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EQUILIBRIUM AND KINETIC STUDIES ON THE REMOVAL OF HEAVY METAL IONS WITH NATURAL LOW-COST ADSORBENTS

Adsorption isotherms and kinetics of the removal of heavy metal ions (Ni, Pb, Zn) from aqueous solutions by natural adsorbents (zeolite, bentonite, clay) were investigated in a lab-scale batch study. The effect of various parameters such as adsorbent dosage, initial concentration of heavy metal ions, temperature, and agitation time were studied to optimise the conditions. Under those optimized conditions (180 rpm agitation rate, 120 min agitation time, pH 4.0, 298 K, 100 mg/dm³ initial adsorbate concentration), the removal percentages of heavy metal ions for natural adsorbents have been determined. The adsorption mechanisms and characteristic parameters of the process were analyzed by two and three parameter isotherm models (Langmuir, Freundlich, Temkin, Redlich–Peterson, Toth and Sips), and kinetic models (Lagergren’s pseudo-first order, Ho and McKay’s pseudo-second order). Adsorption thermodynamics of heavy metal ions (changes of standard enthalpy, entropy and free energy) on zeolite, bentonite and clay were also studied at 298, 318 and 338 K.

1. INTRODUCTION

Heavy metals have been immoderately released into the environment due to rapid industrial development and cause a major problem worldwide. The pollution of heavy metal ions can arise from many sources but most commonly arises from metal plating, mining activities, pesticides, battery production, tanneries and photographic industries, etc. [1]. Heavy metal ions are reported priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [2]. Heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed [3]. Several methods have been employed to remove heavy metal ions from wastewater such as precipitation, flotation, ion exchange, adsorption, membrane-

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-related processes, electrochemical technique and biological processes [4]. In regards of its simplicity and high-efficiency characteristics even for a minute amount of heavy metal ions, adsorption is considered a better technology. Basically, adsorption is a mass transfer process from the liquid phase to the surface of a solid, and adsorbate becomes bound by physical and/or chemical interactions. In recent years, the search for low-cost adsorbents that have metal binding capacities has intensified. Materials locally available in large quantities such as natural materials can be utilized as low-cost adsorbents [5]. Natural zeolite, natural bentonite and natural clay can be evaluated as appropriate low cost adsorbents due to their physical and chemical properties as large specific area, cation exchange capacity, and adsorptive affinity for organic and inorganic ions.

Natural zeolites are aluminosilicates with a cage-like structure suitable for ion exchange due to isomorphous replacement of Al^{3+} with Si^{4+} in the structure, giving rise to deficiency of positive charge in the framework [6]. Bentonite is a clay consisting essentially of smectite mineral of the montmorillonite group [7]. Clay minerals with the negative charged structure gives the capability to attract metal ions [8]. In particular crystalline zeolites are some of the most effective cation exchangers known and they have two to three times the cation exchange capacity (CEC) than that of most smectites and vermiculite [9]. Zeolites, bentonites and clays are easily available, naturally occurring structured and phyllosilicate minerals.

Even a number of studies are already available which deal with elimination of heavy metal ions using various kinds of adsorbents, this work attempts to summarize recent studies in the removal of Pb, Ni and Zn using zeolite, bentonite and clay and compare the results with the present study. Based on the above-mentioned facts, the specific objectives of this study were: (1) to investigate the adsorption capacity of natural zeolite, natural bentonite and natural clay in removal of Pb, Ni and Zn from the aqueous solution; (2) to compare the performance and effectiveness of the studied low-cost natural materials in present study with literature; (3) to determine the effect of adsorbant dosage, contact time, initial concentration of heavy metal ions and temperature on the adsorption capacity of the used adsorbents; (4) to study the applicability of various two and three-parameter isotherm models and kinetic equations for determination of the adsorption mechanisms and characteristic parameters for the present application and (6) to determine adsorption thermodynamics of heavy metal ions on the used low-cost adsorbents.

2. EXPERIMENTAL

Adsorbents. In this study, natural zeolite, natural bentonite, and natural clay materials used as adsorbents for the adsorption of the heavy metal ions were obtained from the Rota Mining Incorporated Company and Evginler Mineral Crushing Limited

Company. Prior to the adsorption process, adsorbents were washed with distilled water to eliminate impurities, dried at 103 °C for 24 h, and then sieved to get desired sizes. The results of several geotechnical analyses and the chemical composition of adsorbents [10] are given in Table 1.

Table 1
Chemical composition of the studied liner materials [10]

Liner materials	Chemical composition [%]							
	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	MgO	Na ₂ O	K ₂ O	TiO ₂
Clay	0.11	23	2.4	62	0.5	0.02	2.3	1.25
Bentonite	2.4	18.10	2.66	69.51	4.5	0.02	2.2	0.03
Zeolite	3.4	11.8	1.7	71	1.4	0.4	2.4	0.10

According to the Soil Classification System (USCS), the clay material used in this study belongs to the class of CL-Class clays ($w_L < 50\%$) such as low plasticity clays and inorganic clays, silty clays, gravelly clays and sandy clays. As seen in Table 2, the present clay material has the clay content of 35% and silt content of 65% based on the soil grading curve [11]. Based on the USCS, it can also be specified as CL-Class low plasticity silty clay. Likewise, according to the USCS, the bentonite used as an other liner material in this work belongs to the class of CH-Class clays ($w_L > 50\%$) such as clays and inorganic clays of high plasticity. The present bentonite material has the clay content of 89% and a silt content of 11% (Table 2).

Table 2
Geotechnical properties of the clay material used

Property	Clay	Bentonite	Zeolite
Specific weight, g/cm ³	2.63	3.75	2.08
Clay content, %	35	89	9
Silt content, %	65	11	91
Liquid limit (w_L), %	33	382	65
Plastic limit (w_P), %	17	53	NP ^a
Plasticity index ($IP = w_L - w_P$), %	16	329	NP ^a
Activity coefficient	0.46	3.62	NS ^b
Swelling potential	Low	Very high	NS ^b

^aNP – non-plastic.

^bNS – non specified.

Based on the USCS, it can be classified as CH-class high-plasticity clay. Moreover, the tests of consistency limits showed that plastic limit and plasticity index could not be obtained for the zeolite material indicating a non-plastic (without plasticity) soil

type. The present zeolite material has the silt content of 91%, and it can be specified as MH-Class non-plastic silty soil according to the USCS [10].

Reagents. The stock solutions containing 1000 mg/dm³ of Ni, 1000 mg/dm³ of Pb or 1000 mg/dm³ of Zn were prepared by dissolving 4.05 g NiCl₂·6H₂O, 1.6 g of Pb(NO₃)₂ and 2.6 g of ZnCl₂ in 1 dm³ of distilled water, respectively. In this study, the concentrations of Ni, Pb and Zn prepared from the stock solutions ranged from 100 to 500 mg/dm³, from 50 to 500 mg/dm³, and from 25 to 100 mg/dm³, respectively.

Batch adsorption experiments. Batch adsorption experiments were carried out by allowing an accurately weighed amount of adsorbents to reach equilibrium with Ni, Pb and Zn solutions of various initial concentrations at 298, 308 and 318 K. Known weights of adsorbents were added to 250 cm³ conical flasks, each containing 100 cm³ of solution. The bottles were shaken in a temperature-controlled shaker (Gallenkamp Orbital Incubator) at a constant speed of 180 rpm. Equilibrium period was determined by preliminary experiments at 298 K. At the end of the equilibrium period, the contents of the bottles were filtered and the supernatant was subsequently analyzed for residual concentration of Ni, Pb, and Zn with an atomic absorption spectrophotometer.

In adsorption isotherm studies, solutions with various initial concentrations were added, pH was not adjusted and the equilibrium time was set at 120 min, which was determined by preliminary experiments. Each experiment was duplicated under identical conditions. The amount of heavy metal ions in the solid phase q_e (mg/g) was calculated by the equation

$$q_e = V \frac{C_0 - C_e}{m} \quad (1)$$

where C_0 and C_e are the amounts of initial and retained heavy metal ion concentrations in the solutions at time t (mg/dm³), respectively, V is the volume of the solution (dm³) and m is the weight of the adsorbent (g).

Kinetic studies were performed following a similar procedure with three adsorbents at 298 K, pH of the solutions was not adjusted, and the initial concentration was set as 100 mg/dm³ for Ni, Pb and Zn. The uptake of the adsorbate at time t , q_t (mg/g) was calculated by the following equation:

$$q_t = V \frac{C_0 - C_t}{m} \quad (2)$$

where C_t is the concentration of the adsorbate (mg/dm³) in the solution at time t .

3. RESULTS AND DISCUSSION

3.1. EFFECT OF ADSORBENT DOSAGE

In the experimental studies, the optimum adsorbent dosage for heavy metal ions removal was investigated with an initial adsorbate (Ni, Pb, Zn) concentrations of 100 mg/dm^3 at 298 K. The effect of the adsorbent (natural zeolite, natural bentonite, natural clay) dosages on the adsorption of heavy metal ions is shown in Fig. 1. Adsorbent dosages were varied in the range of $1\text{--}20 \text{ g/dm}^3$ for all the three adsorbents. The time required to reach equilibrium was determined to be 120 min in preliminary studies. It can be concluded from Fig. 1 that the removal of heavy metal ions increases with the increase in adsorbent dosages. The increase in adsorption efficiency with the adsorbent dosage may be attributed to a higher surface area and the availability of more adsorption sites, as reported by other authors [8, 12, 13].

As can be seen in Fig. 1, the adsorbed amount increases with adsorbent concentration but this increase does not show a linear trend. This result is consistent with the results obtained by several authors [14–16]. It can be indicated from the results that the optimum zeolite dosages for Ni, Pb and Zn were determined to be 10, 6 and 6 g/dm^3 , bentonite dosages 10, 1.2 and 5 g/dm^3 and clay dosages 6, 10 and 10 g/dm^3 . For higher than those dosages, no significant changes were observed in heavy metal ions removal efficiencies.

3.2. EFFECT OF INITIAL CONCENTRATION AND CONTACT TIME

Figures 2–4 present the plot of heavy metal ions removal versus contact time for natural adsorbent at 298 K with a contact time of 120 min, at initial concentrations between $100\text{--}500 \text{ mg/dm}^3$, $50\text{--}500 \text{ mg/dm}^3$, $25\text{--}100 \text{ mg/dm}^3$ concentrations for Ni, Pb and Zn, respectively. Heavy metal ions removal efficiency was strongly correlated with increase in contact time. Rapid removal was noticed initially which declined gradually until reaching equilibrium and remained constant thereafter. The initial rapid phase may be explained by availability of more vacant sites at the initial stage. In the last stage, a plateau is seen to be reached for all curves representing that the adsorbent is saturated at this stage, as similarly reported by Hameed et al. [14]. Results showed that the removal efficiencies of heavy metal ions by natural adsorbents decreased as the initial concentration increased. These results are consistent with the results obtained by Peric et al. [6]. It is noted that described procedure of removal of heavy metal ions is the most efficient in processes containing lower pollution concentrations [6].

3.3. ADSORPTION ISOTHERMS

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Several two and three parameter models of adsorption have been published in order to describe experimental results. In this study, two and three parameter isotherm models (Langmuir, Freundlich, Temkin, Redlich–Peterson, Toth, and Sips) have been utilized to describe the adsorption equilibrium of heavy metal ions onto natural adsorbents.

Isotherm studies were conducted at the effective initial pH of 4, agitation rate of 180 rpm and equilibration time of 120 min. The batch isothermal data fitted to the six models used in this study solved by using the curve fitting toolbox of MATLAB program. The residual degrees of freedom (R^2) of the obtained models were calculated so as to evaluate the goodness of fit. The correlation coefficients and constants of adsorption isotherm models are given in Tables 3–5.

3.3.1. TWO-PARAMETER ISOTHERMS

Langmuir isotherm further based on the assumption that all the adsorption sites are energetically identical (monolayer adsorption) and adsorption occurs on a structurally homogeneous adsorbent. In its formulation, binding to the surface is primarily by physical forces and implicit in its derivation is the assumption that all adsorption sites have equal affinities for adsorbate molecules and that the presences of adsorbed molecules at one site do not affect the adsorption of molecules at an adjacent site [13, 16]. The Langmuir isotherm is defined as:

$$q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e} \quad (3)$$

where Q_0 is the maximum pollutant uptake (mg/g); k_L – the Langmuir equilibrium constant (dm^3/mg), q_e (mg/g) and C_e (mg/dm^3) are the amount of pollutant adsorbed per unit mass of adsorbent and pollutant concentration in solution at equilibrium, respectively.

As can be seen from Tables 3–5, the Langmuir model effectively described the adsorption data for Ni and Zn with all R^2 values greater than 0.90. The adsorption isotherms of Ni and Zn exhibited Langmuir behavior which indicates a monolayer adsorption. The maximum adsorption capacities of Ni, Pb and Zn at 298 K were obtained by utility of bentonite as adsorbents. Q_0 values were found to be 62.89, 158.73 and 18.30 mg/g for Ni, Pb and Zn onto bentonite, respectively. According to the Q_0 (mg/g) parameter, the sorption efficiency of Ni and Pb may be ordered in the he following sequence: bentonite > zeolite > clay while sorption of Zn in the following one: bentonite > clay > zeolite.

Table 3

Isotherm model parameters for heavy metal ions adsorption on low-cost adsorbents at 298 K

Model	Parameters	Zeolite			Bentonite			Clay		
		Ni	Pb	Zn	Ni	Pb	Zn	Ni	Pb	Zn
Langmuir	Q_0	30.03	56.99	6.25	62.89	158.73	18.30	8.25	20.85	15.82
	k_L	0.04	0.12	0.11	0.02	0.04	0.09	0.03	0.06	0.01
	R^2	0.93	0.97	0.97	0.98	0.84	0.96	0.98	0.99	0.91
Freundlich	k_F	5.17	15.61	1.37	5.72	35.94	5.06	0.91	2.65	0.38
	n	3.24	3.97	2.79	2.36	3.95	3.76	2.48	2.11	1.33
	R^2	0.99	0.94	0.99	0.97	0.98	0.99	0.99	0.99	0.93
Temkin	a_T	1.17	3.53	1.37	0.22	3.23	1.56	0.17	0.68	0.24
	b_T	5.10	2.79	19.15	1.80	1.15	7.20	11.69	5.40	9.72
	R^2	0.98	0.98	0.99	0.97	0.95	0.99	0.99	0.98	0.85
Sips	k_S	4.72	11.85	1.32	2.45	35.85	4.52	0.36	2.08	–
	b_S	0.40	0.66	0.48	0.77	0.24	0.46	0.78	0.71	–
	a_S	0.06	0.18	0.09	0.03	0.12	0.14	0.03	0.06	–
	R^2	0.99	0.99	1.00	0.98	0.98	0.99	0.99	1.00	–
Redlich–Peterson	k_{RP}	6178	10.16	2.67	1.76	45.65	462	0.25	2.37	482.0
	a_{RP}	6408	0.28	1.43	0.07	0.98	2454	0.06	0.03	2189
	g	0.37	0.90	0.71	0.82	0.79	0.50	0.84	0.72	0.08
	R^2	0.66	0.98	0.99	0.98	0.96	0.55	0.99	0.99	0.94
Toth	A	29.80	58.27	6.07	67.59	168.2	18.30	9.00	47.34	–
	B	21.21	6.03	5.99	35.52	1.78	7.12	48.69	2.96	–
	d	0.96	0.89	0.92	0.91	0.50	0.91	0.99	0.42	–
	R^2	0.93	0.98	0.97	0.98	0.92	0.96	0.99	0.99	–

The Freundlich isotherm is originally empirical in nature but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface. Freundlich isotherm model is represented as follows [17];

$$q_e = k_f C_e^{1/n} \quad (4)$$

where k_f is the Freundlich constant (dm^3/g) and n is the Freundlich exponent. A greater value of k_f indicates a higher adsorption capacity. The value of the exponent n gives an indication on the favorability of adsorption. The values of n in the range of 2–10 represent good adsorption characteristics, 1–2 – moderately difficult, and lower than 1 – poor. At 298 K, adsorption capacity of Pb on bentonite has the maximum k_f value 35.94 mg/g as compared with adsorption capacities of other heavy metal ions onto natural adsorbents and that of Pb on zeolite and clay. As can be seen from Tables 3–5, natural zeolite and natural bentonite are good adsorbents for Ni, Pb and Zn ($2.367 < n < 3.977$). Natural

clay is also a good adsorbent for Ni and Pb but adsorption process is moderately difficult for Zn onto clay.

Table 4

Isotherm model parameters for heavy metal ions adsorption on low-cost adsorbents at 318 K

Model	Parameters	Zeolite			Bentonite			Clay		
		Ni	Pb	Zn	Ni	Pb	Zn	Ni	Pb	Zn
Langmuir	Q_0	30.30	51.81	3.15	67.11	156.30	16.31	15.69	20.20	8.53
	k_L	0.05	0.02	0.10	0.01	0.04	0.03	0.03	0.20	0.01
	R^2	0.92	0.91	0.95	0.97	0.87	0.99	0.99	0.97	0.97
Freundlich	k_F	5.26	7.26	0.86	2.53	33.33	1.99	1.62	4.75	0.27
	n	3.20	3.01	3.51	1.83	3.83	2.56	2.33	2.45	1.48
	R^2	0.99	0.98	0.99	0.99	0.98	0.99	0.97	0.99	0.99
Temkin	a_T	1.50	1.99	1.47	0.11	2.38	0.29	0.25	2.55	0.18
	b_T	5.17	3.65	39.62	1.71	1.13	6.76	6.77	5.98	14.56
	R^2	0.98	0.88	0.98	0.95	0.98	0.99	0.99	0.99	0.94
Sips	k_S	5.44	7.46	0.80	2.15	34.83	1.19	0.60	5.24	–
	b_S	0.08	0.29	0.02	0.60	0.36	0.66	0.89	0.58	–
	a_S	0.39	0.03	0.14	0.01	0.12	0.05	0.03	0.15	–
	R^2	0.99	0.98	0.99	0.99	0.99	1.00	0.99	0.99	–
Redlich–Peterson	k_{RP}	4524	153.60	2.66	–	–	0.84	0.49	–	623.40
	a_{RP}	3292	20.98	2.74	–	–	0.15	0.04	–	2633
	g	0.42	0.67	0.74	–	–	0.79	0.94	–	0.29
	R^2	0.70	0.98	0.99	–	–	1.00	0.99	–	0.99
Toth	A	29.41	63.53	3.76	–	–	16.16	15.76	–	–
	B	14.75	8.19	2.84	–	–	32.62	34.92	–	–
	d	0.94	0.63	0.63	–	–	0.99	0.99	–	–
	R^2	0.93	0.93	0.97	–	–	0.99	0.99	–	–

The Temkin isotherm is based on the assumption that decrease in the heat of sorption is linear rather than logarithmic, unlike the Freundlich equation. The heat of sorption of all the molecules in the layer would decrease linearly with coverage depending on sorbate–sorbent interactions. The Temkin isotherm has been used in the following form:

$$q_e = \frac{RT \ln(a_t C_e)}{b_t} \quad (5)$$

where b_t is the Temkin constant related to the heat of sorption (J/mol); a_t – the Temkin isotherm constant (dm³/g), R – the gas constant (8.314 J/(mol·K)) and T the absolute temperature (K). The parameters of the Temkin model as well as the correlation coefficients are given in Tables 3–5. The Temkin isotherm can describe adequately the ad-

sorption isotherm of heavy metal ions on low-cost adsorbents except for Zn adsorption on clay.

Table 5

Isotherm model parameters for heavy metal ions adsorption on low-cost adsorbents at 338 K

Model	Parameters	Zeolite			Bentonite			Clay		
		Ni	Pb	Zn	Ni	Pb	Zn	Ni	Pb	Zn
Langmuir	Q_0	32.57	25.39	1.35	62.11	172.4	13.97	16.20	21.79	6.24
	k_L	0.05	0.06	0.23	0.01	0.03	0.04	0.03	0.18	0.02
	R^2	0.92	0.51	0.96	0.94	0.88	0.98	0.99	0.98	0.88
Freundlich	k_F	6.27	8.81	0.53	2.02	28.90	2.32	1.81	4.44	0.32
	n	3.35	4.83	4.51	1.77	3.31	2.97	2.38	2.17	1.75
	R^2	0.99	0.87	0.97	0.98	0.99	0.95	0.96	0.97	0.91
Temkin	a_T	2.47	12.89	5.55	0.10	1.13	0.45	0.28	2.03	0.21
	b_T	5.16	7.36	108.0	1.88	0.93	8.40	6.57	5.27	19.37
	R^2	0.97	0.77	0.98	0.92	0.93	0.98	0.99	0.98	0.8
Sips	k_S	6.50	1.24	0.54	3.57	27.62	0.71	0.53	4.63	–
	b_S	0.08	0.02	0.52	0.31	0.23	0.91	0.99	0.74	–
	a_S	0.38	0.86	0.29	0.10	0.09	0.05	0.03	0.16	–
	R^2	0.99	0.92	0.98	0.98	0.99	0.98	0.99	0.99	–
Redlich–Peterson	k_{RP}	4439	22.38	0.64	–	–	–	0.51	–	–
	a_{RP}	3415	2.34	0.82	–	–	–	0.03	–	–
	g	0.39	0.81	0.87	–	–	–	1.01	–	–
	R^2	0.63	0.83	0.98	–	–	–	0.99	–	–
Toth	A	32.24	46.46	1.40	–	–	–	16.28	–	–
	B	14.59	5.87	2.96	–	–	–	31.07	–	–
	d	0.95	0.54	0.85	–	–	–	0.99	–	–
	R^2	0.93	0.75	0.97	–	–	–	0.99	–	–

If the two-parameter models used in this study are compared, the Freundlich and Temkin models are more suitable than the Langmuir model for the description of the experimental data of the study.

3.3.2. THREE-PARAMETER ISOTHERMS

Redlich and Peterson [18] developed an empirical isotherm advanced with respect to those of Langmuir and Freundlich, incorporating the features of the two isotherms into a single equation. This three-parameter isotherm can be represented as [18]:

$$q_e = \frac{k_{RP} C_e}{1 + a_{RP} C_e^g} \quad (6)$$

where k_{RP} is the Redlich–Peterson isotherm constant (dm^3/g), a_{RP} is another constant (dm^3/mg), and g is an exponent taking values between 0 and 1. There are two limiting behaviors: Langmuir form for $g = 1$, and Henry's law form for $g = 0$. The isotherm parameters and R^2 values are given in Tables 3–5. The g values obtained for Ni and Pb removal on bentonite and clay and Pb and Zn removal on zeolite were close to unity. Therefore, the Langmuir equation could precisely depict the equilibrium data over the concentration range in this study [14].

Derived from the potential theory, the Toth isotherm has been proven to be useful in describing adsorption in heterogeneous systems [19]. This isotherm can be represented by the following equation [20]:

$$q_e = \frac{AC_e}{(B + C_e^D)^{1/D}} \quad (7)$$

where A is the maximum adsorption capacity (mg/g), B is the Toth model constant and D is the Toth model exponent. It is obvious that for $D = 1$, this isotherm reduces to the Langmuir isotherm [21]. The Toth model constant B and exponent D values are given in Tables 3–5. In this study, the D values were found to be close to unity except for Pb adsorption on bentonite and clay and Zn adsorption on clay. Results indicated that the heavy metal ions adsorption data correlated well with the Toth model and as confirmed by high determination coefficient ($R^2 = 0.90$) values.

The Sips or Langmuir–Freundlich isotherm has the following form [19, 22]:

$$q_e = \frac{k_s C_e^{b_s}}{1 + a_s C_e^{b_s}} \quad (8)$$

where k_s (dm^3/g) and a_s (dm^3/mg) are the Sips model constant and b_s is the exponent. At low adsorbate concentrations, it effectively reduces to a Freundlich isotherm and thus it does not obey the Henry's law. At high adsorbate concentrations, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm [13, 16, 19]. The Sips equation fits adequately the experimental results. Based on the maximum adsorption capacity values (Tables 3–5), the results are identical to those obtained using the Langmuir isotherm. The parameter k_s changes similarly as the constants k_L of the Langmuir equation.

If just the three-parameter models used in this study are compared, the Sips and Redlich–Peterson models are more suitable than the Toth model for the description of the experimental data.

3.4. ADSORPTION KINETICS

Adsorption kinetics is used to explain the adsorption mechanism and characteristics. Pseudo-first order and pseudo-second order kinetic models were applied to experimental data in order to investigate the kinetics of sorption of heavy metal ions onto natural adsorbents and kinetic parameters were calculated by the MATLAB program. Kinetic study were conducted in optimum conditions determined in the preliminary experiments (initial concentration – 100 mg/dm³, solution volume – 100 cm³, temperature – 298 K, zeolite dosages for Ni, Pb and Zn – 10, 6 and 6 g/dm³, bentonite dosages – 10, 1.2 and 5 g/dm³, and clay dosages 6, 10 and 10 g/dm³, respectively). Kinetic model equations used in this study and the calculated kinetic parameters are given in Table 6.

Table 6

Kinetic parameters for heavy metal ions adsorption onto low-cost adsorbents at 298 K

Order	Kinetic parameters	Zeolite			Bentonite			Clay		
		Ni	Pb	Zn	Ni	Pb	Zn	Ni	Pb	Zn
Pseudo-first	k_1	0.0270	0.0209	0.2897	0.0217	0.0218	0.2706	0.0193	0.0322	0.2525
	q_e	8.9948	19.439	5.37	14.963	80.409	14.17	5.4738	8.7988	4.45
	R^2	0.5953	0.7743	0.8767	0.8973	0.5874	0.6221	0.5932	0.6411	0.9063
Pseudo-second	k_2	0.1345	0.0202	0.1175	0.0219	0.0071	0.0571	0.0832	0.2689	0.9162
	q_e	8.9384	19.096	5.3000	14.629	79.441	14.025	5.4016	8.7691	4.4409
	R^2	0.9847	0.9767	0.9620	0.9737	0.9651	0.9502	0.9881	0.9418	0.9725

3.4.1. PSEUDO-FIRST-ORDER REACTION KINETIC

The pseudo-first order equation or the so called Lagergren equation can be expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (9)$$

where k_1 is the adsorption rate constant, q_t is the amount of heavy metal ions adsorbed at time t (mg/g) and q_e is the amount of heavy metal ions adsorbed at saturation. The integrated form of the equation is

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (10)$$

The plots of $\log(q_e - q)$ versus t give a straight line, and k_1 and q_e values can be determined from its slope and intercept. Figure 5 shows the plots of the linearized form of the pseudo-first-order equation. Kinetic parameters along with correlation coefficients of the kinetic models are shown in Table 6.

3.4.2. PSEUDO- SECOND ORDER REACTION KINETIC

The pseudo-second-order kinetic equation was first proposed by Blanchard et al. [23] and since then it has been frequently employed to analyze sorption data obtained from various experiments as reviewed by Ho et al. [24]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (11)$$

The linearized form of the equation is obtained as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

where q_e is the amount of the solute sorbed at equilibrium (mg/g), k_2 is the equilibrium rate constant of pseudo-second order model (g/mg min). The q_e and k_2 values of the pseudo-second-order kinetic model can be determined from the slope and the intercept of the plots of t/q versus t , respectively. Figure 5 gives the results of the linearized form of the pseudo-second-order kinetic model. The calculated q_e values are closer to the experimental data than the calculated values of pseudo-first-order model. Therefore, the adsorption of heavy metal ions can be approximated more favorably by the pseudo-second-order model. Correlation coefficients as shown in Table 6 are also considerably higher for pseudo-second-order kinetic model as compared with that for pseudo-first-order kinetic model reinforcing the applicability of this model.

3.5. THERMODYNAMIC STUDIES

Standard change in free energy G of the adsorption can be calculated from:

$$\Delta G^\circ = -RT \ln K \quad (13)$$

where T is the absolute temperature and R is the gas constant.

Using the K values determined from the adsorption isotherms, the corresponding values of ΔG° can be determined at various temperatures. ΔG° is the function of standard change in enthalpy of adsorption (ΔH°) as well as standard change in entropy (ΔS°)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

If equation (13) is inserted in equation (14), it becomes

$$\ln K = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (15)$$

ΔH° and ΔS° can be determined from the slope and the intercept of the linear plot of $\ln K$ versus $1/T$. The equilibrium constants obtained from the Langmuir model at 298, 308, and 318 K were used to determine the standard changes of the Gibbs free energy. The values of the thermodynamic parameters at 298–338 K are given in Table 7.

The negative value of ΔH° suggests the exothermic nature of the adsorption while its positive value points to the endothermic nature of the adsorption. It can be concluded from Table 7 that adsorption of all the heavy metal ions on bentonite has exothermic nature while adsorption of all the heavy metal ions on clay has endothermic nature. It can also be seen that Pb and Zn adsorption on zeolite has exothermic nature as Ni adsorption on zeolite has endothermic nature (Table 7). Basically, the heat evolved during physical adsorption is of the same order of magnitude as the heat of condensation, i.e., 2.1–20.9 kJ/mol, while the heat of chemisorption generally falls into the range of 80–200 kJ/mol [25]. Therefore, it seems that heavy metal ion adsorption onto natural low-cost adsorbents is of physical nature except for Zn adsorption on clay. Zn adsorption onto clay would be attributed to a type of transition between physical and chemical adsorption rather than a pure physical or chemical adsorption process.

4. CONCLUSIONS

In this study, heavy metal ions (Ni, Pb, Zn) adsorption onto natural low-cost, abundant and locally available adsorbents, zeolite, bentonite and clay were studied at 298–338 K. The adsorption mechanisms and characteristic parameters for the present application were also explored as an important objective using various isotherm and kinetic models. The optimum conditions for heavy metal ions removal by zeolite, bentonite and clay were found to be: pH = 4.0, agitation rate = 180 rpm and equilibration time = 120 min. Optimum zeolite dosages for Ni, Pb and Zn were obtained to be 10, 6 and 6 g/dm³, bentonite dosages 10, 1.2 and 5 g/dm³ and clay dosages 6, 10 and 10 g/dm³, respectively. Among the two-parameter isotherms, the experimental data showed better fits with the Freundlich and Temkin isotherm equations. Three-parameter isotherms had higher determination coefficients than two-parameter isotherms. The Sips and Redlich–Peterson isotherms were found to be the best-fitted three-parameter isotherm models to describe the experimental data.

The applicability of all isotherm models implies that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions studied. The adsorption of heavy metal ions is thus complex, involving more than one mechanism. Adsorption kinetics was found to follow both first and second-order rate expressions. Among these kinetic models, the experimental data showed better fits with pseudo-second order model with considerably higher correlation coefficients. The

present results on temperature effect show that adsorption of all the heavy metal ions on bentonite has exothermic nature while their adsorption on clay has endothermic nature. It can also be seen that Pb and Zn adsorption on zeolite has exothermic nature as Ni adsorption on zeolite has endothermic nature. Heavy metal ion adsorption onto natural low-cost adsorbents has physical nature except for Zn adsorption on clay. Zn adsorption onto clay would be a type of transition between physical and chemical adsorption rather than a pure physical or chemical one.

Consequently; zeolite and bentonite showed better adsorptive characteristics for the removal of heavy metal ions (Ni, Pb, Zn) from aqueous solutions than clay. Although bentonite is a good adsorbent for heavy metal ions high amounts of bentonite constitute a great problem. Since, bentonite becomes a gel-like sticky material by interaction with the aqueous phase, this feature may be disadvantage for the practical use of high mass bentonite in the adsorption process. Therefore, zeolite should be preferred for heavy metal ions removal from wastewater in practice.

ACKNOWLEDGEMENTS

This research has been supported by The Scientific and Technological Research Council of Turkey (TUBITAK – CAYDAG) (Project No. 105Y334) Ankara, Turkey.

REFERENCES

- [1] WAN NGAH W.S., HANAFIAH M.A.K.M., *Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents. A review*, Bioresour. Technol., 2008, 99, 3935.
- [2] QAISER S., SALEEMI A.R., AHMAD M.M., *Heavy metal uptake by agro based waste materials*, Environ. Biotechnol., 2007, 10, 409.
- [3] DEMIRBAS A., *Heavy metal adsorption onto agro-based waste materials. A review*, J. Hazard Mater., 2008, 157, 220.
- [4] FEBRIANTOA J., KOSASIHA A.N., SUNARSO J., JU Y.H., INDRASWATI N., ISMADJIA S., *Review. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent. A summary of recent studies*, J. Hazard. Mater., 2009, 162, 616.
- [5] KURNIAWAN T.A., CHAN G.Y.S., LO W., BABEL S., *Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals*, Sci. Total Environ., 2006, 366, 409.
- [6] PERIC J., TRGO M., MEDVIDOVIC N.V., *Removal of zinc, copper and lead by natural zeolite. A comparison of adsorption isotherms*, Water Res., 2004, 38, 1893.
- [7] TAHIR S.S., RAUF N., *Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution*, J. Chem. Thermodynamics, 2003, 35, 2003.
- [8] VELI S., ALYÜZ B., *Adsorption of copper and zinc from aqueous solutions by using natural clay*, J. Hazard. Mater., 2007, 149, 226.
- [9] SHETA A.S., FALATAH A.M., AL-SEWAILEM M.S., KHALED E.M., SALLAM A.S.H., *Sorption characteristics of zinc and iron by natural zeolite and bentonite*, Microporous Mesoporous Mater., 2003, 61, 127.
- [10] VARANK G., DEMIR A., TOP S., SEKMAN E., AKKAYA E., YETILMEZSOY K., BILGILI M.S., *Migration behavior of landfill leachate contaminants through alternative composite liners*, Sci. Total Environ., 2011, 17, 3183.

- [11] VARANK G., *Investigation of contaminant transport through solid waste landfills liners and rehabilitation of landfill liners*, Ph.D. Thesis, Institute of Science, Department of Environmental Engineering, Yildiz Technical University, Istanbul, Turkey, 2010 (in Turkish).
- [12] DONAT R., AKDOGAN A., ERDEM E., CETISLI H., *Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions*, J. Colloid Interface Sci., 2005, 286, 43.
- [13] SATHISHKUMAR M., BINUPRIYA A.R., VIJAYARAGHAVAN K., YUN S., *Two- and three-parameter isothermal modeling for liquid-phase sorption of Procion Blue H-B by inactive mycelial biomass of *Panus fulvus**, J. Chem. Tech. Biotech., 2007, 82, 389.
- [14] HAMEED B.H., CHIN L.H., RENGARAJ S., *Adsorption of 4-chlorophenol onto activated carbon prepared from rattan sawdust*, Desalination, 2008, 225, 185.
- [15] HAMDAOUI O., NAFFRECHOUX E., *Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters*, J. Hazard. Mater., 2007, 147, 381.
- [16] VIJAYARAGHAVAN K., PADMESH T.V.N., PALANIVELU K., VELAN M., *Biosorption of nickel(II) ions onto *Sargassum wightii*. Application of two-parameter and three-parameter isotherm models*, J. Hazard. Mater., 2006, B133, 304.
- [17] FREUNDLICH H.M.F., *Über die adsorption in lösungen*, Z. Phys. Chem., 1906, 57, 385.
- [18] REDLICH O., PETERSON D.L., *A useful adsorption isotherm*, J. Phys. Chem., 1959, 63, 1024.
- [19] HO Y.S., HUANG C.T., HUANG H.W., *Equilibrium sorption isotherm for metal ions on tree fern*, Process Biochem., 2002, 37, 1421.
- [20] TOTH J., *State equations of the solid-gas interface layers*, Acta Chem. Acad. Hung., 1971, 69, 311.
- [21] PADMESH T.V.N., VIJAYARAGHAVAN K., SEKARAN G., VELAN M., *Application of two- and three-parameter isotherm models. Biosorption of Acid Red 88 onto *Azolla microphylla**, Bioremediation J., 2006, 10 (1–2), 37.
- [22] SIPS R., *On the structure of a catalyst surface*, J. Chem. Phys., 1948, 16, 490.
- [23] BLANCHARD G., MAUNAYE M., MARTIN G., *Removal of heavy metals from waters by means of natural zeolites*, Water Res., 1984, 18, 1501.
- [24] Ho Y.S., Ng J.C.Y., McKay G., *Kinetics of pollution sorption by biosorbents review*, Sep. Purif. Methods, 2000, 29, 189.
- [25] LIU Y., LIU Y.J., *Biosorption isotherms, kinetics and thermodynamics, review*, Sep. Purif. Technol., 2008, 61, 229.

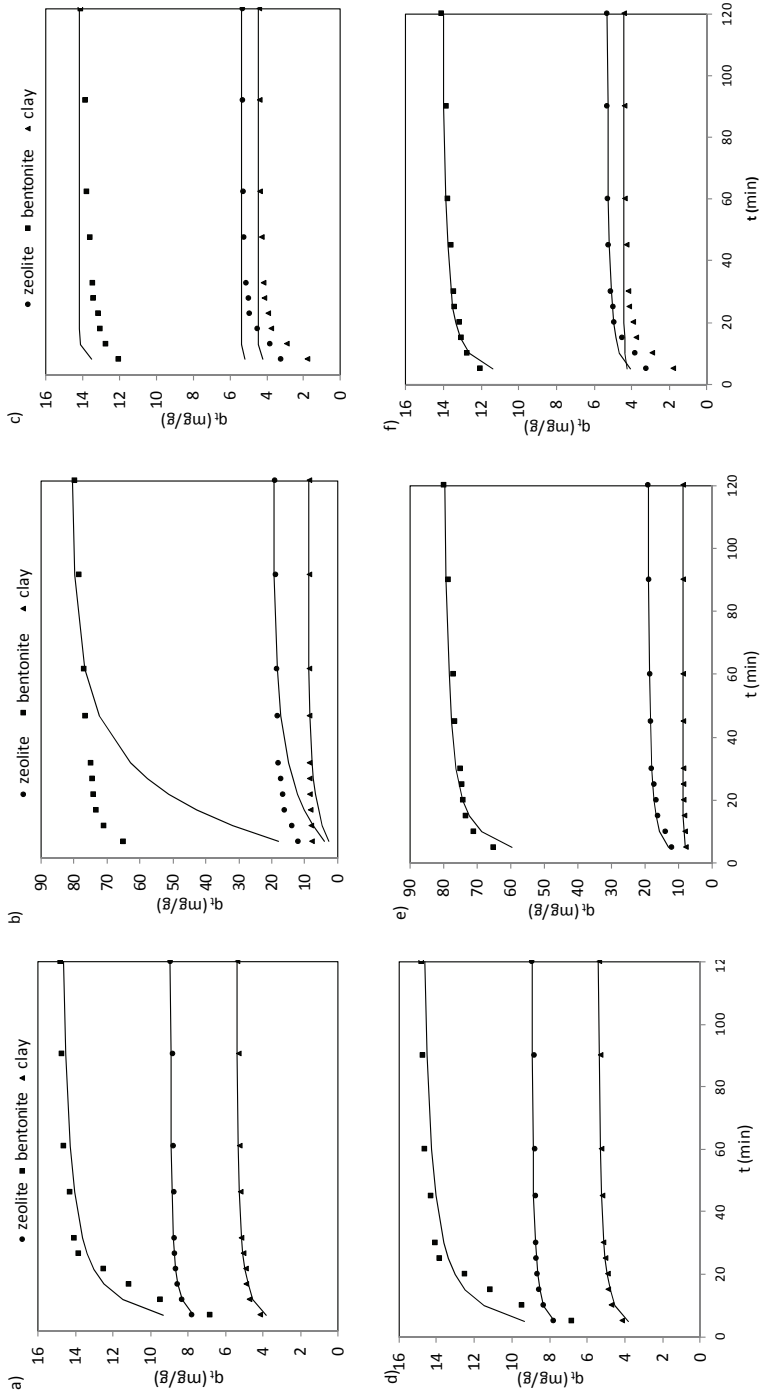


Fig. 5. Adsorption kinetics of heavy metal ions onto low-cost adsorbents at 298 K. Pseudo-first order model for: Ni (a), Pb (b), Zn (c) and pseudo-second order model for Ni (d), Pb (e), Zn (f)

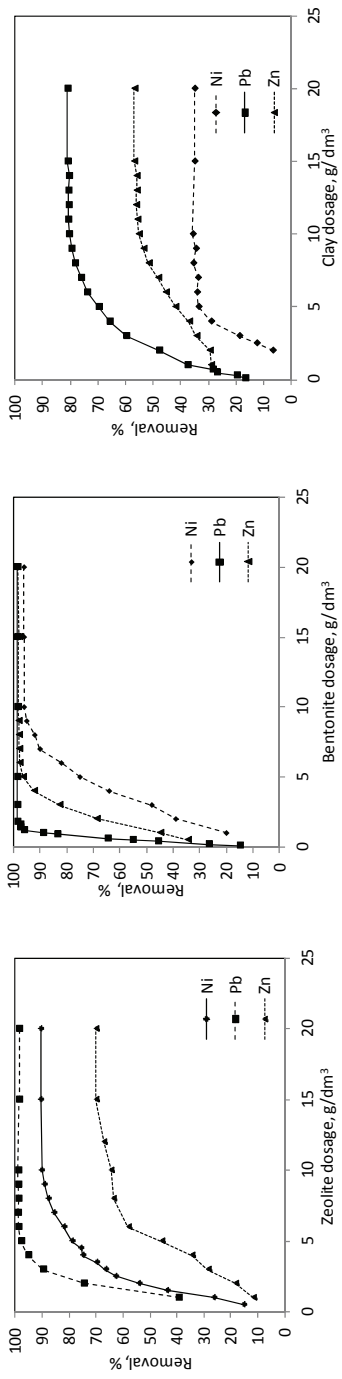


Fig. 1. Effect of adsorbent dosage on heavy metal removal by natural low-cost adsorbents

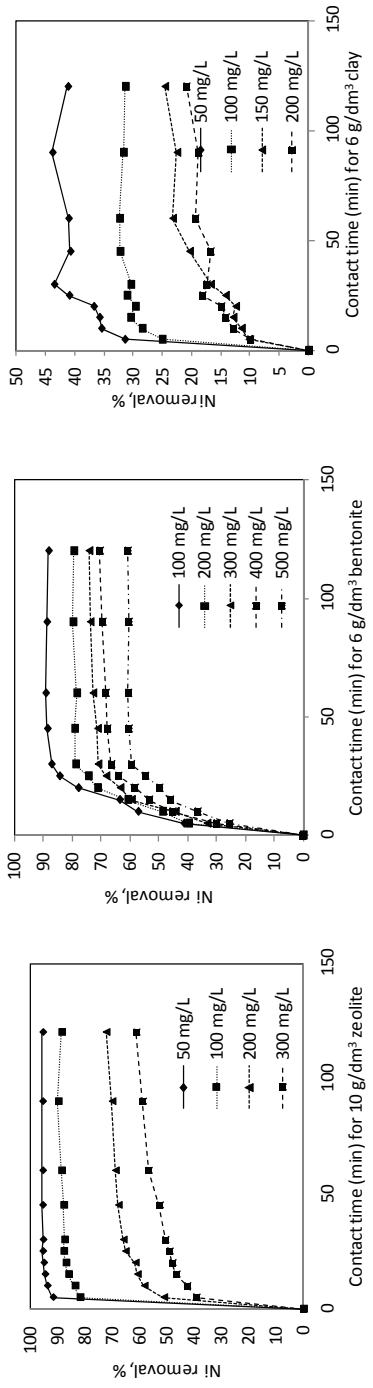


Fig. 2. Effect of contact time and initial concentration on Ni removal by natural low-cost adsorbents at optimum adsorbent dosages

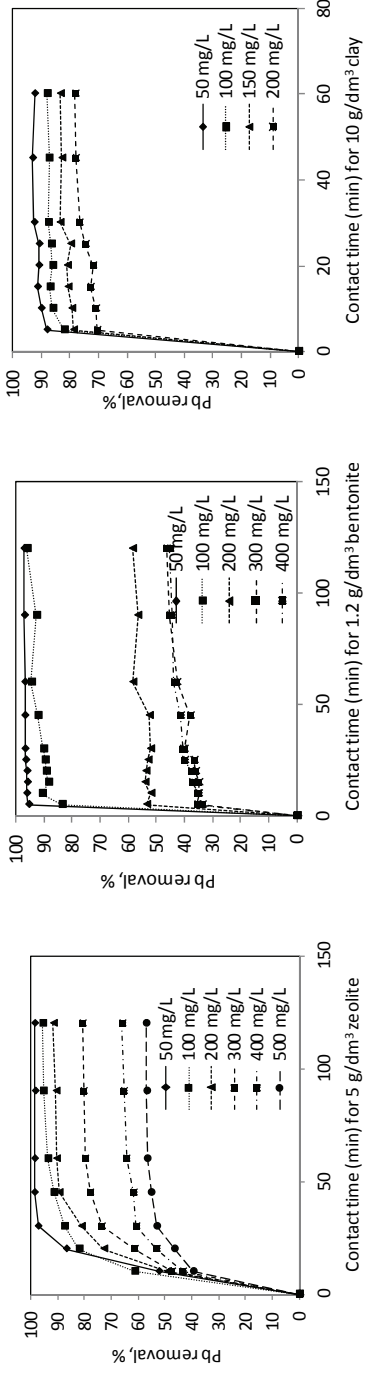


Fig. 3. Effect of contact time and initial concentration on Pb removal by natural low-cost adsorbents at optimum adsorbent dosages

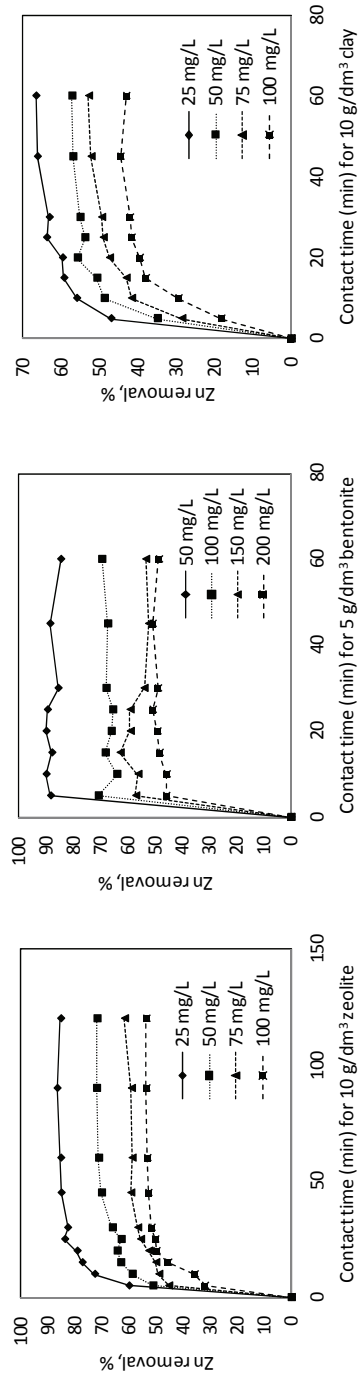


Fig. 4. Effect of contact time and initial concentration on Zn removal by natural low-cost adsorbents at optimum adsorbent dosages

Table 7. Thermodynamic parameters

Adsorbent	Ni					Pb					Zn				
	T [K]	k_L [dm ³ /g]	ΔH° [kJ/mol]	ΔS° [kJ/(mol·K)]	ΔG° [kJ/mol]	k_L [dm ³ /g]	ΔH° [kJ/mol]	ΔS° [kJ/(mol·K)]	ΔG° [kJ/mol]	k_L [dm ³ /g]	ΔH° [kJ/mol]	ΔS° [kJ/(mol·K)]	ΔG° [kJ/mol]		
Zeolite	298	0.039			1.24	0.117			18.02				26.57		
	318	0.048	6.76	-4.18	1.33	0.022			19.23				28.36		
	338	0.054			1.62	0.067			20.44				30.14		
Bentonite	298	0.02			28.96	0.043			16.43				22.02		
	318	0.009	-19.04	-97.26	30.91	0.047			17.54				23.50		
	338	0.008			32.85	0.028			18.65				24.98		
Clay	298	0.026			4.35	0.067			-14.44				6.67		
	318	0.029	4.70	-14.60	4.65	0.203			-15.37				7.12		
	338	0.032			4.94	0.181			-16.34				7.57		