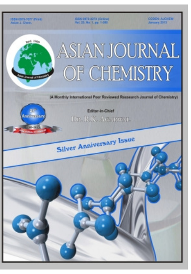
Asian Journal of Chemistry; Vol. 25, No. 4 (2013), 2125-2128

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13355



Kinetic and Thermodynamic Studies on Removal of Selenium from Aqueous Solution by Using Nano-TiO_2

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(*Received*: 29 December 2011; *Accepted*: 17 October 2012) AJC-12295

A novel sorbent, nano-TiO_2 was employed for the removal of selenium from aqueous solution in batch equilibrium experiments, in order to investigate its adsorption properties. The removal percentage of selenium by the sorbent increased with increasing pH in the acidic medium. The adsorption capacities and removal percentage of Se(IV) onto nano-TiO_2 were evaluated as a function of the solution concentration and temperature. The sorption of Se(IV) ions onto nano-TiO_2 followed the second-order rate equation and the Langmuir model could describe the adsorption of nano-TiO_2 to Se(IV) ions successfully over the whole range of concentration studied. The value of standard enthalpy and standard entropy (ΔH^o, $\Delta S^o > 0$) may be interpreted as the endothermic adsorption process. The negative value of ΔG^o showed the adsorptions of Se(IV) by nano-TiO_2 were a spontaneous process.

Key Words: Selenium, Nano-TiO_2, Adsorption, Kinetics, Thermodynamics.

INTRODUCTION

Selenium is a natural trace element found in bedrock, but it is also introduced into the environment by anthropogenic activities, such as mining and combustion of fossil fuels[1,2]. At low concentrations, selenium is an essential micronutrient for mammals, but consumption of quantities exceeding daily recommendations can cause health problems. Its toxicity[3] led the World Health Organization and the European Union to recommend a maximum selenium concentration in drinking water of 10 ppb, while the EPA sets a limit of 50 ppb.

The methods for selenium removal are membrane filtration, microbial reduction and anion exchange. Membrane filtration is expensive, due to low selectivity and fouling problems[4-6]. Microbial treatment, based on reduction to elementary selenium[7,8], is sensitive to oxygen and nitrate and high carbon concentrations are required[9,10]. Ion-exchange resins show selectivity for selenate or selenite[5], but sulfate reduces removal and its precipitation with barium prior to filtration is therefore recommended[11].

The nanometer material is a new functional material, which has attracted much attention due to its special properties. Nano-material is meant clusters of atoms or molecules of metal and oxide, ranging in size from 1 nm to almost 100 nm, falling between single atoms or molecules and bulk materials. Most of the atoms of nano-material is on the surface, where atoms are unsaturated and can easily bind with other atoms and possess high chemical activity. Consequently, nano-material can adsorb selectively metal ions and has a very high adsorption capacity. Besides, the operation is simple, rapid and frees from above mentioned drawbacks. So there is a growing interest in the application of nanoparticles as sorbents[12]. Recently it has been reported that titanium dioxide nanoparticles are used for separation and preconcentration of trace metal ions[13,14]. And we have successfully reported on preconcentration of thallium by nano-TiO_2[15].

In this study, titanium dioxide nanoparticles were employed for the sorption of selenium from aqueous solution. The process was studied in detail by varying the sorption time, pH, selenium concentration, temperature and amount of sorbent. The kinetics and thermodynamics of selenium adsorption on nano-TiO_2 were studied. The results show that the equilibrium time for nano-TiO_2 to absorb selenium is 50 s, the adsorption percentage is 93 % and the adsorption capacity is 32165 μg/g.

EXPERIMENTAL

A stock solution of Se(IV) (1.0000 mg mL^{-1}) was prepared by dissolving 1 g of Se (99.99 % pure, Tianjin Chemical Reagent Co., China) with 10 mL of concentrated nitric acid and 2 mL of (3 + 2) H_2SO_4, then evaporated until without nitric acid. After cooling to room temperature, the solution diluted to a 1 L volumetric flask with doubly distilled water, followed by a model PF6A-2 Non-dispersion Atomic

Fluorescence Spectrophotometer (Beijing Purkinje General Instrument Co., China) analysis.

KBH_4 and HCl (5 %) were used as carrier liquid with current preparation to determine selenium by a model PF6A-2 non-dispersion atomic fluorescence spectrophotometer. A solution of KBH_4 was prepared by dissolving 15.0000 g of KBH\with 100 mL of KOH (5 %), finally diluted to a 1 L volumetric flask with doubly distilled water.

All of the reagents including KBH_4, ammonia, hydrochloric acid, nitric acid and sodium hydroxide, were of analytical grade and obtained from Tianjin Chemical Reagent Co., China. Doubly distilled water was used throughout experiments. Nano-TiO_2 (anatase) that was used as sorbent in this study was provided from Zhoushanmingri Nanometer Material Co. and its particle size was about 10-15 nm.

Procedure: The adsorption experiments were carried out in a series of 50 mL Erlenmeyer flasks containing 0.10 g nano-TiO_2 and 10 mL of 10 mg L^{-1} selenium solution at pH 11. If necessary, an appropriate volume of 0.1 mol/L HCl or NaOH solutions was used to adjust the pH of the solution after addition of nano-TiO_2. The soild/liquid phases were separated by centrifuging at 3000 rpm. The adsorption percentage (ads. %) was calculated as

$$\text{Adsorption percentage} = \frac{(C_i - C_a)}{C_i} \times 100 \tag{1}$$

where C_i and C_a are the initial and the final concentration of Se(IV) in solution phase, respectively.

The fact that q is the amount of Se(IV) adsorbed per unit weight of nano-TiO_2 (μg g^{-1}) was calculated using the equation:

$$q = \frac{(C_i - C_a)v}{m} \tag{2}$$

where m is the mass of the sorbent (g), v is the volume of the solution (mL).

Adsorption isotherm studies were carried out with different initial concentrations of Se(IV) while maintaining the sorbent dosage at constant level. In order to inspect any adsorption of selenium on the container surface, control experiments were carried out without the sorbent. It was found that no adsorption occurred on the container wall.

Kinetic experiments were conducted using a known weight of the sorbent dosage at the different temperatures. After regular intervals of time, suitable aliquots were analyzed for selenium concentration. The rate constants were calculated using the conventional rate expression. The thermodynamic parameters for the process of adsorption were determined at a particular temperature. This procedure was repeated at different temperatures.

RESULTS AND DISCUSSION

Effect of pH: In this study, pH is an important parameter because the pH of solution influences the distribution of active sites on the surface of nano-TiO_2. At the lower pH, the hydrion on the surface of nano-TiO_2 provides the ability of binding anions. The increase of pH leads to the neutralization of surface charge and hydrion is displaced from the surface, so the adsorption of cations onto nano-TiO_2 increases quickly. Fig. 1 shows the effect of pH on the adsorption of Se(IV) by nano-TiO_2. The recovery of selenium increased with an increase in pH. Thus, pH 11 was chosen for the adsorption Se(IV). The adsorption percentage was calculated to be 93 % at pH 11.

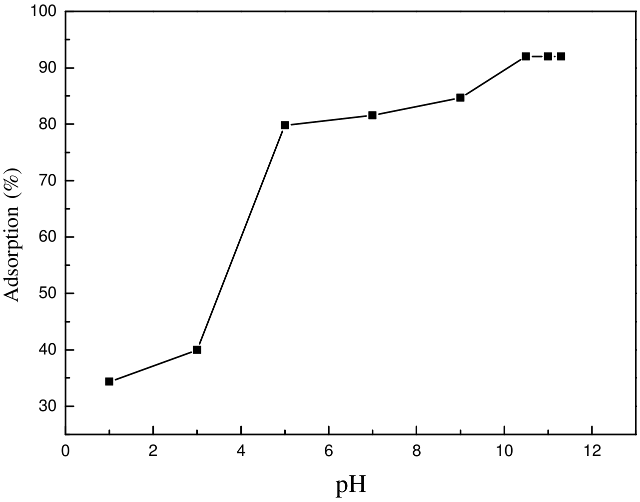

Fig. 1. Effect of pH on the adsorption efficiency of Se(IV) on nano-TiO_2; 100 mg of nano-TiO_2; $C_{Se(IV)}$ 10.0 mg L^{-1}; static for 50 s; temperature 20 ± 0.1 ºC

Adsorption kinetic model: The models of adsorption kinetics were correlated with the solute uptake rate; hence these models are important in water treatment process design. In this study, for a batch of reactions, the adsorption dynamics was followed by conducting the adsorption of Se(IV) on nano-TiO_2 at optimized pH and the sorbent dosage.

Experiments were performed in order to investigate the kinetics of selenium removal by nano-TiO_2.

The sorption kinetics may be described by the pseudo-first-order Lagergren rate model. The equation is as follows[16]:

$$\ln(q_1 - q_t) = \ln q_1 - k_1 t \tag{3}$$

where q_1 and q_t are the amounts of Se(IV) adsorbed on the sorbent (μg g^{-1}) at equilibrium and at time t, respectively and k_1 is the rate constant of the first-order adsorption (s^{-1}). The straight-line plots of ln ($q_1 - q_t$) against t were used to determine the rate constant, k_1 and correlation coefficient, r_1 values of the Se(IV) under different concentration range were calculated from these plots.

The Ho's pseudo-second-order model may also describe the kinetics of sorption of selenium on nano-TiO_2. Thus the kinetic rate law can be rewritten as follows[17]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{4}$$

where k_2 is the rate constant of second-order adsorption (g μg^{-1} s^{-1}). The straight-line plots of t/q_t against t have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data.

The validity of both kinetic models is checked. The results of the kinetic parameters for Se(IV) adsorption are listed in Table-1. Based on the correlation coefficients, the adsorption of Se(IV) is best described by the pseudo-second-order equation.

TABLE-1
KINETIC PARAMETERS FOR Se(IV) ADSORPTION ON NANO-TiO_2 AT THE DIFFERENT TEMPERATURES

T (K)	k_1 (s^{-1})	q_1 (μg g^{-1})	r_1	k_2 (g $μg^{-1}$ s^{-1})	q_2 (μg g^{-1})	r_2
273	0.005458	427.7	0.850	0.0002671	450.8	0.999
293	0.002971	520.5	0.884	0.0003927	467.3	0.999
313	0.002107	511.9	0.862	0.0006057	471.7	0.999

Indicates that model parameters are statistically significant (*t*-test) at 95 % confidence level.

It was possible to calculate the activation energy for adsorption employing Arrhenius equation for the rate constant[18] based on the result in Table-1. Arrhenius equation is as follows:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

where A is the frequency factor (min^{-1}), E_a the activation energy (kJ mol^{-1}), R is the ideal gas constant (J mol^{-1} K^{-1}), T the absolute temperature (K).

Eqn. 5 can be converted into eqn. 6 by taking logarithm

$$\ln k = \ln A - \frac{E_a}{RT} \tag{6}$$

Thus, E_a could be obtained from the slope of the line plotting ln k *vs*. 1000/T (Fig. 2) and the estimated E_a for Se(IV) adsorption on nano-TiO_2 was 14.47 kJ mol^{-1}.

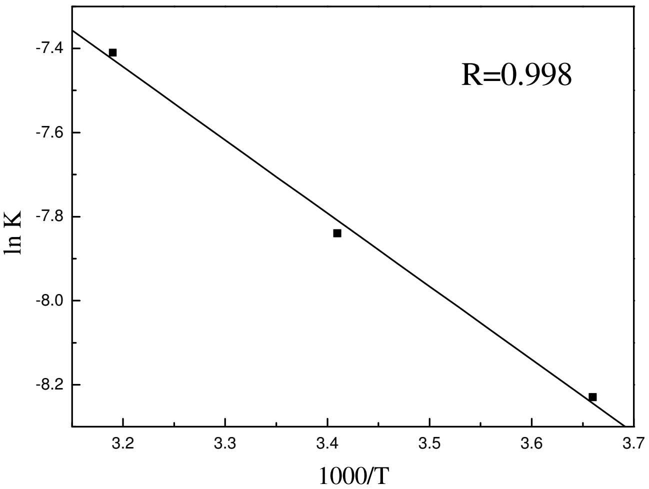

Fig. 2. Plot of ln k *vs*. 1000/T (the points correspond to 273, 293, 313 K); 100 mg of nano-TiO_2; $C_{Se(IV)}$ 10 mg L^{-1}; pH 11

Adsorption isotherm and adsorption capacity: The equilibrium adsorption of Se(IV) on nano-TiO_2 as a function of the initial concentration of Se(IV) is shown in Fig. 3. There was a gradual increase of adsorption for Se(IV) ions until the equilibrium was attained. Adsorption isotherm is important to describe how solutes interact with the sorbent. The Langmuir models are often used to describe equilibrium sorption isotherms. The most widely used Langmuir equation, which is valid for monolayer sorption on a surface with a finite number of identical sites, is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{7}$$

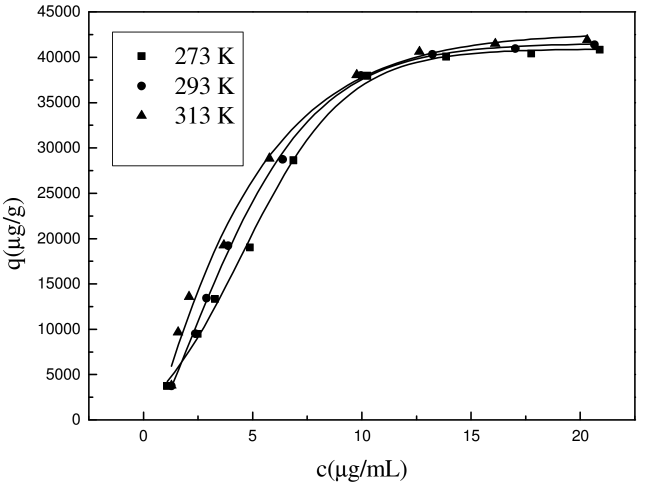

Fig. 3. Isotherm of Se(IV) adsorption on nano-TiO_2 at different temperatures (273, 293, 313 K); 100 mg of nano-TiO_2; the initial Se(IV) concentration range was 0-200.0 mg L^{-1}; static for 50 s; pH 11

where q_{max} is the maximum adsorption at monolayer (μg g^{-1}), C_e is the equilibrium concentration of Se(IV), q_e is the amount of Se(IV) adsorbed per unit weight of nano-TiO_2 at equilibrium concentration (μg g^{-1}) and b is the Langmuir constant related to the affinity of binding sites. A linearized plot of C_e/q_e against C_e gives q_{max} and b (Fig. 4).

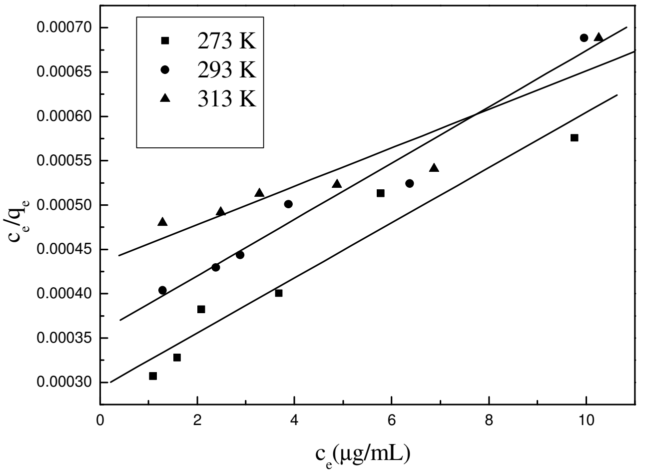

Fig. 4. Langmuir adsorption isotherm at different temperatures (273, 293, 313 K); 100 mg of nano-TiO_2; the initial Se(IV) concentration range was 0-200 mg L^{-1}; static for 50 s; pH 11

The calculated results of the Langmuir isotherm constants are given in Table-2. Fig. 4 shows that the adsorption of Se(IV) on nano-TiO_2 was correlated well ($R > 0.99$) with the Langmuir equation. The maximum adsorption capacity of selenium ions on nano-TiO_2 was 31506, 32165 and 46104 μg/g at 0, 20 and 40 ºC, respectively.

Thermodynamic studies: The experiments were carried out at 273, 293 and 313 K for different concentrations, respectively. The values of ΔHº were calculated from the slopes and intercepts of linear regression of ln C *versus* 1/T using the Clausius-Clapeyron equation[19,20]

$$\ln C = \frac{\Delta H^{o}}{RT} + D \tag{8}$$

TABLE-2
LANGMUIR ISOTHERM CONSTANTS AND CORRELATION COEFFICIENTS AT THE DIFFERENT TEMPERATURES

T (K)	Langmuir equation $\frac{C_e}{q_e}=\frac{C_e}{q_{max}}+\frac{1}{bq_{max}}$	b	q_m (µg/g)	R
273	C/q = 0.00003174C + 0.0002935	0.1059	31506	0.990
293	C/q = 0.00003109C + 0.0003568	0.0890	32165	0.991
313	C/q = 0.00002169C + 0.0004344	0.0500	46104	0.998

Indicates that model parameters are statistically significant (*t*-test) at 95 % confidence level.

where C is the equilibrium concentration of Se(IV) in solution (mg/L) and D is the intercept of the plot of ln C *versus* 1/T. ΔH° was assumed to be constant for a constant surface coverage.

To calculate the values of the other parameters (ΔG°, ΔS°) the following equations were used:

$$K_C = \frac{C_{Be}}{C_{Ae}} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_C \quad (10)$$

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \quad (11)$$

where C_{Be} and C_{Ae} are the equilibrium concentrations of Se(IV) on the sorbent and solution, respectively, K_C is the equilibrium constant, ΔS° is standard entropy, ΔG° is standard free energy. Table-3 represents the estimated thermodynamic parameters for Se(IV) adsorption.

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF Se(IV) ON NANO-TiO_2

T (K)	273	293	313
K_c	19.00	17.37	14.53
ΔG° (kJ mol^{-1})	-3.54	-3.94	-4.94
ΔH° (kJ mol^{-1})	–	22.03	–
ΔS° (kJ mol^{-1} K^{-1})	0.09366	0.08863	0.08617

It can be seen from Table-3 that positive ΔH° indicates that the adsorption reaction of Se(IV) on nano-TiO_2 is endothermic. The free energy value for all the systems are negative and decrease in the value of ΔG° with increase of temperature shows that the reaction is easier at high temperature. Metal ions in aqueous media are hydrated. When the ions get absorbed on the sorbent surface, water molecules previously bonded to the metal ion get released and dispersed in the solution; the results in an increase in the entropy[21].

Conclusion

The experimental results indicate that nano-TiO_2 is an effective sorbent for the adsorption of Se(IV) from aqueous solutions. The percentage of Se(IV) removal from solution by nano-TiO_2 is 93 % at pH 11.0. For all studied systems of kinetics, the pseudo-second-order model provides better correlation of the adsorption data than the pseudo-first-order model. The adsorption isotherms could be well fitted by the Langmuir adsorption isotherm equation. The thermodynamic parameters ΔG°, ΔH° and ΔS° are calculated and the positive values of enthalpy confirm the endothermic nature of adsorption.

ACKNOWLEDGEMENTS

The authors acknowledged the Ankang University Special Foundation of High-level Personnel (No. AYQDZR200933) for financial support. 'The authors also thank our colleagues and other students who participated in this work.

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