

Experimental and modeling adsorption of Cs⁺ on bentonite and nanobentonite

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Abstract— The adsorption properties of local bentonite (SemnanIran) and nanobentonite prepared from this bentonite towards Cs⁺ adsorption, were investigated by batch equilibration. The influence of equilibration time, sorption isotherms, kinetic sorption, solution pH and presence of EDTA and NaCl on these properties was studied and discussed. Kinetic data were found to be well fitted with pseudo-second order kinetic model. Cs⁺ is preferably adsorbed by bentonite and nanobentonite. The Freundlich isotherm model has the best fit with experimental data than other sorption isotherm models. The maximum sorption of Cs⁺, representing the highest negative charge density on the surface of the adsorbent was observed at pH 8, where the negative charge density on the surface of the adsorbents was the highest. The lowest observed sorption was observed at pH 12.30 for bentonite. Presence of EDTA and NaCl decreased the amount of Cs⁺ sorption.

Keywords— bentonite; nanobentonite; Cs⁺; Equilibrium isotherm; Kinetics

I. Introduction

¹³⁷Cs (T_{1/2}=30.2 years) and ¹³⁴Cs (T_{1/2}=2.4 years) are important radionuclides in radioactive waste for many reasons: very high solubility, long half-life, and easy incorporation into terrestrial and aquatic organisms (because of its chemical similarity to K) (Vejsada et al., 2005). The bioavailability of Cs in natural systems depends on sorption properties of the solid phases (Bellenger & Staunton, 2008; Vejsada et al., 2005). The sorption of Cs has been studied on many sorbents examining their properties for safety assessment.

The fundamental safety concept for radioactive waste disposal is to isolate the waste from accessible environments for a period sufficiently long to allow substantial decay of the radionuclides and to limit release of residual radionuclides into environment [1]. The long-term safety of repository sites relies on a series of engineered and natural barrier systems. The purpose of engineered barrier is to contain the wastes for a period of time such that short-lived nuclides have been decayed and then limiting the release of surviving radionuclides. The purpose of natural barrier is to retard radionuclide migration so that the radioactive inventory is considerably reduced by decaying and dilution of the most long-lived nuclides [1&2].

Sorption reactions are useful in limiting migration of radionuclides thereby reducing the potential radiological hazard to humans resulting from disposal of radioactive waste (Ibrahim et al, 2008). Sorption models are required to quantify the extent to which this hazard can be reduced [3].

Use of NaCl as de-icing chemical in roads and widespread use of EDTA ethylene diaminetetraacetic acid can lead to their increased concentration in groundwater and other water sources which can form complexes with free metal ions,

thereby preventing precipitation and sorption of metals in clay barrier systems (Furukawa et al., 2007; Darban et al., 2000). The present work investigates adsorption of cesium on bentonite and nanobentonite using batch adsorption method. The primary objective of this work was to study kinetic sorption and sorption isotherms of Cs⁺ on bentonite and nanobentonite. The effect of pH, Eh, NaCl and EDTA on Cs⁺ adsorption were also studied.

II. Materials and methods

Raw bentonite and nanobentonite were used. The clay used in sorption tests were collected from the Semnan Iran deposit. Bentonite content of this clay is > 65 % by weight. Raw clay were dried, crushed, powdered, and sieved through the 80µm sieve and homogenized. The bulk chemical composition of raw clay used were determined by XRF (X-ray fluorescence vacuum spectrograph, Philips) and is listed in Table 1. Mineralogical analysis using X-ray diffraction is presented in Figure 1.

To prepare nano-bentonite, Lagaly method was used which requires removal of carbonated and organic matter as well as reduction of Fe⁺² (Lagaly & Ziesmer, 2003; Tributh & Lagaly).

Chemicals and reagents

All the reagents used in this work were of RA grade chemicals and were used without further purification. Cesium was supplied as cesium nitrate, from Sigma-Aldrich Company.

Batch sorption studies

Batch experiments were performed under kinetic and equilibrium conditions. To determine the pH range at which maximum uptake of Cs⁺ takes place, a series of 50mL Cs⁺ solution (500mg/l) with 1g bentonite were diluted and shaken for 60s to attain equilibrium. Within this time sorption process completed. The suspension obtained was centrifuged to separate the solid from the liquid phase. The clear liquid phases thus obtained were analysed using ICP. The initial pH

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was adjusted to values ranging from 1.90 to 13.0 using dilute solution of nitric acid or sodium hydroxide.

To investigate effects of EDTA and NaCl on Cs⁺ sorption, 50 ml of Cs⁺ solution (500mg/l) was applied to bentonite with increasing amount of EDTA and NaCl. EDTA and chloride concentration were used within the range of 0.001 to 0.01 mol/l, and 0.01 to 0.1 mol/l, respectively. Upon equilibrium, the suspension was centrifuged at 6000 rpm for 30 min.

Table 1: Chemical composition of raw clay

Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	TiO ₂
%Wt.	3.541	1.88	11.189	65.99	0.69	1.43	1.065	1.136

Kinetic experiments

Kinetic studies were performed at room temperature (298 K) using an initial ion concentration of 500 mg/L. For these investigations, 1g of bentonite was brought into contact with 50mL solution containing known concentration of Cs⁺ ions and shaken for different times. The amount of ions sorbed per unit time were determined by using:

$$q_t = (C_0 - C_t) \frac{V}{m}$$

Where C₀ and C_t are the initial and equilibrium concentrations (mg/L) of metal ion in solution, V the volume (L) and m is the weight (g) of the bentonite.

In the experiments of sorption isotherm measurements, 50mL of the Cs⁺ ion solution of varying concentrations (200–800 mg/L) were agitated with 1g of bentonite and nano bentonite (with separately) at room temperature (298K) and at initial pH of 6.0. After the established contact time (1 h) was reached, the suspension was centrifuged and then amount of Cs⁺ in the bentonite phase (mmol/kg) was estimated.

Effect of solution pH

The effect of solution pH was studied within the range 1.80-12.30. Initial concentration Cs⁺ was 500 mg/l, and equilibration time was 1 h.

Effect of EDTA addition

The adsorption of Cs⁺ ions in presence of EDTA was investigated by equilibration of bentonite, with solutions containing 500mg/L Cs⁺ and different concentrations of the complexing agent (0.01-0.001M) at pH 6, for 1 h.

Effect of NaCl addition

The adsorption of Cs⁺ ions in presence of NaCl was investigated by equilibration of bentonite, with solutions containing 500mg/L Cs⁺ and different concentrations of the NaCl (0.1-0.01M) at pH 6, for 1h.

III. Results and discussion

Effect of pH

The effect of pH on Cs⁺ sorption from aqueous nitric solution using bentonite was investigated over the pH range from 1.80 to 12.30 and the results are shown in Figure 2.

The q_e is relative low at acid pH and this may be attributed to H⁺ competition for available Cs⁺ sorption sites. H⁺ ions are effective in removing Cs⁺ ions that are fixed at the lattice edges of clay minerals [8]. In addition at the acid pH levels there is a greater dissolution of clay minerals with a destruction of some of the sites responsible for fixing Cs⁺ resulting to lower cesium sorption [9]. The maximum sorption of Cs⁺ results was observed at pH= 8. High sorption levels of Cs⁺ indicate a high fixation capacity of the studied soil for cesium ions in this pH region.

The increase in q_e, pH 8 could be attributed to significantly high negative charge density of clay minerals at that pH. As pH increased, the number of protons on the soil surface decreased and more electrostatically attractive surface to the cations became available, allowing more Cs⁺ to be sorbed. At high pH, Cs sorption on bentonite may be dominated by surface complexation (Missana et al., 2004) and thus the distribution coefficient of Cs⁺ is higher at high pH values than those at low pH [10]. According to Oscarson et al less Cs⁺ is sorbed at pH of 5 than at pH 8.5.

Significantly less Cs sorbed by the studied soil at the alkali regain up pH 10 to 12.30. A possible formation of carbonate or hydroxide species at this high pH level is likely to caused complexation of Cs⁺ ions resulting to lower Cs amount of available for sorption.

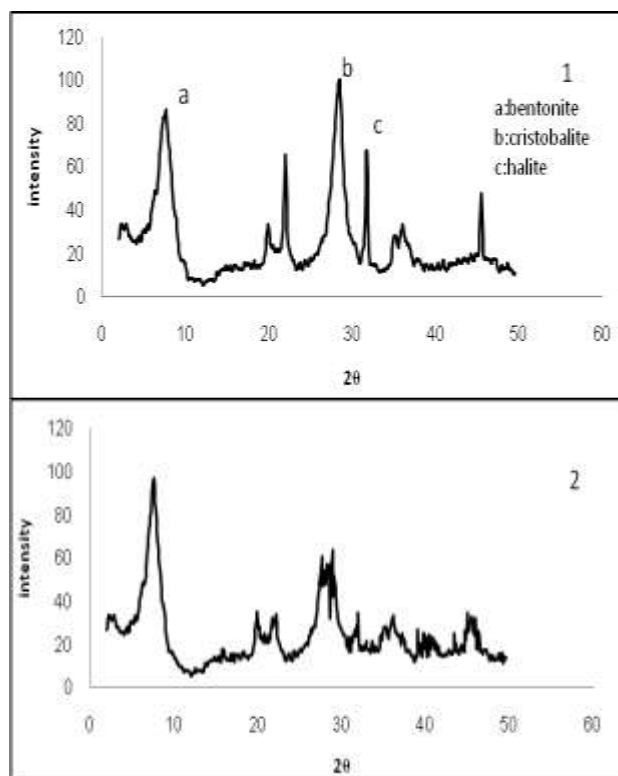


Figure1. X-ray diffraction pattern for (1) raw bentonite and (2) nanobentonite

Sorption equilibrium experiments

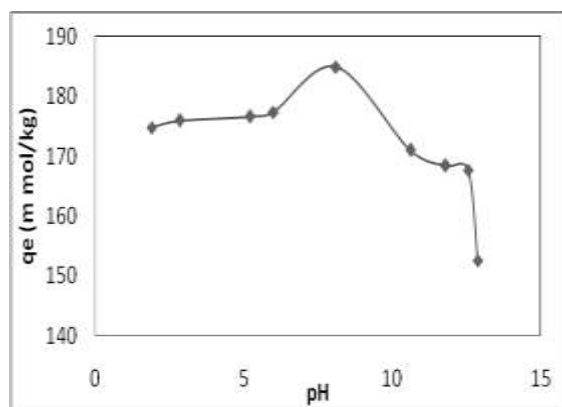


Figure 2: The q_e values of Cs as a function of pH of bentonite.

Sorption isotherms

Equilibrium sorption isotherms are one of the most important data to understand sorption. Adsorption equilibrium is usually described by an isotherm equation whose parameters state the surface properties and affinity of the sorbent, at a fixed temperature and pH. An adsorption isotherm describes the relationship between the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Sorption isotherms of Cs⁺ ions from aqueous nitric solutions onto bentonite sorbent were determined and shown in Figure 3 – Figure5. The isotherm parameters were evaluated using Langmuir, Freundlich, and D-R. (Dubinin–Radushkevich) isotherm models.

Langmuir isotherm model

The linearized form of the Langmuir equation is given by the following formula (El-Kamash, 2008):

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{Q_0 b}\right) + \left(\frac{1}{Q_0}\right) C_e$$

Where C_e is the equilibrium concentration of metal ion in equilibrium solution (mmol/l), q_e the amount of metal ion sorbed per unit weight of sorbent (mmol/kg), Q_0 the monolayer adsorption capacity (mmol/kg) and b is a constant related to the free energy of adsorption ().

The graphic presentations of C_e/q_e versus C_e give straight lines for Cs⁺ ions sorbed onto bentonite and nanobentonite, as represented in Figure3 and Figure4, confirming that this expression is indeed a reasonable representation of chemisorptions isotherm. The numerical values of constants Q_0 and b evaluated from the slope and intercept of each plot are given in Table2. The value of saturation capacity Q_0 corresponds to the monolayer coverage and defines the total capacity of the sorbent for Cs metal ion. As it can be seen from Table2 the monolayer sorption capacity (Q_0) values define the total capacity of the prepared bentonite and nanobentonite towards Cs⁺ ions. (Ibrahim et al., 2008)

$$R_L = \frac{1}{1 + bC_0}$$

Freundlich isotherm model

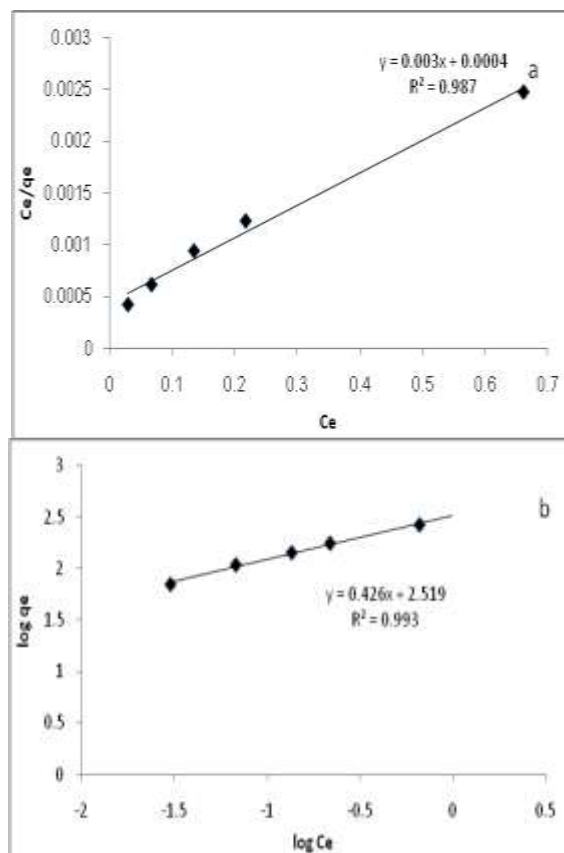
The logarithmic form of Freundlich equation may be written as (El-Kamash, 2008)

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$$

Where K_f is constant indicative of the relative adsorption capacity of the sorbent (mmol/kg) and $1/n$ is the constant indicative of the intensity of sorption process. The pictorial illustration of $\log q_e$ versus $\log C_e$ is shown in Figures 3 and 4 which suggests that the sorption of Cs⁺ ions obey Freundlich isotherm over the entire range of sorption concentration studied. The sorption isotherms for Cs⁺ ions onto both bentonite and nanobentonite were determined.

Table 2: Langmuir, Freundlich and D-R isotherm parameters for the sorption of Cs⁺ onto bentonite and modified bentonite

	Langmuir model parameters				Freundlich model parameters		
	Q_0 (mmol/kg)	b (l/mmol)	R_L	R^2	K_f (mmol/kg)	n	R^2
Bentonite	333.33	7.5	0.41497	0.98	330.36	2.3	0.993
nanobentonite	333.33	25	0.11738	0.96	503.5	2.7	0.997



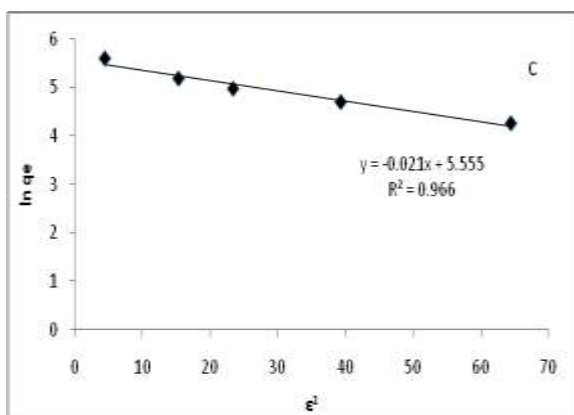


Figure3 Isotherm plots of Cs^+ ions sorbed onto bentonite at 298K:

(a) Langmuir; (b) Freundlich; (c) D–R.

Effect of EDTA

The effect of EDTA on Cs^+ sorption is presented in Figure 8. EDTA acts as complexing agent for Cs^+ ions therefore free Cs^+ concentration becomes reduced resulting in decrease in Cs^+ sorption. The dominant form of EDTA complex for many metal ions is $\text{M-EDTA}(z_4)^+$ at pH 4.5 and 7.0 (Furukawa et al., 2007). Polyvalent metal ions readily form $\text{M-EDTA}(z_4)^+$, while Rb^+ and Cs^+ are dissolved as free metal ions under this condition since their EDTA complexes are not very stable therefore EDTA have low affect on Cs^+ sorption.

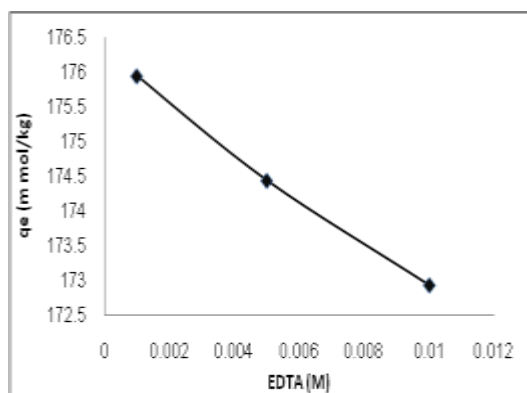


Figure4: Effect of EDTA concentration on Cs^+ sorption

Effect of NaCl

The effect of NaCl on Cs^+ sorption is presented in Figure 9. Ion exchange is one of the most important processes of adsorption on bentonite. In natural environment, the liquid phase composition may significantly influence cesium adsorption on clay minerals, especially due to the presence of ions that can compete in adsorption process. The most important competitive ions for cesium adsorption are NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} . On the other hand NaCl is a complexing agent. The role of exchangeable cations could be successfully interpreted by analyzing their influence on the reaction mechanism of adsorption of dye cations (Darban et

al., 2000). The aggregation of dye cations takes place almost instantaneously after the clay dispersion is mixed with the dye solution. The cation aggregation probably proceeds in the vicinity of clay particles in the zones of the electrical double layer and precedes adsorption. The dye aggregates are often unstable and after adsorption on the clay surface decompose with time. Parameters characterizing the electric double layer are crucially dependent on the type and number of ions present. For example, the polarizing power of the ions greatly affects the polarity of water, which may be essential for dye aggregation. The aggregation of the dye cations is a consequence of energetically disadvantageous interactions between relatively hydrophobic molecular planes of heteroaromatic groups of dye cations and polar water molecules. Therefore the dye aggregation in solutions increases with the polarity, i.e., the dielectric constant, of the solvent and increases with the presence of salts. Effects of salts on the aggregation of thiazine dyes were studied and explained in terms of the formation of hydration shells around the ions forming the salt).

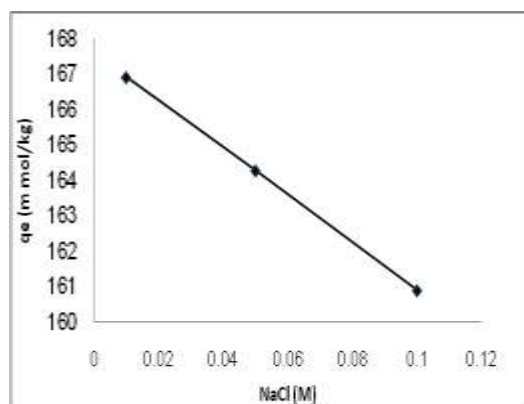


Figure5: Effect of NaCl concentration Cs^+ sorption on bentonite

Conclusion

Bentonite and nanobentonite were investigated as inorganic ion exchange material for the removal of cesium ions from aqueous nitric solutions. The kinetics of both metal ions was experimentally studied and the obtained data were analyzed using simple kinetic models. Results explained that the pseudo second-order sorption mechanism is predominant and the overall rate constant of each sorption process appears to be controlled by chemical sorption process. Equilibrium isotherms have been determined and tested for different isotherm expressions and the sorption data were successfully modeled using Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) approaches. Freundlich have been found best consistent with experimental data. Based on the D–R model expression, The values of mean free energy, E , of sorption was in all cases in the range of <8.0 kJ/mol, which physical forces may affect the sorption mechanism and k_f parameter (Freundlich) were 330 and 503 mmol/kg for bentonite and nanobentonite, respectively. Maximum sorption

of Cs^+ for bentonite was observed at pH 8. In cases of EDTA and NaCl addition, amount of sorption were decreased with increase in EDTA and NaCl concentrations. Also the best result was achieved in Eh value of 0.

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