Distribution coefficient of Nickel on Alluvium soil of Anarak Nuclear Repository in Iran

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ABSTRACT

In this study, the distribution coefficient of Nickel on the Anarak nuclear repository was studied considering the effects of contaminant concentration, soil particle size, and soil/solution ratio. For this purpose, two experiments were designed. The soil sample was collected from inside the trench of the Anarak Nuclear Repository by the channel method and its characteristics was determined using ASTM method. The batch method was employed while different concentration and volume of contaminant solution was added to the soil and was stirred for 24 h at room temperature. The nickel distribution coefficient in the concentration range of 0.05-1 mg/L was determined as 13.63-997.89 mL/g with the mean value of 256.24 mL/g. Adsorption behavior of Nickel in Anarak soil is better followed by Langmuir adsorption isotherm. The results indicated the contrary conversion of K_d with soil particle size and soil/solution ratio. Moreover, the results confirmed the high dependency of K_d on the contaminant concentration.

Keywords: Adsorption, Anarak, Distribution coefficient, Nickel, soil

I. Introduction

With the development of near-surface disposal facilities, releases of radionuclides and heavy metals and movement in the geosphere and groundwater systems which could contaminate the local drinking water and also the food chain, should be considered in the safety assessment calculations [1]. The metals and nuclide's interaction in soils and their mobility in aquatic environments are characterized by solid–liquid distribution coefficient, K_d, that is used in the transport and risk assessment modeling due to their conceptual simplicity. K_d represents the partition of the solute in the matrix and pore water and is defined as the ratio of the metal concentration in the solid phase to that in solution at equilibrium [2,3].

The values for Kd are extremely variable, not only vary significantly for different contaminants, but also vary with key environmental attributes such as aqueous and solid-phase chemistry and the experimental method used for its quantification [4]. Kd is affected by soil mineralogy (clay content and type, iron oxides and hydroxides), organic matter content, and soil geochemistry (pH, presence of colloids, presence of counter-ions), [5] while the key variables are considered as pH, clay content and organic carbon content of soil [4].

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Whereas K_d values for different radionuclides and heavy metals are reported in the literature, an evident discrepancy is observed between the data, which can be related to the soil characteristics. Environmental Protection Agency of United States (EPA) explicitly states that utilization of the generic or default Kd values for predicting the absolute impacts of contaminant migration can result in a significant error. As a result, for site-specific calculations, Kd values measured at site-specific conditions are absolutely essential [6]. The Batch method is known as the most common laboratory method through the well-known procedures for determining K_d values [7,8]. In the EPA method, one of the most common variations of the batch K_d procedure is the concentration of the dissolved contaminant. In contrast, the other variations can be considered as the ratio of solids to liquid and liquid composition [6].

The objective of this study was to establish the distribution coefficient of nickel in representative soil of Anarak Nuclear Repository, which is the primary low and intermediate level radioactive waste disposal site located in Anarak District, Isfahan Province, Iran. The release of nickel in ecosystems are in significant consideration because of the observed effects on the human nervous system [9,10]. Two experiments were designed to determine the K_d values by the batch method considering the concentration of contaminant, the ratio of solid to liquid ratio, and the size of soil particles as the variables.

II. Material and methods

Representative soil of Anarak Nuclear Repository was provided from sampling inside the trench by the channel method. No. 5 (4 mm) and No. 200 (0.075 mm) stainless steel sieves were utilized to establish the soil with arbitrary size particles. $Ni(NO_3)_2 . 6H_2O$, with chemical purity of more than 99%, was purchased from Sigma Aldrich company. High precision scales, shaker, and centrifuge devices manufactured by Sartorius (Germany), Memmert (Germany) and Mistral (USA) Company were used for batch tests. ICP-AES, optima 7300 DV (USA), ICP MS ELAN DRC 9000 (PerkinElmer, USA), and AAS Varian Spectra AA 200 (USA) were used for the measurement of ions and anions. XRD, Philips PW 1800 (Netherlands), and XRF, Philips 2404 (Netherlands) were utilized for the determination of the main minerals as well as the oxide compounds in the soil.

II. I. Soil sampling

The soil sample was collected from inside the trench of Anarak Nuclear Repository, up to a depth of 1 meter by the channel method. The geographic coordinates of the sampling point are presented in Table 1.

Table 1. Geographic coordinates of sampled soil (TR3).

Longitude (UTM)	Latitude (UTM)
729800	3694745

II. II. Soil and groundwater characteristics

The soil sample was air-dried and passed through the No.5 stainless steel sieve, and stored in plastic bags until the time of the investigation. The main characteristics of the sample, including soil texture, pH, density, moisture content, Organic Matter Content (OM), Cation Exchange Capacity (CEC), and ingredient minerals which are effective in the distribution coefficient of heavy metals, were assessed.

The soil characteristics were all determined using the standard methods of ASTM [11-15]. While, soil texture analysis was carried out using the hydrometric method by determining the amounts of clay, silt, and sand, CEC of the soil was specified using the Bower method [16]. The amounts and types of constituent minerals were assigned using X-ray diffraction (XRD) analysis and X-ray fluorescence (XRF) analysis.

According to the effect of groundwater on the distribution coefficient of heavy metals, the groundwater of the Anarak nuclear repository was prepared and filtered through a 0.45-µm polycarbonate membrane, and the number of ions and anions were determined by ion chromatographic analysis (IC) and atomic emission spectrometry (AES) before using in the distribution coefficient measurement.

II. III. Distribution Coefficient determination

The distribution coefficient of Nickel in the Anarak alluvium soil was obtained by the two designed experiments, which are described below.

III. Experimental
Experiment 1

In this experiment, the distribution coefficients were evaluated by the batch method, whereas the effects of contaminant concentration and soil particle size were studied. For this purpose, soil granulation was performed using No. 5 and 200 sieves. Thus, experiments were accomplished with three different types of granulation: natural (passing through No. 5 sieve), the soil between No. 5, and No.200 sieves, and fine-grained (passing through No. 200 sieve).

Then, 0.5 g of the three soil granulations were weighed and placed in polyethylene containers while 20 ml of different concentrations of 50, 100 and 200 mg/l of nickel solution was added to each granulation. The samples were shaken at room temperature (25 °C) at 200 rpm for 24 hours, and then centrifuged at 5000 rpm for 15 minutes. The supernatant solution was separated and the amount of nickel was analyzed by ICP analysis. The distribution coefficient was calculated utilizing Equation1 [17]:

$$K_d = \frac{B - A}{A} * \frac{V}{m} \tag{1}$$

Where B is the amount of nickel before ion exchange in the soluble phase (mg/L), A is the amount of nickel after ion exchange in the soluble phase (mg/L), V is the volume of solution containing contaminants (mL), and M is the weight of the exchanger (g).

Experiment 2

In the second experiment, the effects of contaminant concentration and the soil/solution ratio were investigated using the batch method. Six different concentrations of nickel, all below one mg/L, were selected. To 0.5 g of soil, other volumes of contaminant solution (10, 15, and 20 ml) with specific concentrations were added and shaken for 24 h at room temperature. The supernatant solution was separated after centrifuging at 5000 rpm for 15 minutes. The distribution coefficient was again calculated using Equ.1. All experiments were repeated three times.

IV. Results
IV. I. Soil analysis

While various studies have been performed to determine the distribution coefficients of radionuclides and heavy metals, the results show the values with different ranges depending on the soil type and the physical and chemical conditions of soils. Therefore, in this study, according to the EPA instructions, soil and groundwater of Anarak Nuclear Repository were analyzed. The result of soil analysis covering pH, %TNV (percentage of equivalent calcium carbonate), %OM, CEC, specific gravity, moisture content, and soil texture is represented in Table 2. Furthermore, XRD analysis for clay minerals is indicated in Fig. 1.
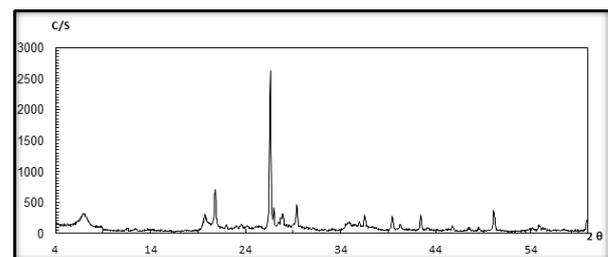

**Fig.1**. XRD analysis for clay minerals of soil sample.

According to the results of XRD analysis, the main minerals of Anarak nuclear repository soil include montmorillonite (32%), quartz (24%), albite (15%), muscovite (8%), microcline (6%), calcite (6%), Chlorite (5%), and gypsum (2%). Furthermore, the results of XRF analysis show that the principal soil oxides include SiO_2, Al_2O_3, CaO, and Fe_2O_3 with a weight percentages of 64.23%, 8.70%, 7.20%, and 3.35%, respectively.

Table 2. Soil characteristics of Anarak Nuclear Repository.

pH	7.56
% TNV	51.19
% OM	0.26
CEC (meq/100g)	8.85
Specific gravity (g/cm³)	2.74
Moisture content	1.77
% clay	78
% silt	10
% sand	12
Texture	S. L

III. II. Distribution coefficient determination

The values of nickel distribution coefficient achieved in the first experiment for different contaminate concentrations and soil particle size are demonstrated in Fig. 2.
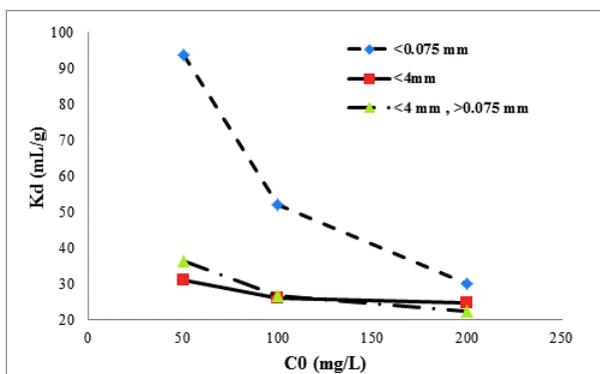
Fig. 2. Distribution coefficient of nickel versus its primary concentration for different soil particle size.

The results of the second experiment are indicated in Fig. 3. The amounts of nickel absorbed in the soil (yield from the second experiment) are also presented in Table 3.

The absorption data of nickel was examined for the kind of adsorption isotherms, linear, Freundlich, and Langmuir, followed by equations 1, 2, 3, respectively. Where, a and b are constants, k_f and n show the adsorption capacity, and binding strength and q_m and k_L are the maximum adsorption and the constant related to binding energy [18,19].
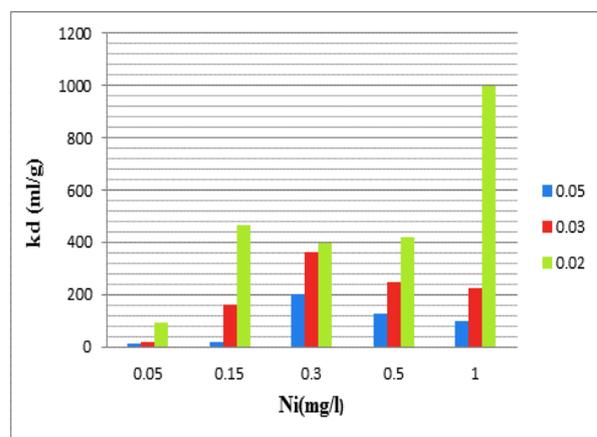
$$q = a + b \, (c_e) \tag{2}$$

$$Ln(q_e) = Ln(k_f) + \frac{1}{n} \, Ln(c_e) \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L q_m} \cdot \frac{1}{c_e} \tag{4}$$

Table 3. The amounts of nickel absorbed (μg in g soil).

Soil/solution ratio	nickel concentration (mg/L)				
	0.05	0.15	0.3	0.5	1.0
0.025	1.04	6.04	7.44	10.86	18.96
0.033	0.42	4.14	5.82	7.98	13.05
0.050	0.3	1.5	3.82	5.06	8.2

Fig. 3. Distribution coefficient of nickel based on primary nickel concentration for different soil/solution ratios.

In Langmuir adsorption isotherm, the dimensionless parameter R_L is defined to evaluate the optimal adsorption as follow:

$$R_L = \frac{1}{1 + k_L c_0} \tag{5}$$

Where, C_0 is the maximum initial concentration of the absorbed component in milligrams per liter. So that $R_L > 1$ and $R_L < 1$ show undesirable and desirable adsorption, respectively, and $R_L = 0$ is defined as irreversible adsorption.

The results show that the adsorption behavior of nickel in soil is better followed by Langmuir adsorption isotherm. Langmuir absorption equation for nickel, and Langmuir isotherm parameters are displayed in Table 4.

IV. Discussion

In this study, the distribution coefficient of nickel in Anarak Nuclear Repository soil was calculated for different concentrations of contaminant, soil particle size, and soil/solution ratio. The results of the first experiment indicated the increment of

distribution coefficient with the reduction of nickel concentration, where the concentrations of the contaminants were selected between 50-200 mg/L. However, for the concentration range below one mg/L (second experiment), no regular variations of the distribution coefficient in terms of concentration were observed. The low K_d values at high concentrations can be related to the sites available on the soil surface, which may be saturated and, as a result, cannot adsorb more.

This result is under the results of Reddy and Dunn's (1986) study which shows the increment of nickel distribution coefficient with the reduction of initial nickel concentration in the solution. According to the results of this group, the values of the distribution coefficient for the concentrations studied in this research and for loamy sandy soil (the texture of Anarak soil) should be about 20-30 ml/g. In this study, the average value obtained for natural soil is equal to 27.28, which is inconsistent with the results of this group [1].

Table. 4. Linear, Freundlich and Langmuir absorption equations of Ni on Anarak alluvium soil for different soil/solution ratio.

		linear	Freundlich	Langmuir
	Equation	y = 0.0169x + 0.002	Y=0.9129x -3.8387	y = 48.321x – 37.383
	Correlation factor	0.9643	0.9309	0.9687
Soil/solution ratio=0.025	q_m (mg /g soil)			0.026
	K_L			0.78
	R_L			0.56
	Equation	y = 0.0121x + 0.0014	y = 1.097x -4.0259	y = 125.04x – 226.01
	Correlation factor	0.9492	0.8959	0.9529
Soil/solution ratio=0.033	q_m(mg /g soil)			0.004
	k_L			1.80
	R_L			0.35
	Equation	y = 0.0081x + 0.0005	y = 1.1159x - 4.5389	y =174.1x – 232.79
	Correlation factor	0.958	0.9639	0.9837
Soil/solution ratio=0.05	q_m (mg /g soil)			0.004
	K_L			1.34
	R_L			0.42

The effect of particle size was also showed the growth of the distribution coefficient with the diminution of particle size. However, this subject is not so consistent for the distribution coefficient of nickel for soils with the particle sizes of <4 mm and <4 mm, >0.075 mm. The increment of nickel distribution coefficient with the reduction of soil particle size may be related to various reasons such as the growth of cation exchange capacity, the increase in the amount of clay minerals, organic matter, oxides and hydroxides of iron and manganese, and so on. While reducing the particle size, the percentage of clay minerals such as montmorillonite increases. Montmorillonite is the main component of bentonite and has high adsorption and swelling. This clay mineral has exchangeable Na$^+$ positive ions in its structure, which ion exchange with water-soluble ions such as nickel and cause its adsorption.

The distribution coefficient of nickel was reduced when the soil/ solution ratio was increased, which complies with ^{137}Cs distribution coefficient fluctuation with the soil/solution ratio [20]. As expected, the amounts of nickel absorbed highly increase with the growth of its concentration which confirms the observation of the previously reported literature [1,21]. The adsorption of Ni by soil is also enhanced with the diminution of the soil/solution ratio. The results indicated that the soil/solution ratio could affect the parameters of adsorption isotherms as well as the distribution coefficient. The value of R_L for all soil/solution ratios is achieved below one that can show the desired adsorption.

The results of the first and second experiments for the same soil/solution ratio (0.025) and soil particle size, by the batch method, represent high dependency of the distribution coefficients on the contaminant concentrations. The values achieved are exhibited in Table. 5.

Table. 5. The values of distribution coefficient (ml/g) gained in this study for the soil/solution ratio of 0.025 and natural soil.

Experiment 1 (concentration range: 50-200 mg/l)			Experiment 2 (concentration range: 0.05-1mg/l)		
max	min	Mean value	max	min	Mean value
33.73	21.79	26.95	997.89	94.54	474.19

Numerous studies have been performed for the determination of nickel distribution coefficient in different soils (Table. 6) [4,18,21-28]. Regarding the high difference in these values and EPA recommendation to the deployment of the site-specific values, in this study, the distribution coefficient of nickel in Anarak soil at different conditions was investigated. The median values obtained in this study were compared with the other database.

In 1990, Thibault et al. measured the distribution coefficient of nickel and a number of the other elements in 20 samples of Canadian agricultural soil. Shepard et al. determined the distribution coefficients of a number of elements in the soil of seven sites in the Farsmark and Simpovarp regions of Sweden, in 2009. This group expressed pH, organic carbon content and the clay and sand percentage of soil as the parameters affecting the distribution coefficient while pH and clay content attributed to the greatest effect [5]. Garcia et al. also presented the values of nickel distribution coefficient in soil based on soil type and pH. According to their research, the most important factors affecting the distribution coefficient were soil type, pH and amount of soil organic matter.

In 2013, Baraz et al. measured the distribution coefficient of cobalt and nickel in 21 samples of East Amazon soil by the batch method and based on the adsorption isotherm [6]. For this purpose, the contact time of 24 hours was considered. These values are provided for concentrations less than 5 mg / L. The results showed that the pH and the

amount of oxide in the soil have a greater effect on the distribution coefficient of than the amount of soil organic matter. The results of the mentioned researches as well as the amounts achieved in this study are presented in Table. 6. It should be noted that the results of this study presented in the table are only the obtained values from the second experiment.

Table. 6. Comparison of the distribution coefficients of nickel obtained in this study with the other database.

database	Nickel distribution coefficients		
	K_d-GM	K_d-max	K_d-min
Tibault et al. 1990	300-1100		
IAEA 1994	300		
Yu 2001 (RESRAD)	1000		
Sheppard et al.2009	980	3800	**450**
Gil-Garcia et al. 2009	280	7250	**3**
Braz et al. 2013	23.7	524.2	**47**
This study	256.24	997.89	**13.63**

The values of the obtained distribution coefficient for Ni are much lower than the values given by the International atomic energy and the amounts recommended by the RESRAD software. These values, however, are much similar to the K_d best estimates presented by Garcia and his colleagues, but they are still lower [28]. The difference between the values of this study with the other previously reported studies can be related to the soil and groundwater characteristics, contact time, the method of measurement and so on. The results of Reddy and dunn's (1986) study on the determination of Ni K_d indicated that sandy loam with low exchange capacity possesses the lowest

K_d value. Hence, the lower values may be related to the soil texture (sandy loam) assessed in this study.

V. Conclusion

In this study, the distribution coefficient of nickel was surveyed. The results show that the values of K_d are relevant to the primary concentration of the metals. In the concentration range of 50 to 200 mg/l, the mean value of nickel distribution coefficient was obtained as 37.94 ml/g. The data show the inverted change of K_d with the concentration. Following the above results, in the concentration range of 0.05-1.0 mg/l, the mean value of the nickel distribution coefficient was determined as 256.24 ml/g. However, in this concentration range, regular variations did not observe. Furthermore, the results indicated the growth of Kd with the reduction of soil particle size. The adsorption of nickel increases with the increment of their concentration and diminution of soil/solution ratio. Adsorption behavior of nickel in Anarak soil is better followed by Langmuir adsorption isotherm. The results indicated that the soil/solution ratio could affect the parameters of adsorption isotherms and the distribution coefficient. The values of the obtained distribution coefficients are much lower than the values of IAEA and RESRAD but are much similar to the K_d best estimates presented by Garcia and his colleagues.

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