



Influence of solution chemistry on the removal of Ni(II) from aqueous solution to titanate nanotubes

Guodong Sheng*, Shitong Yang, Jiang Sheng, Donglin Zhao, Xiangke Wang*

Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, 230031 Hefei, PR China

ARTICLE INFO

Article history:

Received 29 November 2010

Received in revised form

20 December 2010

Accepted 20 December 2010

Keywords:

Titanate nanotubes

Adsorption

Humic acid

Fulvic acid

ABSTRACT

In this work, adsorption of Ni(II) from aqueous solution to titanate nanotubes (TNTs) as a function of various water quality parameters was investigated under ambient conditions. The results indicated that the adsorption of Ni(II) to TNTs was strongly dependent on pH and ionic strength. A positive effect of humic acid (HA)/fulvic acid (FA) on Ni(II) adsorption was found at pH < 6.0, whereas a negative effect was observed at pH > 6.0. At low pH, the adsorption of Ni(II) was dominated by outer-sphere surface complexation or ion exchange with Na⁺/H⁺ on TNT surfaces, whereas inner-sphere surface complexation was the main adsorption mechanism at high pH. The TNTs are suitable material for the preconcentration of Ni(II) from large volumes of aqueous solutions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The increasing levels of toxic heavy metals or radionuclides, which have been discharged into the environment as industrial wastes, pose a serious threat to human health, living resources and ecological systems. Among the potentially contaminants, nickel is one of the most widespread pollutants in the environment. It is generally regarded that the wastewater containing nickel is mainly derived from industrial production processes including mining, electrolysis, electroplating, batteries dyes metallurgy, pesticides, etc. [1]. ⁶³Ni(II) ($T_{1/2} = 96$ a), an important product of the neutron activation of the reactor materials, is present in liquid wastes released from pressurized water from the nuclear power reactors and is also widely used in research and medical applications. The presence of nickel in drinking water above the permissible limit of 0.02 mg/L (WHO drinking-water quality standards) can cause adverse health impacts such as anemia, diarrhea, encephalopathy, hepatitis and the dysfunction of central nervous system. For ecosystem stability and public health sake, it is of great importance to remove nickel from wastewaters. Among most methods of wastewater management, sorption technique has been widely used for the treatment of wastewater and retention of nuclear waste due to its simplicity of design, high sorption efficiency and low cost. In Sweden, the Svensk Kärnbränslehantering AB (SKB, the Swedish Nuclear Fuel and Waste

Management Co.) presents an R&D program every three years to manage spent nuclear fuel and other radioactive waste [2]. The studies on the sorption of radionuclides have been extensively conducted. Many R&D programs and various results have been reported [3–8]. For the long-term performance assessment of nuclear waste, it is of great significance to obtain in-depth understanding on the sorption mechanism of radionuclides at solid/water interfaces.

Since the innovative work of Kasuga et al. [9–11], titanate nanotubes (TNTs) have been of particular research interest for their potential application as hydrogen sensors, catalyst supports, ion-exchange materials and superior sorbents due to their fascinating microstructures and excellent physicochemical properties [12]. In the past few years, various investigations have been conducted to study the adsorption potential of TNTs towards the removal of gas [13], organic dyes [14–17], Ag(I) [18], Pb(II) [18–20], Cu(II) [18,21] and As(V) [22]. It was first reported by Umek et al. [13] that gaseous NO₂ could be physically adsorbed on the surface of TNTs by p_y orbital of the oxygen atoms. Adsorption of organic dyes on TNTs was studied by Lee et al. [14,15], and they indicated that the amount of Na(I) within TNT structure appears to dominate the adsorption potential of TNTs. Regarding the adsorption of heavy metal by TNTs, An et al. [18] and Lin et al. [21] indicated that TNTs showed high adsorption capacity for Cu(II), Pb(II), and Ag(I), and the results revealed that a decrease in adsorption was owing to the strengthening O–H bond and the intercalation of H(I) in TNT structure. However, these limited studies only focused on the adsorption kinetic and thermodynamic of TNTs towards organic dyes and heavy metals and little attention has been paid to the adsorption characteristic of radionuclides onto TNTs.

* Corresponding authors. Tel.: +86 551 5591368; fax: +86 551 5591310.

E-mail addresses: gsheng@mail.ustc.edu.cn (G. Sheng), xkwang@ipp.ac.cn (X. Wang).

Table 1
¹³C NMR characteristics (chemical shift, ppm) of HA and FA [27–29].

	0–50	51–105	106–160	161–200	Aromaticity
HA	15	21	47	17	57
FA	16	28	19	39	30

Table 2
The concentrations of functional groups of HA and FA calculated from potentiometric titration by using FITEQL 3.1 [27].

	Log K_a			C (mol/g) ^a			Surface sites density (mol/g)	WSOS/DF
	L ₁	L ₂	L ₃	HL ₁	HL ₂	HL ₃		
HA	–5.04	–7.40	–9.60	2.20×10^{-3}	1.08×10^{-3}	3.18×10^{-3}	6.46×10^{-3}	2.37
FA	–5.19	–7.77	–10.53	1.83×10^{-3}	1.08×10^{-3}	2.42×10^{-3}	2.71×10^{-2}	0.10

^a HL₁, HL₂ and HL₃ represent the carboxyl groups (–COOH), the phenolic groups (Ar–OH) and the amine groups (–NH₂) of HA and FA, respectively.

Despite of the extensive studies on the adsorption of metal ions [18–22] or organic compounds [14–17] on TNTs, according to our literature survey, there is still little information with respect to the influence of organic compounds on the adsorption of metal ions. However, it should be noted that metal ions and organic compounds exist simultaneously at many contaminated sites. For example, the presence of natural organic matter (NOM), such as humic acid (HA) and fulvic acid (FA), may influence the fate of metal ions in natural environment. In our previous studies [23–26], the effect of HA/FA on metal ion adsorption to minerals had been extensively studied. It was generally found that the adsorption was increased at low pH values but decreased at high pH values. However, the effect of HA/FA on metal ion adsorption to TNTs is still scarce. Therefore, to better understand the practical application of TNTs as a potential adsorbent in the wastewater management, it is greatly important to investigate the adsorption of metal ions to TNTs in the presence of HA/FA.

In this work, we investigated the adsorption of Ni(II) on TNTs under various solution chemistry conditions. Ni(II) was selected as a model metal ion because of its extensive existence in water environment, and as a representative radionuclide because radionickel is one of most important radionuclides in nuclear waste. The objectives of this work are: (1) to study the adsorption of Ni(II) on TNTs under various common conditions; (2) to discuss the adsorption mechanism of Ni(II) on TNTs.

2. Materials and methods

2.1. Materials

All chemicals used in the experiments were purchased as analytical purity and used directly without any further purification. All the reagents were prepared with Mill-Q water. HA and FA were extracted from the soil of Hua-Jia county (Gansu Province, China) and were characterized in detail [27–29]. Cross-polarization magic angle spinning (CPMAS) ¹³C NMR spectra of HA and FA were divided into four chemical shift regions, i.e., 0–50 ppm, 51–105 ppm, 106–160 ppm and 161–200 ppm. The four regions were referred to as aliphatic, carbohydrate, aromatic, and carboxyl regions. The percentage of the total intensity of each region was estimated by integrating CPMAS ¹³C NMR spectra for each region. The fractions of aromatic groups calculated by expressing aromatic C as percentage of the sum of aliphatic C (0–105 ppm) and aromatic C (106–160 ppm) are tabulated in Table 1. HA and FA have also been characterized as a suite of 3 discrete acids with pK_a values listed in Table 2. The concentrations of functional groups of HA and FA determined by fitting the potentiometric acid–base titration data using FITEQL 3.1 are given also in Table 2. In addition, the weight-averaged molecular weights (M_w) of dissolved HA and FA

are evaluated according to the method of Chin et al. [30], and the M_w values of dissolved HA and FA are 2108 and 1364, respectively. The preparation and characterization of TNTs have been described in detail in our previous study [31].

2.2. Batch adsorption procedures

All the experiments were carried out by using batch technique in polyethylene centrifuge tubes under ambient conditions. The stock suspension of TNTs and NaClO₄ solution was pre-equilibrated for 24 h and then Ni(II) stock solution was added to achieve the desired concentrations of different components. The pH was adjusted to desired values by adding negligible volumes of 0.1 or 0.01 M HClO₄ or NaOH. After the suspensions were oscillated for 24 h, the solid and liquid phases were separated by centrifugation at $7788 \times g$ for 30 min. To take into account of Ni(II) adsorption on tube wall, calibration curves were obtained separately under otherwise identical conditions as the adsorption process but no TNTs. Based on the obtained calibration curves, the amount of Ni(II) adsorbed on TNTs was calculated by subtracting the mass in the solution from the mass spiked. Radionuclide ⁶³Ni was used in the experiments as radiotracer. The concentration of radiotracer ⁶³Ni was analyzed by Liquid Scintillation counting using a Packard 3100 TR/AB Liquid Scintillation analyzer (PerkinElmer). The sorption percentage (sorption % = $(C_0 - C_{eq})/C_0 \times 100\%$) and distribution coefficient ($K_d = (C_0 - C_{eq})/C_{eq} \times V/m$) of ⁶³Ni(II) on TNTs were derived from the initial concentration of Ni(II) (C_0), the equilibrium concentration of Ni(II) (C_{eq}), the mass of TNTs (m) and the volume of the suspension (V). All experimental data were the average of triplicate determinations and the relative errors were about 5%.

3. Results and discussion

3.1. Effect of ionic strength

Fig. 1 shows the pH dependence of Ni(II) adsorption to TNTs in 0.001, 0.01, and 0.1 mol/L NaClO₄ solutions, respectively. As indicated in Fig. 1, solution pH is an important factor to influence the removal of Ni(II) from aqueous solution to TNTs. The removal of Ni(II) increases slowly at pH ranging from 2.0 to 4.0, then increases abruptly at pH 4.0–6.0, and at last maintains the high level with increasing pH at pH > 6.0. About 90% of Ni(II) is adsorbed on TNTs at pH > 6.0. It is well known that the species of Ni(II) in aqueous solution are important to Ni(II) sorption. The species of Ni(II) in aqueous solution are strongly dependent on pH values. Fig. 2 shows the relative distribution of Ni(II) species calculated from the overall hydrolysis constants (Log $K_1 = -9.9$, Log $K_2 = -19$, Log $K_3 = -30$ and Log $K_4 = -27.7$) ($K_n = [Ni(OH)_n^{2-n}] \cdot [H^+]^n / [Ni^{2+}]$) [32]. It can be clearly found from Fig. 2 that Ni(II) presents in

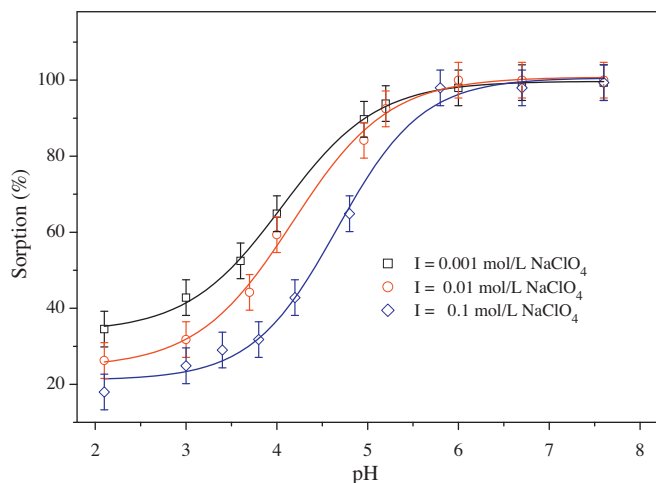


Fig. 1. Effect of ionic strength on Ni(II) adsorption onto TNTs as a function of pH, $T = 20^\circ\text{C}$, $C_{\text{Ni(II)initial}} = 10\text{ mg/L}$, $m/V = 0.5\text{ g/L}$.

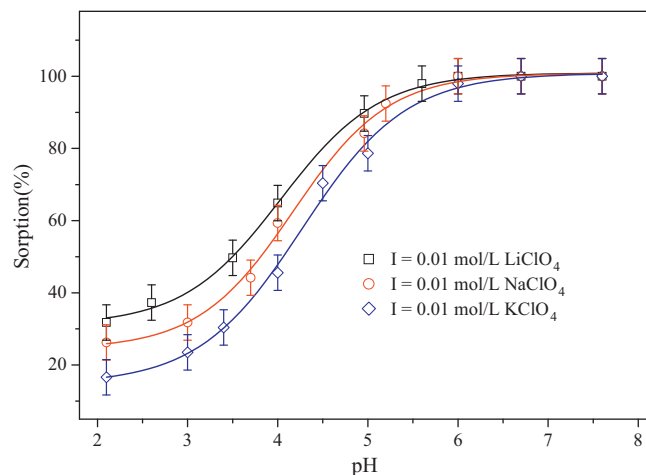


Fig. 3. Effect of foreign cations on Ni(II) adsorption onto TNTs as a function of pH, $T = 20^\circ\text{C}$, $C_{\text{Ni(II)initial}} = 10\text{ mg/L}$, $m/V = 0.5\text{ g/L}$.

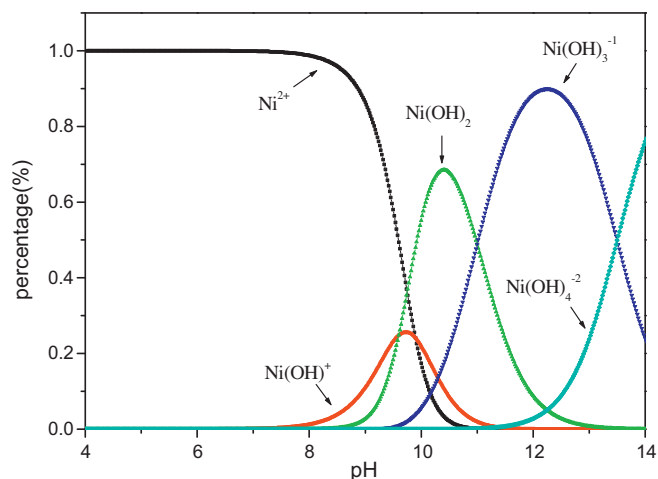


Fig. 2. Relative proportion of Ni(II) species as a function of pH.

the species of Ni^{2+} , $\text{Ni}(\text{OH})^+$, $\text{Ni}(\text{OH})_2^0$, $\text{Ni}(\text{OH})_3^-$ and $\text{Ni}(\text{OH})_4^{2-}$ at different pH values. At low pH values, Ni^{2+} and $\text{Ni}(\text{OH})^+$ are the main species of Ni(II) in aqueous solution. Because of the protonation reaction (i.e., $\equiv\text{TiOH} + \text{H}^+ \leftrightarrow \equiv\text{TiOH}_2^+$) on TNT surfaces, the concentration of protonated sites ($\equiv\text{TiOH}_2^+$) decreases with pH increasing. Therefore, the removal of Ni^{2+} and $\text{Ni}(\text{OH})^+$ is difficult as a result of coulombic repulsion at pH range 2.0–4.0. However, at high pH values, the concentration of deprotonated sites ($\equiv\text{TiO}^-$) increases with pH increasing because of the surface deprotonation reaction (i.e., $\equiv\text{TiOH} \leftrightarrow \equiv\text{TiO}^- + \text{H}^+$). The deprotonated sites ($\equiv\text{TiO}^-$) are more available to retain Ni(II) ions and surface complexation between Ni^{2+} , $\text{Ni}(\text{OH})^+$ and TNTs is facilitated, thus resulting in sharp increase of Ni(II) sorption at pH 4.0–6.0.

Fig. 1 also demonstrates the influence of ionic strength on the removal of Ni(II) from solution to TNTs. It is generally regarded that ClO_4^- does not form complexes with Ni(II) in solution or on TNT surfaces. The influence of NaClO_4 concentration on Ni(II) sorption is mainly contributed to the competition of H^+/Na^+ with Ni(II) on the surfaces of TNTs. It can be clearly seen that the removal of Ni(II) at $\text{pH} < 6.0$ is obviously influenced by ionic strength, while no drastic difference of Ni(II) sorption to TNTs is found at $\text{pH} > 6.0$ in the three different solution concentrations of NaClO_4 . The effect of ionic strength effects on Ni(II) sorption is consistent with those reported in the literatures [33,34].

Based on the triple-layer model, a possible equilibrium adsorption reaction of Ni(II) with the TNT surface can be expressed as follows: (i) if Ni(II) ions react similarly to a background electrolyte with TNTs, then ion-pairs are formed at the β -plane, on which the adsorption process is nonspecific and the reaction product is an outer-sphere surface complex; (ii) if the adsorption of Ni(II) ions is visualized as a chemically specific reaction, then the reaction can be considered as an inner-sphere coordination process. Ni(II) ions with 1 and 2 mol of reactive surface hydroxyl of TNTs forms inner-sphere monodentate and bidentate surface complexes, respectively; (iii) if hydrate Ni(II) ions react with TNTs, inner-sphere and outer-sphere surface complexes can be formed, respectively [35,36]. The background electrolyte concentration influences the thickness and interface potential of the double layer, affecting the binding of the adsorbing species. Hayes and Leckie [37] proposed that the influence of the background electrolyte on the adsorption reaction can be applied to predict the adsorption reaction. β -Plane adsorption can be assumed to proceed when the background electrolyte easily influences the adsorption reaction; otherwise, α -plane adsorption may occur. The results of this work suggest that Ni(II) participates in a β -plane complex reaction at low pH values, as the adsorption is greatly affected by the β -plane complex reaction of the background electrolyte (i.e., Na^+ and NO_3^-). Meanwhile, Ni(II) participates in an α -plane complex reaction at high pH values, without being affected by the β -plane complex reaction of the background electrolyte (i.e., Na^+ and NO_3^-). From the discussion mentioned above, we can draw a conclusion that the pH- and ionic strength-dependent adsorption of Ni(II) suggests that the removal of Ni(II) to TNTs is dominated by ion exchange or outer-sphere surface complexation at $\text{pH} < 6.0$, whereas the pH-dependent and ionic strength-independent Ni(II) adsorption indicates that the removal of Ni(II) is mainly due to inner-sphere surface complexation at $\text{pH} > 6.0$ [33,34,38,39].

3.2. Effect of cation

Fig. 3 shows the removal of Ni(II) from aqueous solution to TNTs as a function of pH in 0.01 mol/L LiClO_4 , NaClO_4 and KClO_4 solutions, respectively. The removal of Ni(II) to TNTs is clearly affected by cations in the TNT suspension. One can see that the removal percent of Ni(II) to TNTs at $\text{pH} < 6.0$ is in the following order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, which indicates that cations can change the surface properties of TNTs and thus influences the adsorption of Ni(II) onto TNTs. Cations in TNT suspension will compete for interaction with the surface of TNTs, and Ni(II) has higher charge and higher affinity to the surface of TNTs than that of the alkali metal ions. As support for this compe-

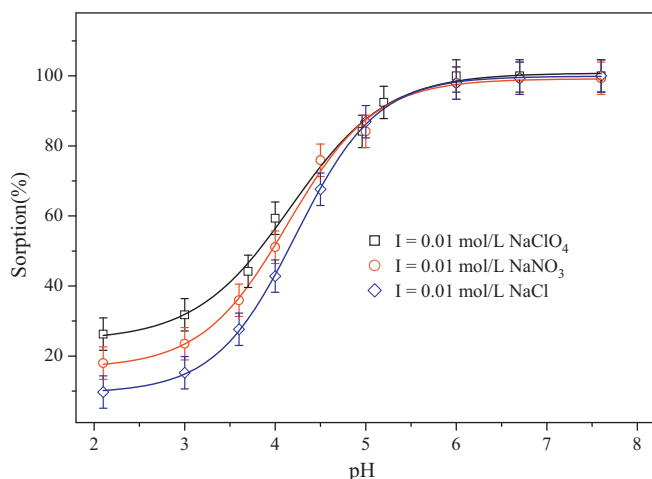


Fig. 4. Effect of foreign anions on Ni(II) adsorption onto TNTs as a function of pH, $T = 20^\circ\text{C}$, $C_{\text{Ni(II)initial}} = 10\text{ mg/L}$, $m/V = 0.5\text{ g/L}$.

tition principle, the order of Ni(II) uptake under the same pH value is found to be the lowest for K^+ and the highest for Li^+ , which is the order of their radii of hydration: $\text{K}^+ = 2.32$, $\text{Na}^+ = 2.76$ and $\text{Li}^+ = 3.4\text{ \AA}$ [33,34]. The adsorption of Ni(II) to TNTs can be considered as a competition of Ni(II) with Li^+ (or Na^+ , K^+) at the TNT surfaces. The radius of Li^+ is larger than those of the other two cations and thus the influence of Li^+ on Ni(II) adsorption to TNTs is smaller than those of Na^+ and K^+ . However, at $\text{pH} > 6.0$, no drastic difference of Ni(II) sorption to TNTs in LiClO_4 , NaClO_4 and KClO_4 solutions is observed, which may be attributed to the inner-sphere surface complexation or surface precipitates at high pH values as mentioned in the above section. Hu et al. [33,34] investigated the effect of Li^+ , Na^+ and K^+ on the sorption of Ni(II) in goethite/water and illite/water suspensions, respectively, and similar results were also found.

3.3. Effect of anion

Fig. 4 demonstrates the adsorption curves of Ni(II) onto TNTs as a function of pH in 0.01 mol/L NaClO_4 , NaNO_3 and NaCl solutions, respectively. The results suggest that the anions affect Ni(II) adsorption onto TNTs obviously at $\text{pH} < 6.0$. The removal percent of Ni(II) from aqueous solution to TNTs is the lowest in NaCl solution and the highest in NaClO_4 solution under the same pH values. This phenomenon can be ascribed to the factors that: (I) Cl^- and NO_3^- can form soluble complexes with Ni(II) ions in solution (e.g. $\text{Ni(II)Cl}_x^{(2-x)-}$, $\text{Ni(II)(NO}_3)_x^{(2-x)-}$), while ClO_4^- does not form soluble complexes with Ni(II) in solution. Ni(II) has the highest affinity to Cl^- and the lowest affinity to ClO_4^- ; (II) idiocratic adsorption of Cl^- to TNT surface is a little easier than that of NO_3^- and ClO_4^- , and Cl^- adsorption on TNT surface alters the surface properties of TNTs and decreases the availability of binding sites for Ni(II); (III) the inorganic acid radicals radium sequence is $\text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^-$, the smaller radium inorganic acid radicals can take up more ionic exchange sites and lead to the decline of Ni(II) adsorption on TNTs [33,34].

3.4. Effect of HA/FA

Fig. 5 shows the pH dependent of Ni(II) adsorption onto TNTs in the absence and presence of HA/FA. A positive effect of HA/FA on Ni(II) adsorption onto TNTs is observed at low pH values, while a negative effect of HA/FA on Ni(II) adsorption to TNTs is observed at high pH values. Fig. 6 shows the adsorption of HA and FA to TNTs as a function of pH. It can be obviously found that about 90% of HA/FA is adsorbed on TNT surface at $\text{pH} < 6.0$, and then the adsorption

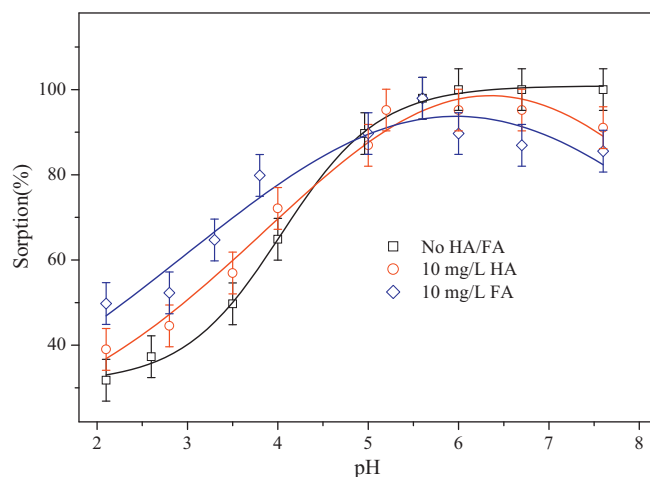


Fig. 5. Effect of HA/FA on Ni(II) adsorption onto TNTs as a function of pH, $T = 20^\circ\text{C}$, $I = 0.01\text{ mol/L NaClO}_4$, $C_{\text{Ni(II)initial}} = 10\text{ mg/L}$, $m/V = 0.5\text{ g/L}$.

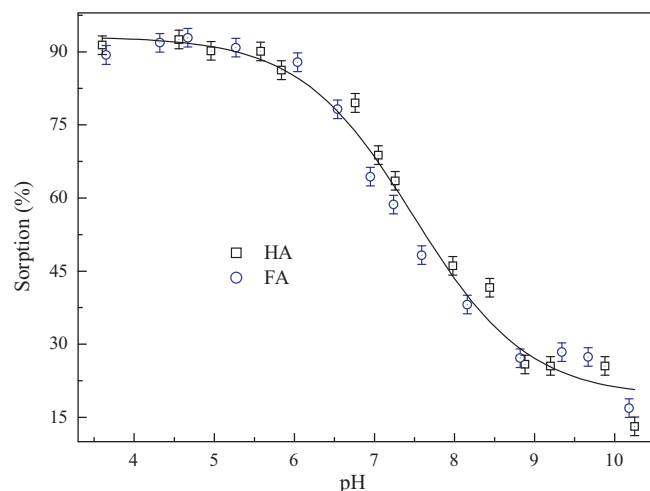


Fig. 6. Adsorption of HA and FA to TNTs as a function of pH, $C_{\text{HA/FA}} = 10.0\text{ mg/L}$, $m/V = 0.5\text{ g/L}$, $I = 0.01\text{ mol/L NaClO}_4$, $T = 20^\circ\text{C}$.

decreases with increasing pH. Ghosh et al. [40] and Yang and Xing [41] had determined the zeta potential of HA and FA as a function of pH, respectively, and it was found that both HA and FA were negatively charged in the pH range of 3.0–10.0. The observations are in agreement with previous potentiometric titration results [27]. Therefore, at low pH values, the negatively charged HA/FA can be easily adsorbed on the positively charged surfaces of TNTs because of the electrostatic attraction. The strong complexation between surface adsorbed HA/FA and Ni(II) leads to the enhancement of Ni(II) adsorption to TNTs at low pH values. However, at high pH values, the adsorption of the negatively charged HA/FA on the negatively charged surfaces of TNTs becomes difficult because of the electrostatic repulsion. Thus the HA/FA in solution forms soluble complexes of HA/FA–Ni(II) in solution, and thereby reduces Ni(II) adsorption to TNTs.

It is also seen from Fig. 5 that the influence of FA on the removal of Ni(II) is a little stronger than that of HA at the whole pH range when the mass concentrations of HA and FA are the same. Although the samples of HA and FA were extracted from the same soil samples and both of them contain functional groups such as carboxyl, amine and phenolic, the proportions and configurations of these functional groups and surface sites density are different. As is illustrated in Table 2, the surface site density of FA (i.e., $2.71 \times 10^{-2}\text{ mol/g}$) is much higher than that of HA (i.e.,

6.46×10^{-3} mol/g), which can provide more available surface sites for the binding of Ni(II). Therefore, it is reasonable that FA has a stronger effect on Ni(II) removal than HA at the whole pH range.

4. Conclusion

Batch technique was adopted to investigate the adsorption of Ni(II) from aqueous solutions onto TNTs as a function of various environmental factors such as pH, ionic strength, coexisting electrolyte ions and humic substances under ambient conditions. The adsorption increases with increasing pH values at $\text{pH} < 6.0$, and then maintains high level at $\text{pH} > 6.0$. The adsorption of Ni(II) is dependent on ionic strength and foreign ions at low pH values, and independent of these factors at high pH values. The presence of HA/FA enhances the adsorption of Ni(II) at $\text{pH} < 6.0$, while reduces Ni(II) adsorption at $\text{pH} > 6.0$. By integrating all the above-mentioned analysis together, one can conclude that the adsorption of Ni(II) on TNTs is dominated by ion exchange or outer-sphere surface complexation at low pH values, and by inner-sphere surface complexation at high pH values. Considering the accessibility and low cost of TNTs, one can conclude that this material has a great application potential for the cost-effective disposal of Ni(II)-contaminated wastewaters. Based on the results noted for Ni(II), TNTs may also be suitable for the removal of other heavy metals and radionuclides. Hence, more investigations on the adsorption properties of TNTs towards various environmental pollutants are ongoing in our laboratory so as to have a more thorough view of the possibility of using TNTs as a promising material for wastewater management.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (21071147; 20971126; 21077107; 21007074), 973 project (2007CB936602; 2011CB933700), the Knowledge Innovation Program of CAS and Special Foundation for High-level Waste Disposal (2007-840) are greatly acknowledged.

References

- [1] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium of Co(II), Cr(III), and Ni(II) onto coir pith, *Process Biochem.* 41 (2006) 609–615.
- [2] B. Rosborg, L. Werme, The Swedish nuclear waste program and the long-term corrosion behavior of copper, *J. Nucl. Mater.* 379 (2008) 142–153.
- [3] D. Cui, T.E. Eriksen, Reduction of Tc(VII) and Np(V) in solution by ferrous ion. A laboratory study of homogeneous and heterogeneous redox processes. SKB Technical Report, TR-96-03, 1996.
- [4] F. El Aamrani, I. Casas, J. de Pablo, L. Duro, M. Grivé, J. Bruno, Experimental and modeling study of the interaction between uranium (VI) and magnetite. SKB Technical Report, TR-99-21, 1999.
- [5] M.A. Glaus, B. Baeyens, M. Lauber, T. Rabung, L.R. Van Loon, water-extractable organic matter from opalinus clay: effect on sorption and speciation of Ni(II), Eu(III) and Th(IV). Nagra Technical Report 01-07, 2001.
- [6] N. Marmier, A. Delisée, F. Fromage, Surface complexation modeling of Yb(III), Ni(II), and Cs(I) sorption on magnetite, *J. Colloid Interf. Sci.* 211 (1999) 54–60.
- [7] Å. Gustafsson, M. Molera, I. Puigdomenech, Study of Ni(II) sorption on chlorite—a fracture filling mineral in granites, in: *Scientific Basis for Nuclear Waste Management XXVIII*. Materials Research Society Symposium proceedings, vol. 824, 2004, pp. 373–378.
- [8] S. Holgersson, Oskarshamn site investigation. Batch experiments of I, Cs, Sr, Ni, Eu, U and Np sorption onto soil from the Laxemar area. SKB P-09-29, 2009.
- [9] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Formation of titanium oxide nanotube, *Langmuir* 14 (1998) 3160–3163.
- [10] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Titania nanotubes prepared by chemical processing, *Adv. Mater.* 11 (1999) 1307–1311.
- [11] J. Suetake, A.Y. Nosaka, K. Hodouchi, H. Matsubara, Y. Nosaka, Characteristics of titanate nanotube and the states of the confined sodium ions, *J. Phys. Chem. C* 112 (2008) 18474–18482.
- [12] H.H. Ou, S.L. Lo, Review of titania nanotubes synthesized via the hydrothermal treatment: fabrication, modification, and application, *Sep. Purif. Technol.* 58 (2007) 179–191.
- [13] P. Umek, P. Cevc, A. Jesih, A. Gloter, C.P. Ewels, D. Arcon, Impact of structure and morphology on gas adsorption of titanate-based nanotubes and nanoribbons, *Chem. Mater.* 17 (2005) 5945–5950.
- [14] C.K. Lee, K.S. Lin, C.F. Wu, M.D. Lyu, C.C. Lo, Effects of synthesis temperature on the microstructures and basic dyes adsorption of titanate nanotubes, *J. Hazard. Mater.* 150 (2008) 494–503.
- [15] C.K. Lee, C.C. Wang, L.C. Juang, M.D. Lyu, S.H. Hung, S.S. Liu, Effects of sodium content on the microstructures and basic dye cation exchange of titanate nanotubes, *Colloids Surf. A* 317 (2008) 164–173.
- [16] D.V. Bavykin, K.E. Redmond, B.P. Nias, A.N. Kulak, F.C. Walsh, The effect of ionic charge on the adsorption of organic dyes onto titanate nanotubes, *Aust. J. Chem.* 63 (2010) 270–275.
- [17] L. Xiong, Y. Yang, J.X. Mai, W.L. Sun, C.Y. Zhang, D.P. Wei, Q. Chen, J.R. Ni, Adsorption behavior of methylene blue onto titanate nanotubes, *Chem. Eng. J.* 156 (2010) 313–320.
- [18] H.Q. An, B.L. Zhu, H.Y. Wu, M. Zhang, S.R. Wang, S.M. Zhang, S.H. Wu, W.P. Huang, Synthesis and characterization of titanate and CS_2 -modified titanate nanotubes as well as their adsorption capacities for heavy metal ions, *Chem. J. Chin. U.* 29 (2008) 439–444.
- [19] H. Kochkar, A. Turki, L. Bergaoui, G. Berhault, A. Ghorbel, Study of Pd(II) adsorption over titanate nanotubes of different diameters, *J. Colloid Interf. Sci.* 331 (2009) 27–31.
- [20] Y.C. Chen, S.L. Lo, J. Kuo, Pb(II) Adsorption capacity and behavior of titanate nanotubes made by microwave hydrothermal method, *Colloids Surf. A* 361 (2010) 126–131.
- [21] S.S. Liu, C.K. Lee, H.C. Chen, C.C. Wang, L.C. Juang, Application of titanate nanotubes for Cu(II) ions adsorptive removal from aqueous solution, *Chem. Eng. J.* 147 (2009) 188–193.
- [22] H.Y. Niu, J.M. Wang, Y.L. Shi, Y.Q. Cai, F.S. Wei, Adsorption behavior of arsenic onto protonated titanate nanotubes prepared via hydrothermal method, *Micro. Mater.* 122 (2009) 28–35.
- [23] C.L. Chen, X.K. Wang, Influence of pH, soil humic/fulvic acid, ionic strength and foreign ions on adsorption of thorium(IV) onto $\gamma\text{-Al}_2\text{O}_3$, *Appl. Geochem.* 22 (2007) 436–445.
- [24] X.L. Tan, X.K. Wang, C.L. Chen, A.H. Sun, Effect of soil humic and fulvic acids, pH and ionic strength on Th(IV) sorption to TiO_2 nanoparticles, *Appl. Radiat. Isotopes* 65 (2007) 375–381.
- [25] D. Xu, X.K. Wang, C.L. Chen, X. Zhou, X.L. Tan, Influence of soil humic acid and fulvic acid on adsorption of thorium(IV) on MX-80 bentonite, *Radiochim. Acta* 94 (2006) 429–434.
- [26] D. Xu, D.D. Shao, C.L. Chen, A.P. Ren, X.K. Wang, Effect of pH and fulvic acid on adsorption and complexation of cobalt onto bare and FA bound MX-80 bentonite, *Radiochim. Acta* 94 (2006) 97–102.
- [27] X.L. Tan, X.K. Wang, H. Geckeis, T.H. Rabung, Sorption of Eu(III) on humic acid or fulvic acid bound to alumina studied by SEM-EDS, XPS, TRLFS and batch techniques, *Environ. Sci. Technol.* 42 (2008) 6532–6537.
- [28] Z.Y. Tao, J. Zhang, J. Zhai, Characterization and differentiation of humic acids and fulvic acids in soils from various regions of China by nuclear magnetic resonance spectroscopy, *Anal. Chim. Acta* 395 (1999) 199–203.
- [29] J. Zhang, J.J. Zhai, F.Z. Zhao, Z.Y. Tao, Study of soil humic substances by cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance and pyrolysis-capillary gas chromatography, *Anal. Chim. Acta* 378 (1999) 177–182.
- [30] Y.P. Chin, G. Alken, E. O'Loughlin, Molecular weight polydispersity, and spectroscopic properties of aquatic humic substances, *Environ. Sci. Technol.* 28 (1994) 1853–1858.
- [31] G. Sheng, S. Yang, J. Sheng, G. Montavon, X. Wang, Investigation of Eu(III) Sorption and local atomic structures on titanate nanotubes by a combination of batch and EXAFS study, *Environ. Sci. Technol.* (submitted for publication).
- [32] A. Shukla, Y. Zhang, P. Dubej, J. Margrave, S. Shukla, The role of sawdust in the removal of unwanted materials from water, *J. Hazard. Mater.* 95 (2002) 137–152.
- [33] B. Hu, W. Cheng, H. Zhang, G. Sheng, Sorption of radionickel to goethite: effect of water quality parameters and temperature, *J. Radioanal. Nucl. Chem.* 285 (2010) 389–398.
- [34] B. Hu, W. Cheng, H. Zhang, S. Yang, Solution chemistry effects on sorption behavior of radionuclide ^{63}Ni (II) in illite-water suspensions, *J. Nucl. Mater.* 406 (2010) 263–270.
- [35] C.H. Wu, C.F. Lin, P.Y. Horng, Adsorption of copper and lead ions onto regenerated sludge from a water treatment plant, *J. Environ. Sci. Health A* 39 (2004) 237–252.
- [36] C.H. Wu, Studies of the equilibrium and thermodynamics of the adsorption of Cu^{2+} onto as-produced and modified carbon nanotubes, *J. Colloid Interf. Sci.* 311 (2007) 338–346.
- [37] K.F. Hayes, J.O. Leckie, Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces, *J. Colloid Interf. Sci.* 115 (1987) 564–572.
- [38] G. Sheng, J. Hu, H. Jin, S. Yang, X. Ren, J. Li, Y. Chen, X. Wang, Effect of humic acid, fulvic acid, pH, ionic strength and temperature on ^{63}Ni (II) sorption to MnO_2 , *Radiochim. Acta* 98 (2010) 291–299.
- [39] S. Yang, J. Li, Y. Lu, Y. Chen, X. Wang, Sorption of Ni(II) on GMZ bentonite: effects of pH, ionic strength, foreign ions, humic acid and temperature, *Appl. Radiat. Isotopes* 67 (2009) 1600–1608.
- [40] S. Ghosh, H. Mashayekhi, B. Pan, P. Bhowmik, B.S. Xing, Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter, *Langmuir* 24 (2008) 12385–12391.
- [41] K. Yang, B. Xing, Adsorption of fulvic acid by carbon nanotubes from water, *Environ. Pollut.* 157 (2009) 1095–1100.