Colloids and Surfaces A: Physicochem. Eng. Aspects 380 (2011) 16–24

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Impact of environmental conditions on the adsorption behavior of radionuclide ^{63}Ni(II) on γ-Al_2O_3

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ARTICLE INFO

Article history:
Received 31 July 2010
Received in revised form 9 November 2010
Accepted 30 November 2010
Available online 10 December 2010

Keywords:
^{63}Ni(II)
γ-Al_2O_3
Adsorption
pH
Humic substances
Thermodynamic data

ABSTRACT

The fate and transport of toxic metal ions and radionuclides in the environment is generally controlled by adsorption reactions. The removal of ^{63}Ni(II) from wastewaters by γ-Al_2O_3 was studied as a function of various environmental parameters such as shaking time, pH, ionic strength, foreign ions, and humic substances under ambient conditions. The results indicated that the adsorption of ^{63}Ni(II) on γ-Al_2O_3 was strongly dependent on pH and ionic strength. At low pH, the adsorption of ^{63}Ni(II) was dominated by outer-sphere surface complexation and ion exchange with Na^+/H^+ on γ-Al_2O_3 surfaces, whereas inner-sphere surface complexation was the main adsorption mechanism at high pH. The Langmuir and Freundlich models were used to simulate the adsorption isotherms of ^{63}Ni(II) at three different temperatures of 298.15, 323.15 and 343.15 K. The thermodynamic parameters (ΔH°, ΔS° and ΔG°) calculated from the temperature dependent adsorption isotherms indicated that the adsorption process of ^{63}Ni(II) on γ-Al_2O_3 was endothermic and spontaneous.

1. Introduction

Water pollution by hazardous metal ions is a worldwide problem and has aroused widespread concern of scientists and environmentalists. In recent years, the levels of toxic metal ions in surface waters increase obviously due to the pollution caused by industrial and agricultural wastewater discharges. Radionuclides ^{63}Ni(II) ($T_{1/2}$ = 96a) are present in liquid wastes released from pressurized water nuclear power reactors, and ^{63}Ni(II) is widely used in research and medical applications. The adsorption of radionickel to clay or metal (hydr)oxides changes the physical–chemical forms of radionickel and controls the diffusion/migration of radionickel in the environment. Therefore, the research of ^{63}Ni(II) is important for the evaluation of the behavior of radionickel in the natural environment.

Iron and/or aluminum oxides and hydroxides regulate the transport and concentration distribution of cations and anions in natural environments. The distribution and partitioning of reactive substances and other environmental pollutants are regulated primarily by reactions such as adsorption/desorption and precipitation, which occur at the interface between the aqueous solution and minerals [1]. For the reasons mentioned above, the possibilities of applying multifarious metal (hydr)oxides in wastewater disposal have been studied extensively in recent years and many mechanisms have been postulated such as ion exchange, outer-sphere/inner-sphere surface complexation and precipitation [2,3]. Most of the studies presented on this subject were restricted to the adsorption of single metal solutions in the absence of other electrolyte ions. However, the metal of interest in wastewater is usually found to be in a matrix containing various electrolyte ions. The interaction between these charged particles leads to the formation of an electrostatic field with certain intensity around them, which will further modify the behavior of heavy metal ions towards the sorbent materials [4]. Therefore, to better understand the practical application of metal (hydr)oxides as potential sorbents in sewage disposal, it is of great importance to investigate the adsorption behavior of heavy metal ions on metal (hydr)oxides in the presence of various coexisting electrolyte ions.

In this work, γ-Al_2O_3 is used as a sorbent for the removal of ^{63}Ni(II) from wastewater. The concrete objectives of this paper are: (1) to study the influence of different parameters on ^{63}Ni(II) adsorption, such as contact time, pH, ionic strength, coexisting electrolyte ions, humic substances and temperature by using batch technique; (2) to determine the thermodynamic parameters of ^{63}Ni(II) adsorption on γ-Al_2O_3; and (3) to presume and discuss the adsorption mechanism of ^{63}Ni(II) on γ-Al_2O_3.

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0927-7757/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.colsurfa.2010.11.077

Table 1
The concentrations of functional groups of HA and FA calculated from potentiometric titration by using FITEQL 3.1 [6].

	Log K_a			C (mol/g)			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^{-2}	2.71×10^{-2}	0.10

HL_1, HL_2 and HL_3 represent the carboxyl groups (–COOH), the phenolic groups (Ar–OH) and the amine groups ($-NH_2$) of HA and FA, respectively.

2. Experimental

2.1. Materials

The hydrous γ-Al_2O_3 (100–200 mesh) was obtained from the Wu-Xi chemical reagent factory (Shanghai, China). Before its use, the sample was firstly washed with 0.1 mol/L HNO_3, then with 0.1 mol/L NaOH up to pH 10 and finally rinsed with Milli-Q water until the conductivity of the washing solution reaching to that of Milli-Q water [5]. The surface area of the free dried sample determined by the N_2-BET method was 105 m^2/g and average particle radius measured by photon correlation spectroscopy (PCS) was about 150 nm. The alumina was characterized by potentiometric acid–base titration and the point of zero charge of the sample was $pH_{pzc} = 9.2 \pm 0.1$ [5].

Soil humic acid (HA) and fulvic acid (FA) were extracted from the soil of Hua-Jia county (Gansu province, China) and were characterized in detail in early study [6]. The concentrations of functional groups of HA and FA determined by fitting the potentiometric acid–base titration data using FITEQL 3.1 are given in Table 1 [6]. Cross-polarization magic angle spinning (CPMAS) ^{13}C 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. In addition, the weight-averaged molecular weights (M_w) of dissolved HA and FA are evaluated according to the method of Chin et al. [7], and the M_w values of dissolved HA and FA are calculated to be 2108 and 1364, respectively.

All chemicals used in this experiment were purchased in analytical purity and used directly without any further purification. All the reagents were prepared with Milli-Q water.

2.2. Adsorption experiments

First, adsorption kinetics was carried out to achieve the equilibrium time. Experiments were carried out at 298.15 ± 1 K using 200 mL of 120 mg of γ-Al_2O_3 and 0.01 mol/L $NaClO_4$ ionic strength and Ni(II) ion solution containing the different pH (6.5, 7.0, and 7.6) in a 500 mL conical flask. The preliminary studies indicated that the rate of Ni(II) adsorption onto γ-Al_2O_3 is very fast and has no obvious effect on Ni(II) adsorption kinetics. Second, other adsorption of ^{63}Ni(II) on γ-Al_2O_3 was investigated by using batch technique in 10 ml polyethylene centrifuge tubes under ambient conditions. Ionic strengths were adjusted to desired values with 0.001, 0.01, 0.1 M $NaClO_4$ electrolyte solution. The pH was adjusted to the desired value by using negligible amount of 0.01 or 0.1 M $HClO_4$ or NaOH solution. After the suspensions were oscillated for 24 h, the solid and liquid phases were separated by centrifugation at 9000 rpm for 30 min. It was necessary to note that the adsorption of ^{63}Ni(II) on the tube wall was negligible according to the blank experiments (i.e., ^{63}Ni(II) adsorption in the absence of γ-Al_2O_3).

The concentration of ^{63}Ni(II) was analyzed by liquid scintillation counting using a Packard 3100 TR/AB liquid scintillation analyzer (PerkinElmer). The scintillation cocktail was ULTIMA GOLD ABTM (Packard). The amount of ^{63}Ni(II) adsorbed on γ-Al_2O_3 was calculated from the difference between the initial concentration and the equilibrium one. The adsorption percentage (adsorption% = $(C_0 - C_e)/C_0 \times 100\%$) and distribution coefficient ($K_d = (C_0 - C_e)/C_e \cdot V/m$) were derived from the difference of initial concentration (C_0), the final one (C_e) in supernatant after centrifugation, the mass of γ-Al_2O_3 (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 shaking time

The adsorption of ^{63}Ni(II) on γ-Al_2O_3 as a function of shaking time was investigated at different pH values (7.6 ± 0.1, 7.0 ± 0.1, 6.5 ± 0.1). As can be seen from Fig. 1, the adsorption of ^{63}Ni(II) on γ-Al_2O_3 occurs quickly and 5 h is enough to achieve the adsorption equilibrium. The adsorption of ^{63}Ni(II) on γ-Al_2O_3 increases with increasing pH. The functional groups at the γ-Al_2O_3 surface contribute to the uptake of ^{63}Ni(II), and these groups are affected by pH values. The surface properties of γ-Al_2O_3 are influenced by pH values, and thereby influence ^{63}Ni(II) adsorption. The whole adsorption dynamics process can be divided into two distinct steps: an initial fast adsorption, followed by a much slower adsorption. The fast ^{63}Ni(II) removal rate in the beginning is attributed to the rapid diffusion of ^{63}Ni(II) from the solution to the external surfaces of γ-Al_2O_3. The subsequent slow adsorption process is attributed to the longer diffusion range of ^{63}Ni(II) into the inner-sphere pores of γ-Al_2O_3 or the exchange with cations in the inner surface of γ-Al_2O_3. According to the above results, the shaking time is fixed at 24 h in the following experiments to ensure that the adsorption reaction can achieve complete equilibrium.

In order to analyze the adsorption rate of ^{63}Ni(II) on goethite, the pseudo-second-order rate equation is used to simulate the kinetic

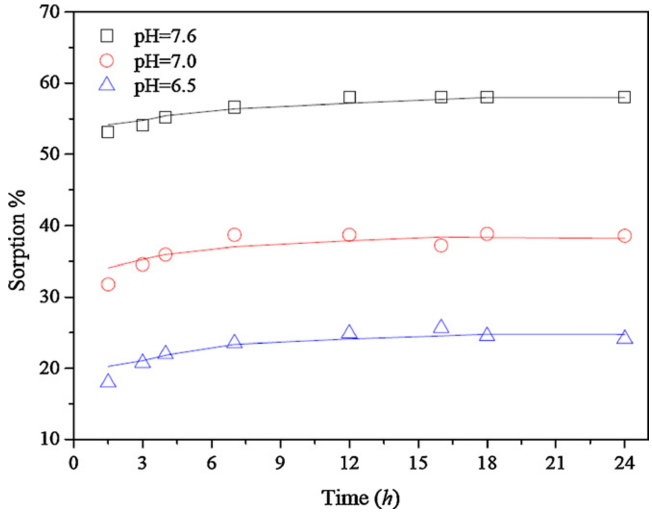

Fig. 1. Variation in adsorption of ^{63}Ni(II) onto γ-Al_2O_3 as a function of shaking time, $C[^{63}Ni(II)]_{initial} = 1.59 \times 10^{-4}$ mol/L, $I = 0.01$ mol/L $NaClO_4$, $m/V = 0.6$ g/L, $T = 298.15 \pm 2$ K.