



Kinetics and thermodynamics of nickel sorption to calcium–palygorskite and calcium–sepiolite: A batch study

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ABSTRACT

Knowing thermodynamic features of sorption/desorption of metals to/from soil minerals is a very efficient tool to assess and control the fate of these chemicals in the environment. In this batch experiment, we assessed the sorption of nickel (Ni) onto palygorskite and sepiolite at temperatures of 25, 35 and 45 °C. Nickel sorption onto both minerals at the three temperatures was adequately described by the Langmuir sorption model ($R^2 > 0.97$ for palygorskite and $R^2 > 0.84$ for sepiolite). Increasing the temperature from 25 to 45 °C caused an increase in both the maximum adsorption capacity of the solid phase (q_m) and the Langmuir sorption coefficient (K_L), indicating the enhanced sorption potential and stronger bonding of Ni to the minerals. Positive values of enthalpy (ΔH) revealed the endothermic nature of Ni sorption and negative free energy ΔG° indicated that sorption of Ni to palygorskite and sepiolite under standard conditions (25 °C) is spontaneous. Time-dependent sorption data at the three temperatures were adequately described by the first order kinetic model ($R^2 > 0.93$ for both minerals). The rate constant of the reaction and the quantity of Ni sorbed on both minerals at equilibrium increased with increasing temperature. However, the lower activation energy (E_a) for sepiolite compared with palygorskite indicated that Ni was more readily sorbed onto sepiolite.

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1. Introduction

Heavy metals are potentially harmful contaminants in the environment. Anthropogenic activities such as mining, agricultural, and industrial practices are mostly responsible for pollution threatening different ecosystems, living organisms, and human health. Such activities can provide various point and non-point source pollution of heavy metals.

Nickel (Ni) is a heavy metal belonging to group VIII B of the periodic table. A variety of industries, such as electroplating, nonferrous metals mineral processing, dyeing, porcelain enameling, and steam-electric power plants have contributed to the contamination of different water bodies with Ni (Yu and Kaewsarn, 2000). Along with Cu^{2+} , Zn^{2+} , Mn^{2+} and Fe^{2+} , Ni is an essential trace element for plant growth, but at high concentrations, Ni can potentially cause human health problems such as dermal allergies and skin reactions (Environment Agency, 2009; Malkoc, 2006). Excess concentrations of Ni can also adversely affect plants and microorganisms (Khan and Scullion, 2002).

Sorption on clay minerals is a very important process determining the mobility, bioavailability and toxicity of metals in natural environments. An understanding of the mechanisms involved in sorption

phenomenon will also assist in setting up managing programs to control pollution (Khan and Scullion, 2002; Wang et al., 2005).

To understand the fate of heavy metals in the environment, understanding the rate of sorption reactions is crucial. It is frequently reported in the literature that metal sorption reactions are initially fast, taking minutes to hours to complete, but may eventually slow down to days or weeks before equilibrium is attained. The initial fast stages are generally explained by adsorption mechanisms and the final slow phases are attributed to precipitation and absorption processes (Sparks, 2003). Results of a study on sorption kinetics of Ni on kaolinite indicated two apparent steps, an initial fast followed step by a slow step. The former attributed to chemical adsorption and the latter to nucleation and precipitation on the mineral surfaces (Eick et al., 2001).

The effect of temperature on reaction rates is a well-known phenomenon. Many published studies have demonstrated a positive linear relationship between reaction rate and temperature (e.g., Scheckel and Sparks, 2001). Temperature also affects thermodynamics of reactions through its effects on both enthalpy (ΔH) and entropy (ΔS) changes (Cemic, 2005). A better understanding of the thermodynamic processes underlying sorption of metals will assist in the development of innovative tools for assessment and control of the fate and environmental impacts of these chemicals. It is therefore not surprising that there has been growing interest in thermodynamics of sorption processes in recent years (Abdel Salam and Burk, 2008; Ghabbour et al., 2006a,

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2006b; Huang et al., 2007b; Jaman et al., 2009; Kumar et al., 2008; Metwally et al., 2008; Mohapatra et al., 2009; Shen et al., 2009; Srivastava et al., 2007; Çelekli et al., 2011).

Palygorskite and sepiolite are fibrous phyllosilicates that occur frequently in arid regions. Occurrence of palygorskite, and to a much lesser extent sepiolite, has been reported in calcareous soils of arid regions worldwide (Galan, 1996; Khademi, 1997; Khormali and Abtahi, 2003). Significant deposits of these two minerals also occur all around the world, including the United States, China, Senegal, Spain, India, Ukraine, Turkey and Iran (Hojati and Khademi, 2013; Murray and Zhou, 2006). Despite their low CEC, palygorskite and sepiolite are capable of retaining relatively high quantities of heavy metals from aqueous environments due to their specific structure, great surface areas and various functional groups that are responsible for metal sorption (Kocaoba and Akyuz, 2005; Murray et al., 2000; Shirvani et al., 2006). Knowledge of the extent and rate of sorption reactions is, therefore, essential to appropriately evaluate the behavior of metals in the arid region soils. Furthermore, application of the sorption processes by using these minerals is considered as a low cost and effective method which is easily designed and operated for water purification purposes. In both natural and controlled environments, temperature fluctuations are common, which can affect the sorption processes. Information on the effects of temperature on sorption properties of palygorskite and sepiolite in general and on the sorption of Ni on these minerals in particular, however, is scarce. The main objectives of this study were, therefore to (i) assess the effects of temperature on equilibrium Ni sorption onto palygorskite and sepiolite, (ii) determine thermodynamic parameters of the Ni sorption reactions and (iii) investigate the effects of temperature on kinetics of Ni sorption to the fibrous clay minerals.

2. Materials and methods

2.1. Characterization of the minerals

The minerals used in this study were Florida palygorskite (PFI-1, Clay Minerals Society's Source Clays Repository, Purdue University, IN) and Iranian sepiolite from Yazd, Iran. Possible carbonates, organic matter, and iron/manganese oxides were removed using acetate–buffer (pH 5), 30% H₂O₂, and citrate–bicarbonate–dithionate extraction, respectively (Kittrick and Hope, 1963). Impurities in the minerals were characterized using an X-ray diffractometer (XD-610, Shimadzu Co. Ltd., Kyoto, Japan) with Cu-K α radiation.

Cation exchange capacity (CEC) of the minerals measured using the Na-acetate method (Rhoads, 1986) were 19.5 and 6.5 cmol kg⁻¹ for palygorskite and sepiolite, respectively. Palygorskite also had a slightly higher specific surface area (120 m² g⁻¹) compared to sepiolite (102 m² g⁻¹) determined by N₂ adsorption using the Brunauer–Emmett–Teller (BET) method.

In order to standardize the procedure, the minerals were powdered in a mortar and sieved through a 230-mesh standard Nickel-free non-metal sieve of round pores. The minerals were saturated with Ca, using 0.5 M CaCl₂, to homogenize the clay surfaces and to eliminate interference of other metal ions that may have been on the mineral surfaces. CaCl₂ was chosen because it furnishes Ca²⁺ as well as Cl⁻, the same anion present in NiCl₂, which was the source of Ni in the experiments.

2.2. Nickel sorption isotherms

A 0.3-g sample of each mineral was suspended in 30 mL of a 0.01 M CaCl₂ solution containing 0, 5, 10, 20, 40, 60, 80 and 100 mg L⁻¹ Ni (NiCl₂) in 50-mL polyethylene centrifuge tubes. Samples were shaken (180 \pm 2 rpm) for 24 h in an orbital shaker set at 25 \pm 1 $^{\circ}$ C, 35 \pm 1 $^{\circ}$ C, and 45 \pm 1 $^{\circ}$ C. Immediately after shaking, samples were centrifuged at 4000 g for 10 min and the supernatants were separated and analyzed for Ni concentration using an atomic absorption

spectrophotometer (AAS) at a wavelength of 232 nm and with a detection limit of 0.05 mg L⁻¹. The quantity of Ni retained by each mineral at the three temperatures (25, 35, and 45 $^{\circ}$ C) was calculated according to Eq. (1):

$$q_e = (C_i - C_e)V/W \quad (1)$$

where, q_e is the amount of nickel retained by mineral surface at equilibrium, C_i and C_e are the initial and the equilibrium concentrations (mg L⁻¹) of Ni, respectively, V is the volume (L) of the solution, and W is the mass (g) of the sorbent. Visual MINTEQ version 3.0 was used to check supersaturation and precipitation of Ni at the three temperatures.

Analysis of variance (ANOVA) using the PROC MIXED procedure (SAS Institute, 2005) was conducted on sorption data, to determine the temperature, Ni concentration, and mineral type effects and their interactions. Treatment means were compared using Tukey–Kramer test at probability level of $P \leq 0.05$. Shapiro–Wilk's normality test showed normal distribution of sorption data as well as residues showing the homogeneity of variance.

2.3. Nickel sorption kinetics

Thirty milliliters of 0.01 M CaCl₂ solution containing Ni at a concentration corresponding to the maximum sorption capacity of each mineral (estimated from sorption isotherms) were transferred into 50-mL polyethylene centrifuge tubes containing 0.3 g of sepiolite or palygorskite. The resulting suspensions were immediately shaken (180 \pm 2 rpm) at 25, 35, and 45 $^{\circ}$ C. After 0.5, 1.5, 3, 6, 12, 18 and 24 h, samples were centrifuged and supernatants were analyzed for Ni concentration by AAS. Pseudo-first order and pseudo-second order kinetic models were tested for their ability to describe the sorption kinetics.

2.4. Data analysis

Kinetic parameters of pseudo-first-order and pseudo-second-order models and equilibrium sorption parameters of the Langmuir and the Freundlich models were derived from experimental data using nonlinear regression analysis of GraphPad Prism version 5.0 for Windows (Graphpad Software Inc., San Diego, CA). The goodness of fit for each model was evaluated using the coefficient of determination (R^2) and standard error of estimate (SEE).

3. Results and discussion

3.1. Mineral properties

X-ray diffraction (XRD) confirmed the studied clay minerals were mainly palygorskite and sepiolite (Fig. 1). The high intensity characteristic (110) reflection peak of palygorskite at 10.4 $^{\circ}$ showed that palygorskite was the main mineral in the sample (Sheikhhosseini et al., 2013). There were also trace amounts of quartz and feldspar in the palygorskite samples (Fig. 1). A sharp and intense peak at 12.3 $^{\circ}$ in the X-ray diffractogram of the Yazd sepiolite sample indicated that it was also a relatively pure sepiolite. The 4.40 and 2.58 $^{\circ}$ peaks were also related to sepiolite. Some quartz ($d = 4.27$ and 3.33 $^{\circ}$) and dolomite ($d = 2.86$ and 2.39 $^{\circ}$) impurities were also present in the sample (Fig. 1) (Sheikhhosseini et al., 2013).

3.2. Effect of temperature on nickel sorption by palygorskite and sepiolite

The results showed that increase of temperature significantly enhanced the sorption of Ni by the both studied minerals (Table 1). Sorption of Ni on palygorskite increased from 1509 to 2034 mg kg⁻¹ and that of sepiolite from 3078 to 3684 mg kg⁻¹ with raising

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