t)^{0.5} \qquad (2)$$

where K_i (mol/g·$h^{1/2}$) is the diffusion rate constant. The plot of q_t vs. $t^{1/2}$ is shown in Fig. 2(a). If the linear plot passes through the origin, the kinetics of the adsorption process may be controlled by intraparticle diffusion. The constant K_i=2.091 h^{-1} is obtained from the slope of the straight line with a correlation coefficient (R^2) of 0.997, which indicates that intraparticle diffusion has important influence on the sorption process. However, the slow rate-limiting step may not be the main mechanism due to the nonzero intercept of the straight line [37].

The liquid film diffusion model is governed by the following equation [38]:

$$\ln(1-F)=-K_{fd}t \qquad (3)$$

where $F=q_t/q_e$, which is the function attainment of equilibrium and K_{fd} (h^{-1}) is the sorption rate constant. The plot of $-\ln(1-F)$ vs. t is given in Fig. 2(b). The constant K_{fd}=0.179 h^{-1} is calculated from the slope of the straight line with a high correlation coefficient (R^2) of 0.970, and the obtained intercept is 0.302. The values indicate that the film diffusion process may not be the singular rate-limiting step in the overall adsorption. Apparently, the correlation coefficient of the intraparticle diffusion model is higher than that of the liquid film diffusion model, which means that Zn(II) adsorption onto γ-alumina is mainly dominated by intraparticle diffusion process [31]. Otherwise, the film diffusion process may play a significant role in the sorption of Zn(II) onto γ-alumina due to its high coefficient.

2. Effect of Solid Amount

The dependence of Zn(II) sorption onto γ-alumina as a function of solid amount was studied with initial Zn(II) concentration of 1.527 $\times10^{-4}$ mol/L at T=298.15 K and pH=6.0±0.1. As can be seen from Fig. 3, the sorption of Zn(II) increases rapidly as the sorbent load increases. With increasing sorbent load, the available sites at γ-alumina surfaces for binding increase, which enhances the formation of complexes with Zn(II) on γ-alumina surfaces.

One can also see from Fig. 3 that the K_d value of Zn(II) sorption decreases gradually with the increase of γ-alumina content. This

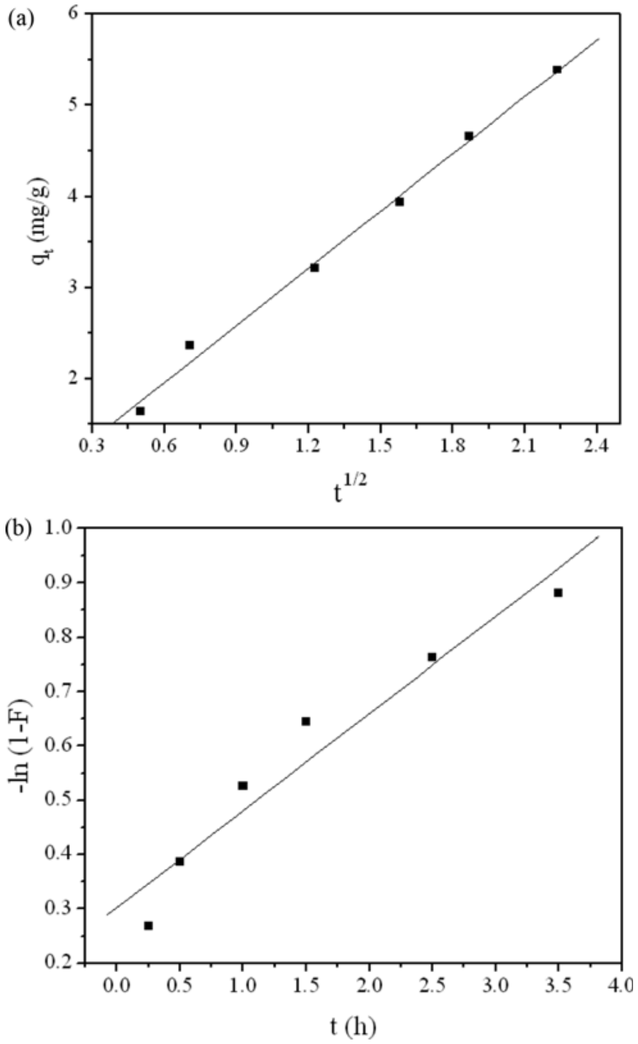

Fig. 2. (a) Sorption of Zn(II) onto γ-alumina as a function of square root of time for the intraparticle diffusion model. (b) Plot of $-\ln(1-F)$ vs. t for Zn(II) sorption onto γ-alumina by the liquid film diffusion model.

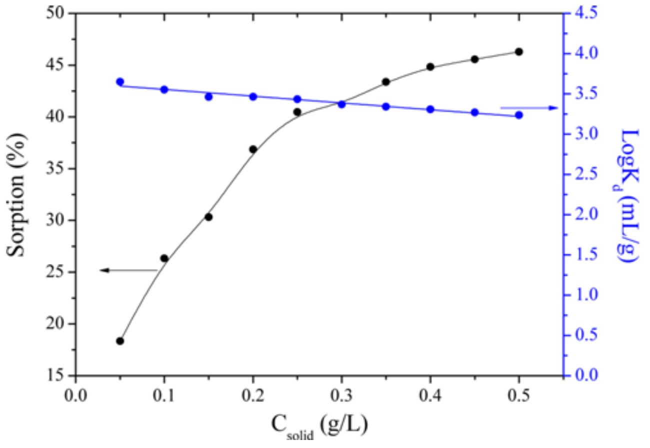

Fig. 3. Sorption of Zn(II) on γ-alumina as a function of clay amount. T=298.15 K, pH=6.0±0.1, $C_{(Zn)initial}$=1.527×10^{-4} mol/L, I=0.01 M $NaClO_4$.

phenomenon may be attributed to the competition of particles among the functional groups at the surface of γ-alumina, which may be termed as a kind of sorbent concentration effect [39]. Such competition reduces the unsaturation of the sorption sites and leads to less sorption at higher solid amount. In addition, particles may aggregate at higher sorbent amount due to the collision between solid particles, causing an increase in diffusional path length and a decrease in the total surface area, both of which can lead to the decrease in the sorption capacity of γ-alumina towards Zn(II) [40,41]. For this reason, appropriate sorbent amount should be chosen according to the concentrations and required removal efficiency of heavy metal ions. The distribution coefficient, K_d, values as a function of the solid amount and sorption percentage were derived from the following equations:

$$K_d=\frac{C_0-C_e}{C_e}\times\frac{V}{m} \quad (4)$$

$$\text{Sorption}\%=\frac{C_0-C_e}{C_e}\times 100\% \quad (5)$$

where m (g) is the mass of γ-alumina and V (mL) is the volume of the suspension.

3. Effect of pH and Ionic Strength

Adsorption of Zn(II) onto γ-alumina is studied over the pH range of 2-11 in 0.001 M, 0.01 M and 0.1 M $NaClO_4$ solutions, respectively. One can see from Fig. 4 that the sorption of Zn(II) is obviously affected by pH values. The sorption of Zn(II) increases gradually with increasing pH at pH 2-5, then the sorption increases sharply with pH increasing in the region of 5-8.5, and at last the sorption gets to a maximum value (97%) at pH>8.5 and maintains the high value with increasing pH values. The effect of pH on Zn(II) removal to γ-alumina may be attributed to the surface properties of γ-alumina in terms of dissociation of functional groups and surface charge. At low pH, the surface charge of γ-alumina becomes positive due to the protonation reaction. Electrostatic repulsion occurs between Zn(II) and the positive charge of γ-alumina, which leads to the low adsorption of Zn(II). However at high pH, the deprotonation process changes the surface charge of γ-alumina from positive to negative and the electrostatic repulsion decreases with raising pH, which increases the sorption of Zn(II) onto γ-alumina [42-44]. Otherwise, the exact speciation of Zn(II) may also have a significant effect on the removal efficiency of γ-alumina towards Zn(II). The fact that Zn(II) in aqueous solution can form different species whose presence depends on the solution pH is well documented [45]. The speciation diagram for Zn(II) can be obtained using the following reactions and equilibrium constants ($LogK_1=-8.96$, $LogK_2=-7.94$, $LogK_3=-11.50$, $LogK_4=-12.80$, $K_n=[Zn(OH)_n^{2-n}]\cdot[H^+]^n/[Zn^{2+}]$) [46]. The results demonstrate that Zn(II) present in the forms of Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ at various pH values (Fig. 5). The speciation diagram for Zn(II) is similar to several companion papers [47]. Accordingly, at pH<8.5, the predominant zinc species is Zn^{2+} and the sorption of Zn(II) is ascribed to ion exchange between Zn^{2+} and H^+/Na^+ on the surface sites, Whereas, the predominant species at pH>8.5 are $Zn(OH)^+$ and $Zn(OH)_2$, thus the removal of Zn^{2+} is possibly accomplished by sorption of $Zn(OH)_2$ and simultaneous precipitation of $Zn(OH)_2$.

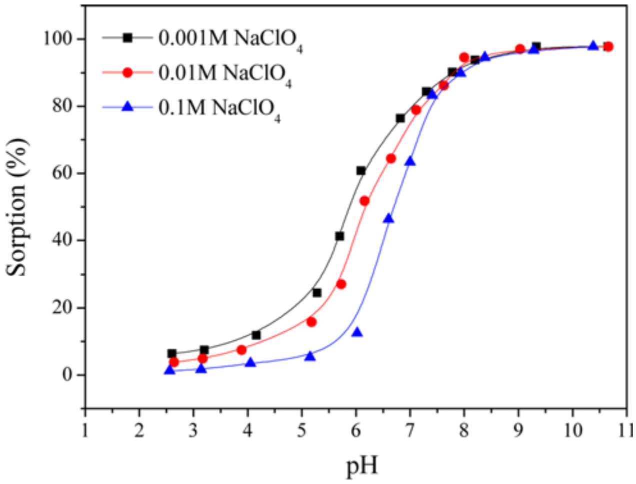

Fig. 4. Effect of ionic strength and pH on Zn(II) sorption onto γ-alumina. T=293.15 K, m/V=0.3 g/L, $C_{[Zn(II)]initial}=1.527\times10^{-4}$ mol/L.

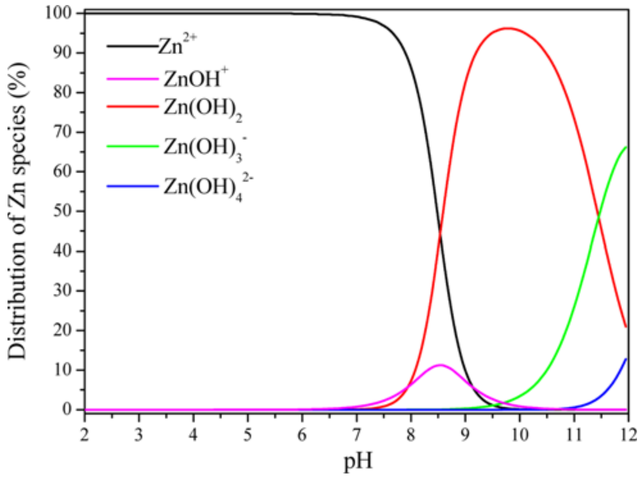

Fig. 5. Distribution of Zn(II) species as a function of pH.

Fig. 4 also shows the effect of ionic strength on Zn(II) sorption as a function of pH values. One can see that sorption of γ-alumina towards Zn(II) is strongly affected by ionic strength at pH<7, whereas the removal is independent of ionic strength at pH>7. The ionic strength may have an effect on the double electrode layer thickness and interface potential, and thus can affect the binding of the adsorbed species. Outer-sphere surface complexes are expected to be more sensitive to changing ionic strength than inner-sphere surface complexes as the background electrolyte ions are placed in the same plane for outer-sphere surface complexes [48,49]. The theory mentioned above suggests that Zn(II) sorption onto γ-alumina at pH<7 is mainly due to cation exchange or outer-sphere surface complexation, whereas the sorption of Zn(II) at pH>7 is dominated by inner-sphere surface complexation [50,51].

To illustrate the variation and relationship of pH, C_e (mol/L, the concentration of Zn(II) remained in solution), and C_s (mol/g, the concentration of Zn(II) adsorbed on solid phase), the experimental data of Zn(II) sorption in 0.1, 0.01 and 0.001 M $NaClO_4$ solutions are plotted as three-dimensional plots of C_s, C_e and pH (Fig. 6). On the pH-C_s plane, the concentration of Zn(II) adsorbed on solid phase is strongly dependent on pH values, which is quite similar to the

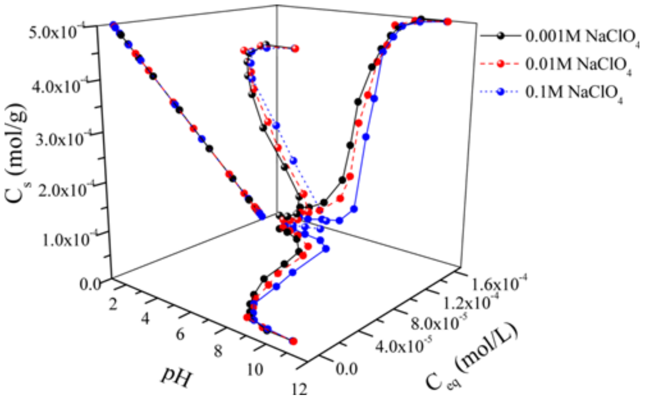

Fig. 6. 3-D plots of Zn(II) sorption onto γ-alumina as the function of pH and ionic strength. T=293.15 K, m/V=0.3 g/L, $C_{[Zn(II)]initial}$ =1.527×10^{-4} mol/L.

results shown in Fig. 4. The concentration of Zn(II) remained in solution decreases with increasing pH at pH<8.5, and then is maintained a low level at pH>8.5 on the pH-C_e plane, which is just the inverted image of the projection on the pH-C_s plane. On the C_e-C_s plane, all experimental data in the projection lie in a straight line due to the initial concentration of Zn(II) and the ratio of solid-liquid are the same, respectively, for all experimental data. The following equation can describe the relationship of C_e-C_s [52]:

$$VC_0=mC_s+VC_e \tag{6}$$

Eq. (6) can be rearranged as:

$$C_s=C_0\frac{V}{m}-C_e\frac{V}{m} \tag{7}$$

where C_0 is the initial concentration of Zn(II), V and m are the volume and the mass of γ-alumina, respectively. The slope (−V/m) and the intercept (C_0·V/m) calculated from C_e-C_s line are −3.333 and 1.527×10^{-4}, which is in quite good agreement with the values of m/V=0.3 (g/L) and $C_0=1.527\times10^{-4}$ (mol/L) in the experiments. The result indicates that the relationship between C_{eq} and C_s is only dependent on the initial concentration of Zn(II) and solid-liquid ratio.

4. Effect of Foreign Ions

Fig. 7 shows the effect of foreign ions on the removal of Zn(II) from aqueous solution onto γ-alumina in 0.01 M NaCl, $NaNO_3$, $NaClO_4$, $LiClO_4$, and $KClO_4$ solutions, respectively, as a function of pH values. The effect of anions on the sorption of Zn(II) onto γ-alumina is given in Fig. 7(a). Clearly, the background electrolyte foreign anions have no obvious influence on the sorption of Zn(II). The inorganic acid radicals radius order is ClO_4^->NO_3^->Cl^-. These negatively charged anions may form complexes with the oxygen-containing functional groups on the surfaces of γ-alumina. However, the effects of ClO_4^-, NO_3^-, or Cl^- on Zn(II) sorption onto γ-alumina are quite weak, which indicates that surface complexes may be formed on γ-alumina surfaces. The effect of foreign anions on Zn(II) removal from solution onto γ-alumina can be negligible. Similar studies of Ni(II) sorption on GMZ bentonite and Pb(II) on oxidized MWCNTs have also been reported [51,53]. Nevertheless, other literature report that Eu(III) sorption on bentonite and Pb(II) on diatomite was obviously influenced by foreign anions [54,55]. The differences may be attributed to the physicochemical properties of metal ions, the surface properties of sorbent or other environmental parameters like pH and ionic strength.

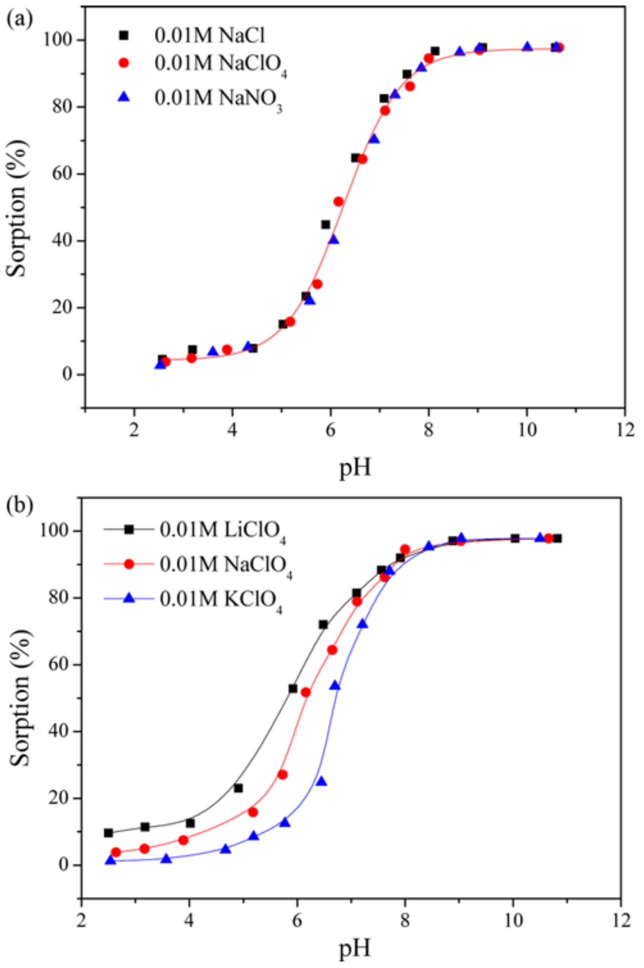

Fig. 7. Effect of foreign anions (a) and foreign cations (b) on Zn(II) sorption onto γ-alumina as a function of pH. T=293.15 K, m/V=0.3 g/L, $C_{[Zn(II)]initial}$=1.527×10^{-4} mol/L.

As can be seen from Fig. 7(b), the sorption of Zn(II) onto γ-alumina is obviously influenced by cations especially at the range of low pH and the effect of cations at high pH can be neglected. At low pH, the sorption percentage of Zn(II) onto γ-alumina is in the following sequence, Li^+>Na^+>K^+, which is in good agreement with the order of their radii of hydration. The results can be easily interpreted by the competition adsorptive capacity of different positive ions with Zn(II) on γ-alumina surfaces. The cations can alter the surface properties of γ-alumina and thus influence the sorption of Zn(II) on γ-alumina. The influence of K^+ on sorption is more obvious than that of Li^+ and Na^+ due to the smallest radius during the three cations. Generally, the cations may follow an order of increasing selectivity for binding to organic matter of alkali metal cations< H^+<alkaline earth cations<transitional group monovalent cations (e.g., Ag^+)<transitional group divalent cations (e.g., Ni^{2+} and Cu^{2+})< trivalent cations [56]. The influence of monovalent alkali ions on the sorption of Zn(II) should be weak according to the orders mentioned above. However, the experimental data show that the influence of Li^+, Na^+ and K^+ on the sorption of Zn(II) is a little drastic at pH 2-7. In the experiments, the concentration of the background

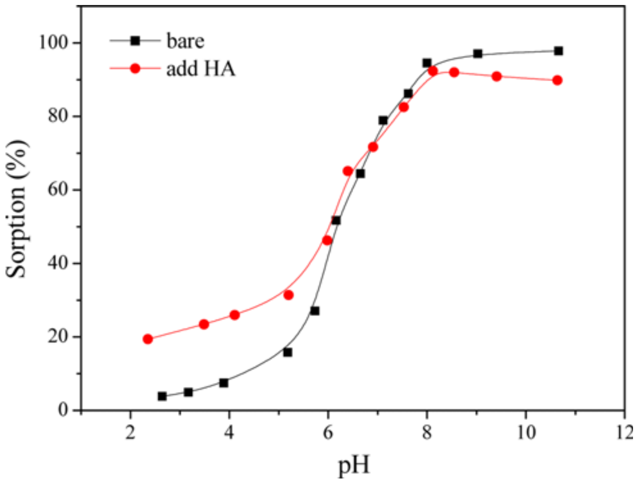

Fig. 8. Effect of HA on Zn(II) sorption onto γ-alumina as a function of pH, T=293.15 K, $C_{[HA]initial}$=10 mg/L, m/V=0.3 g/L, $C_{[Zn(II)]initial}$=1.527×10^{-4} mol/L, I=0.01 M $NaClO_4$.

electrolyte ions (1.00×10^{-2} mol/L) is much higher than that of Zn(II) (1.527×10^{-4} mol/L). The γ-alumina had been pre-equilibrated with background electrolyte ions for 24 h before adding Zn(II) ions. The Zn(II) sorption onto γ-alumina is attributed to ion-exchange reaction between Zn(II) ions and coexisting cations under the experimental conditions. Thereby, it is reasonable that the sorption of Zn(II) onto γ-alumina is influenced by cations. The result is similar to the sorption of Cd(II) and Co(II) [57], and Pb(II) [58] onto graphene oxide.

5. Effect of HA

Fig. 8 shows the pH dependence of Zn(II) sorption onto γ-alumina in the absence and presence of HA. As can be seen, the presence of HA enhances the sorption of Zn(II) on γ-alumina obviously at pH<7, but inhibits the sorption at pH>7. In the low pH region, the negatively charged HA can be easily adsorbed on the positively charged surfaces of γ-alumina which can be explained by electrostatic attraction. The adsorbed HA on γ-alumina surface modifies the long-range electrostatic properties of the aqueous-mineral interface, which results in a more favorable electrostatic environment for Zn(II) sorption and enhances the formation of Zn-HA-alumina ternary surface complexes [45,59], thereby enhancing the sorption of Zn(II) [60]. However, the negative effect of HA at high pH is attributed to the electrostatic repulsion between negatively charged surfaces of γ-alumina and negatively charged HA. Thus, more free HA molecules remain in solution as pH is increasing and increase the formation of strong HA-Zn complexes in solution, which results in the decrease of Zn(II) sorption onto HA-alumina hybrids [61-63].

6. Effect of Temperature and Thermodynamic Study

Batch experiments of Zn(II) sorption onto γ-alumina as a function of temperature are carried out at 298.15, 323.15 and 343.15 K (Fig. 9(a)). One can see that the sorption isotherm is the highest at T=343.15 K and the lowest at T=298.15 K. The result indicates that high temperature is advantageous for Zn(II) sorption on γ-alumina, which may be attributed to several factors. Increasing temperature can increase the proportion and activity of Zn(II) ions in solution and accordingly enhances the affinity of Zn(II) ions to γ-alumina surface. Changes in the γ-alumina pore sizes as well as an increase in the number of sorption sites due to the breaking of some internal bonds near surface edge are expected at higher temperatures [58, 64]. Furthermore, the diffusion rate of Zn(II) into γ-alumina pores may increase with the increasing temperature. To better understand the mechanism and to quantify the sorption data, Langmuir and Fre-

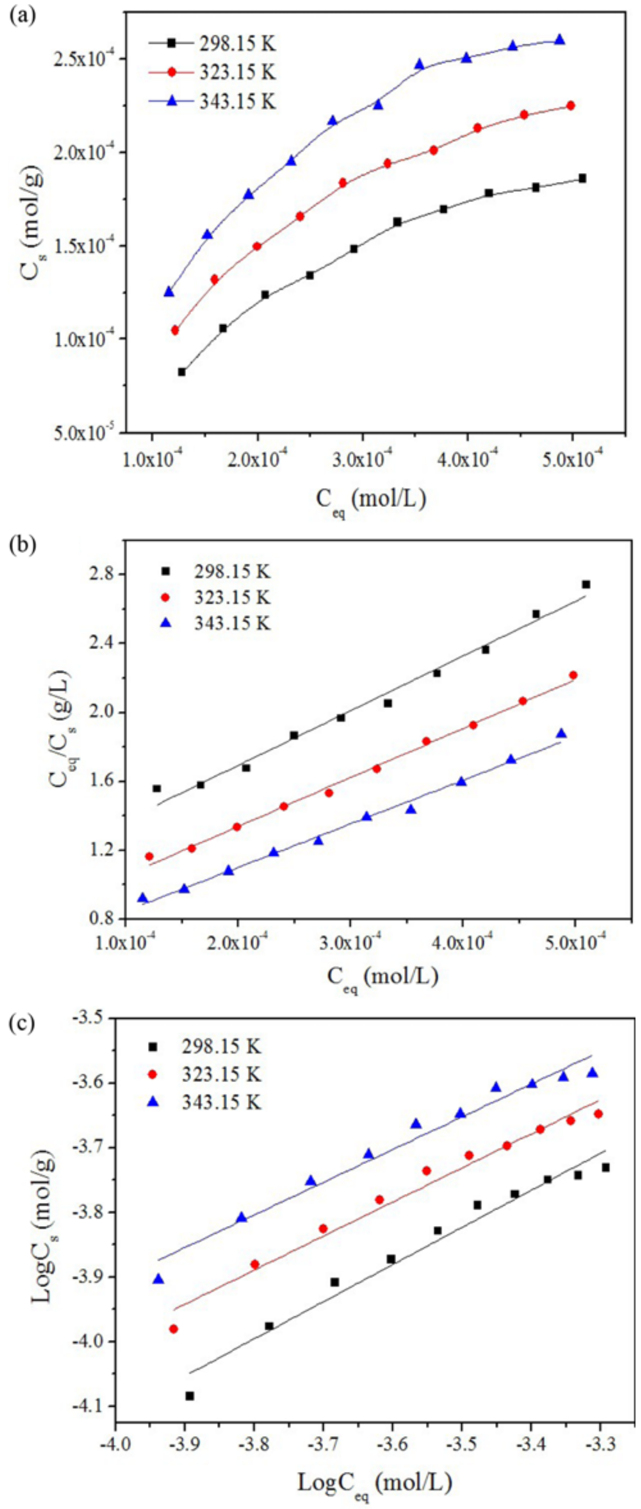

Fig. 9. Sorption isotherms (a), Langmuir (b) and Freundlich (c) isotherms of Zn(II) sorption onto γ-alumina at three different temperatures, pH=6.0±0.1, m/V=0.3 g/L, I=0.01 M $NaClO_4$.

undlich models are conducted to simulate the experimental data.

The Langmuir isotherm model is valid for monolayer sorption on surface containing finite number of identical sorption sites, which is expressed by the following equation [65]:

$$C_s=\frac{bC_{s\,max}C_e}{1+bC_e} \tag{8}$$

where C_e is the equilibrium concentration of Zn(II) remained in solution (mol/L); C_s is the amount of Zn(II) adsorbed on per weight unit of γ-alumina after equilibrium (mol/g); $C_{s\,max}$, the maximum sorption capacity, is the amount of Zn(II) required to form a monolayer (mol/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constant b (L/mol) as below. The values of $C_{s\,max}$ and b can be calculated by the following rearranged equation:

$$\frac{C_e}{C_s}=\frac{1}{bC_{s\,max}}+\frac{C_e}{C_{s\,max}} \tag{9}$$

The Freundlich isotherm model is purely empirical based on sorption on heterogeneous surface and is expressed as follows [66]:

$$C_s=K_FC_e^n \tag{10}$$

where k_F ($mol^{1-n}L^n/g$) represents the sorption capacity when metal ion equilibrium concentration equals to 1, and n represents the degree of dependence of sorption with equilibrium concentration. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as given below:

$$\log C_s=\log K_F+n\log C_e \tag{11}$$

The equilibrium data of Zn(II) sorption (Fig. 9(a)) are analyzed by using the linearized form of the two models, and the results are shown in Fig. 9(b) and Fig. 9(c). The relative values calculated from these models are listed in Table 1. The two models fit the sorption isotherms of Zn(II) on γ-alumina well, which is supported by the high correlation coefficients R^2 (all>0.9). However, it can be concluded from R^2 that the Langmuir model simulates the experimental data better than Freundlich model, which indicates that the sorption of Zn(II) on γ-alumina is almost complete monolayer [67]. The values of $C_{s\,max}$ acquired from the Langmuir model for Zn(II) sorption on γ-alumina are the highest at T=343.15 K and the lowest at T=303.15 K, which indicates that the high temperature is beneficial to the sorption process. The value of n obtained from the Freundlich model is lower than 1, which implies that a nonlinear sorption takes place on γ-alumina surfaces. The parameters calculated from the analysis of the two isotherm models concertedly indicate the sorption of Zn(II) onto γ-alumina is a favorable and chemisorption process.

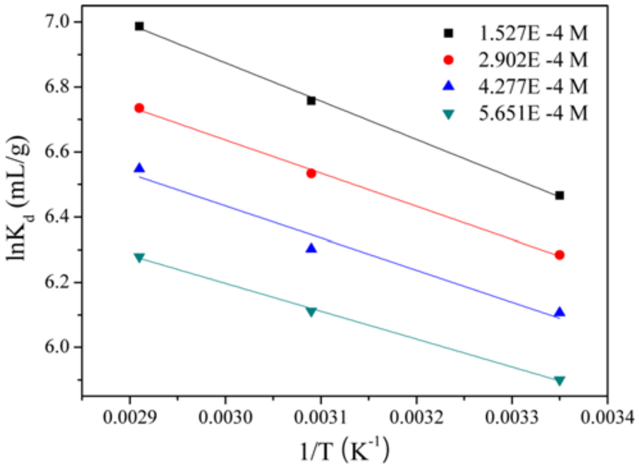

Fig. 10. Linear plots of $\ln K_d$ vs. C_e of Zn(II) sorption onto γ-alumina, pH=6.0±0.1, m/V=0.3 g/L, I=0.01 M $NaClO_4$.

The thermodynamic constants such as enthalpy change ΔH^0, free energy change ΔG^0 and entropy change ΔS^0 for Zn(II) sorption on γ-alumina can be determined from the temperature-dependent sorption isotherms. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of $\ln K_d$ vs. 1/T (Fig. 10) via applying the following equation [68]:

$$\ln K_d=\frac{\Delta S^0}{R}-\frac{\Delta H^0}{RT} \tag{12}$$

The change of Gibbs free energy (ΔG^0) was calculated from the equation:

$$\Delta G^0=\Delta H^0-T\Delta S^0 \tag{13}$$

The thermodynamic data obtained by Eqs. (12) and (13) are in Table 2. The positive enthalpy change (ΔH^0) implies that the sorption process of Zn(II) is endothermic. The positive enthalpy changes can be explained by several factors as follows: first, the sorption of Zn(II) requires a diffusion process, which is endothermic. Second, the sorption of Zn(II) ions may require at least a partial decomposition of their hydration shell, a process needs energy. This energy exceeds the exothermicity of cations to attach to the solid surface [69-71]. Otherwise, the sorption is dominated by ion-exchange, and the exchange of Zn(II) ions with H^+/Na^+ needs to break the O-H/O-Na bond first, which is also an endothermic process. The negative Gibbs free energy change (ΔG^0) values indicate the thermodynamically feasible and spontaneous nature of the sorption. The positive values of entropy change (ΔS^0) reflect the increased randomness at the solid-

Table 1. The parameters for Langmuir and Freundlich isotherms at different temperatures

T (K)	Langmuir			Freundlich		
	$C_{s\,max}$ (mol/g)	b (L/mol)	R^2	k_F ($mol^{1-n}\cdot L^n/g$)	n	R^2
298.15	3.15×10^{-4}	4.26×10^3	0.984	1.55×10^{-2}	0.576	0.967
323.15	3.51×10^{-4}	3.69×10^3	0.995	1.31×10^{-2}	0.528	0.974
343.15	3.95×10^{-4}	3.00×10^3	0.990	1.32×10^{-2}	0.506	0.967

Table 2. The thermodynamic data of Zn(II) sorption on γ-Al_2O_3 at different Zn(II) initial solution concentrations

C_0 (mol/L)	ΔS^0 (J/(mol·K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)		
			298.15 K	323.15 K	343.15 K
1.527×10^{-4}	86.647	9.815	−16.019	−18.185	−19.918
2.902×10^{-4}	80.669	8.483	−15.568	−17.585	−19.199
4.277×10^{-4}	78.116	8.195	−15.095	−17.048	−18.611
5.651×10^{-4}	72.989	7.144	−14.618	−16.442	−17.902

solution interface during the fixation of the Zn(II) ion on the active sites of γ-alumina. The decomposition of the hydration shell will increase the entropy of the solvent.

CONCLUSIONS

From the results of Zn(II) sorption on γ-alumina, we have reached the following conclusions:

(1) The sorption of Zn(II) onto γ-alumina achieves equilibration rapidly. The kinetic sorption can be described by the pseudo-second-order model very well. The mechanisms of the kinetics are controlled by both film diffusion process and intraparticle diffusion process.

(2) The sorption of Zn(II) on γ-alumina is strongly dependent on pH. The sorption increases with increasing pH values at pH<8.5, and then maintains high level at pH>8.5.

(3) The sorption of Zn(II) onto γ-alumina depends on ionic strength at low pH values (pH<7) and is independent of ionic strength at high pH values (pH>7). The sorption is dominated by ion exchange or outer-sphere surface complexation at low pH values and by inner-sphere surface complexation at high pH values.

(4) The sorption of Zn(II) onto γ-alumina is influenced by the foreign cations at low pH and is not influenced by foreign cations at high pH values. The presence of different anions has no obvious influence on the sorption of Zn(II) onto γ-alumina.

(5) The sorption of Zn(II) is significantly influenced by HA. The presence of HA enhances the sorption of Zn(II) onto γ-alumina at pH<7, but decreases the sorption of Zn(II) at pH>7. The enhanced sorption is attributed to the strong surface complexes of Zn(II) with surface adsorbed HA on γ-alumina surfaces; whereas the reduced sorption is attributed to the formation of soluble HA-Zn(II) complexes in solution.

(6) The thermodynamic analysis calculated from temperature dependent sorption isotherms suggests that the sorption of Zn(II) onto γ-alumina is a spontaneous and endothermic process.

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