Scientific paper

Evaluation of the Thermodynamic Parameters for the Adsorption of Cadmium Ion from Aqueous Solutions

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Abstract

Adsorption behavior of Cd(II) onto Tripoli was studied at 0, 20, 30 and 40 °C at pH in the range of 5–6. Thermodynamic equilibrium constant values at infinite dilution, K°, were obtained from the intercept of ℓnK against ionic strength (I) plots by extrapolation of the line obtained to zero ionic strength. The thermodynamic parameters ΔH° and ΔS° of adsorption were calculated from the intercept and the slope of the plot of ℓnK° against 1/T, respectively. These values were used to calculate the values of the free energy (ΔG°) at different temperatures. The adsorption isotherm was found to fit Freundlich model. The adsorption capacity was found to increase with the decrease in temperature. Flam atomic absorption spectrophotometry was used to measure the equilibrium concentrations of cadmium ion.

Keywords: Thermodynamics, adsorption, cadmium, tripoli, Freundlich isotherm

1. Introduction

Due to their toxicity, the presence of heavy metals in the environment is a major concern to many researchers. Unlike organic pollutants they do not degrade into harmless end products. Among these toxic heavy metals is cadmium. The most important sources of cadmium are municipal and medical waste,[1] plastics and dye manufacturing, disposable nickel-cadmium batteries, electroplating industry, burning of coal and use of fertilizers.[2] Removal of cadmium and other heavy metals from aqueous waste is a vital and important issue to prevent its arrival to the food chain. Adsorption onto solid adsorbents is an effective method and have been used to remove cadmium and other heavy metals from aqueous wastes, some of these adsorbents are mentioned by Al-Asheh and Duvnjak[3] and Apra et al.[4]

As there is large variation in temperature during different seasons of the year it is important to study its effect on the adsorption of cadmium, therefore, this work is aimed at the study of the effect of temperature on the adsorption of cadmium onto tripoli. Tripoli is a clay mineral, contains more than 92% SiO_2, available in large quantities in the southern part of Jordan.[5] Commercial tripoli is available with 98% or 99% of silica and minor amounts of alumina and iron oxide, it's color may be white or brownish yellow or reddish depending upon the percentage of iron oxide.[6] Chemical composition of tripoli from other sources is mentioned.[7]

Adsorption onto surfaces is described by an "isotherm". An isotherm is the variation of adsorbate solid concentration per unit mass of adsorbent in units of mmole/g or mg/g as a function of the equilibrium concentration of the adsorbate ion in solution. Paker,[8] had discussed different types of isotherms and divided them into two main categories. The first category is based on the Langmuir isotherm where

$$X = X_{max}KC_e/(1 + KC_e) \qquad (1)$$

and X is the adsorbate solid concentration per unit mass of adsorbent at certain adsorbent solution equilibrium concentration C_e, and K is the equilibrium constant for the adsorption. This isotherm is based on the assumption that all adsorbent sites have the same preference towards an adsorbent ion. The adsorbate solid concentration reaches a constant saturation value at high equilibrium concentration; this isotherm of adsorption is extensively discussed by Attard and Barnes.[9] Diffusion model of adsorption was discussed and applied by Veliev et al.[10]

The second category assumes that the relationship between the adsorbent solid concentration and the equilibrium concentration of the adsorbent in solution, C_e, is exponential and based on the equation:

$$X = a\, C_e^{1/n} \tag{2}$$

where "a" and "n" are constants. This is known as Freundlich isotherm. The linear form of this equation is given by:

$$lnX = \ell na + (1/n)\ell nC_e \tag{3}$$

The equilibrium constant K in the case of Freundlich adsorption can be calculated from the ratio of the adsorbed, C_{ad}, to the equilibrium concentration

$$K = C_{ad.}/C_e \tag{4}$$

where $C_{ad} = C_i – C_e$ and C_i is the initial concentration.[11] The equilibrium constant (K) in terms of molar equilibrium constant (K_m) where molar concentrations are used, and the combination of the activity coefficients (K_γ) is given by,[12-i]:

$$K = K_m \times K_\gamma \tag{5}$$

and the activity coefficient is related to the ionic strength by the equation:

$$\ell og\, \gamma_\pm = – A\, Z_– Z_+\, I^{0.5}/(1 + B\, I^{0.5}) + C\, I \tag{6}$$

where "I" is the ionic strength of the solution, Z is the ionic charge and A, B and C are constants. In non-dilute solutions the second term predominates and therefore $\ell og\gamma_\pm$ (or $\ell ogK_{\gamma\pm}$) is linear in "I".[12-ii] By taking logarithms of equation (5) and combination with equation (6) in non-dilute solutions then,

$$\ell og\, K = \ell og\, K_\mathrm{m} + C\, I \tag{7}$$

According to equation (7), the thermodynamic equilibrium constant or the equilibrium constant at infinite dilution (K^o), can be found from the intercept of ℓogK_m versus ionic strength plot. This method is used by Akgemci and Atalay,[13] and Inel et al,[14] for determination of thermodynamic parameters of some complexes. The relationship between the thermodynamic equilibrium constant K^o and the Gibbs free energy is given by the Vant Hoff equation below:

$$\Delta G^o = – RT\ell n\, K^o \tag{8}$$

and

$$\Delta G^o = \Delta H^o – T\, \Delta S^o \tag{9}$$

combination of equations (8) and (9) and taking the natural logarithms of both sides give:

$$\ell n\, K^o = – \Delta H^o/RT + \Delta S^o/R \tag{10}$$

2. Experimental

2. 1. Materials and Solutions:

Pretreatment of Tripli: tripoli was collected from different places in the university area, cracked by jaw crusher machine, washed many times with 1 M HCl solution to eliminate the soluble part of the rock. The tripoli was then sieved and the slit part (63–150 μm) was taken and washed several times with conc HNO_3 then with excessive amounts of 1 M HCl through a suction filtration apparatus, the washing process continued until having negative EDTA test for heavy metal ions in the filtrate, the test was performed by adding $1.0 \cdot 10^{-3}$ M EDTA solution and 2 mL of NH_3/NH_4Cl buffer to an approximately 5 mL sample of the filtrate, this buffer solution was prepared by adding water to 57 mL of concentrated ammonia and 7 g NH_4Cl to a final volume of about 100 mL.[15] The negative test for the presence of metal ions is indicated by the appearance of the blue color of the EDTA. Tripoli was then washed with excessive amounts of double distilled water until the filtrate gave negative test with 0.1 M $AgNO_3$ solution. The tripoli was then dried overnight in an oven at 105 °C.

Pretreated tripoli was used as the adsorbing media. Analytical grade $Cd(NO_3) \cdot 4H_2O$ provided by Fluka was used to prepare 1000 ppm stock solution, from which solutions of 100, 200, 300, 400 and 500 ppm were prepared by direct dilution using double distilled water. 100 mL of each of these solutions were placed in 250 mL stoppered Erlenmeyer flasks each containing an exactly weighed 2 grams of treated tripoli. Triplicate trials labeled as A, B and C had been performed in a temperature-controlled shaking water bath previously adjusted to 0, 20, 30 and 40 °C.

2. 2. Sample Preparation:

The mixtures were placed in ultrasonic, Quantrex 210 H manufactured by L&R manufacturing company, USA, for 75 minutes then brought to the required temperature by placing them in a temperature controlled shaking water bath, 1083 GFL made by GmbH, with moderate shaking, for 48 hours. Then the samples were taken directly from the water bath and centrifuged, the supernatant solutions were collected in plastic bottles for analysis by atomic absorption spectrophotometry, Perkin-Elmer, Analyst 300 Atomic Absorption spectrophotometer equipped with AS 72 auto-sampler was used for analysis.

The pH of the mixtures were adjusted by adding few drops of 0.1 M NaOH solution when required, pH values were in the range of 5–6. 315 WTW pH meter equipped with WTW pH electrode, provided by WTW GmbH, Germany, was used for the pH measurements. The x-ray diffraction spectra were taken by the use of X-ray Diffraction System, XRD 3003TT, Seifert Machine, Germany.

3. Results and Discussion

The major peak that appears in the XRD spectra for the untreated, (Figure 1), and treated, (Figure 2) tripoli, that appears at 2θ of 26.7 is characteristic of SiO_2. This is shown in a work obtained by Iliescu and co-workers in their study of the chemical composition of quartz crystals by sodium electrodiffusion by XRD method. Some of the other peaks that appear at 2θ of 36. 6, 39.5, 45.86, 50.2 and 60.0 are also characteristic of quartz and other silicon oxide-containing phases.[16]

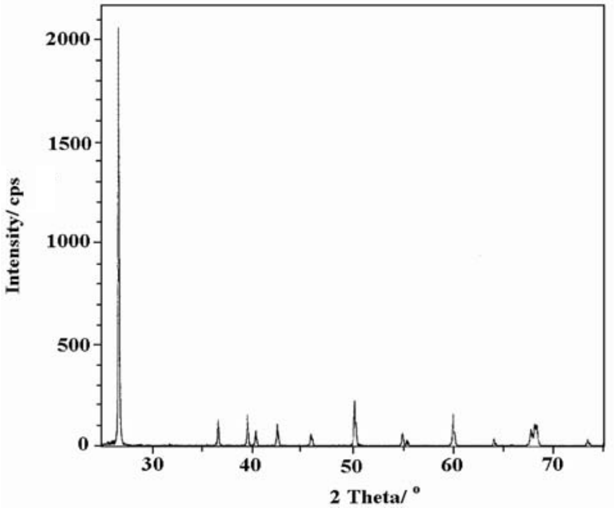

Figure 1. XRD spectrum of untreated tripoli.

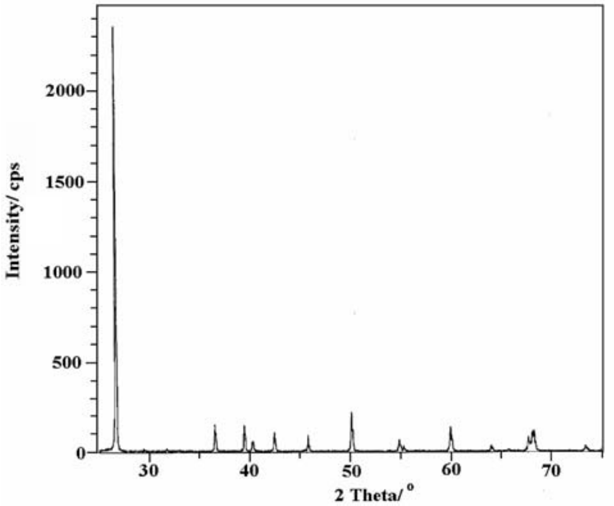

Figure 2. XRD spectrum of untreated tripoli.

The intensity of the major peak in the treated sample (2333.5 cps) was significantly higher than that for the untreated sample (2037.0 cps). This indicates a loss of soluble matter due to the treatment where the percentage of silicate (insoluble) in the sample becomes larger after the acid treatment.

The average solid adsorption capacity, X, in mg of adsorbate per g of adsorbent (mg/g) against equilibrium concentration for the adsorption of Cd(II) onto tripoli at 273, 293, 303 and 313 K are shown in Figure 3

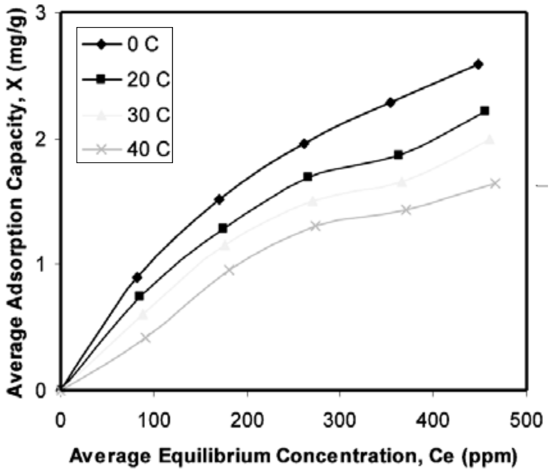

Figure 3. Average adsorption capacity of cadmium ion against average equilibrium concentration, at 0, 20, 30 and 40 °C.

The result of the three trials is exemplified by those obtained at 0 °C, as shown in Figure 4.

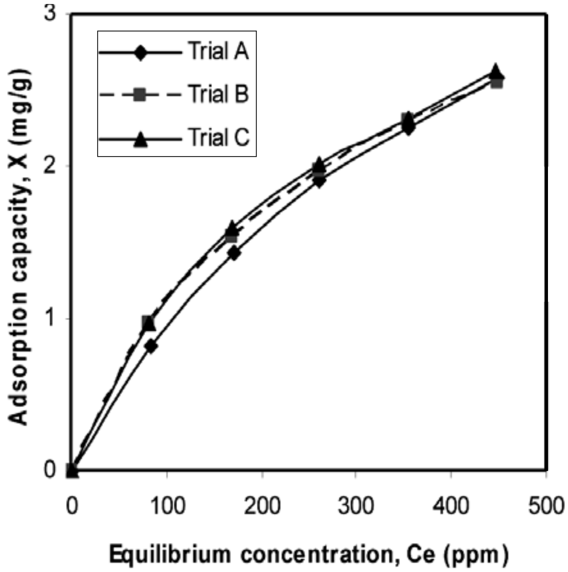

Figure 4. Adsorption capacity of cadmium ion against equilibrium concentration, at 0 °C for the trials A, B and C.

The general appearance of these figures indicates that the adsorption capacity is increasing with the increase of the equilibrium concentration, this behavior is noticed at all temperatures studied in this work. The continuous increase of the adsorption capacity with equilibrium concentration indicates that the adsorption process follows Freundlich isotherm. Logarithmic plots of adsorption capacity, X (mg/g), against equilibrium concentration, Ce, in mg L^{-1} give straight lines. Logarithmic plots (Freundlich lines) of average adsorption capacity, X (mg/g), against average equilibrium concentration, Ce, in mg L^{-1} obtained at different temperatures are shown in Figure 5.

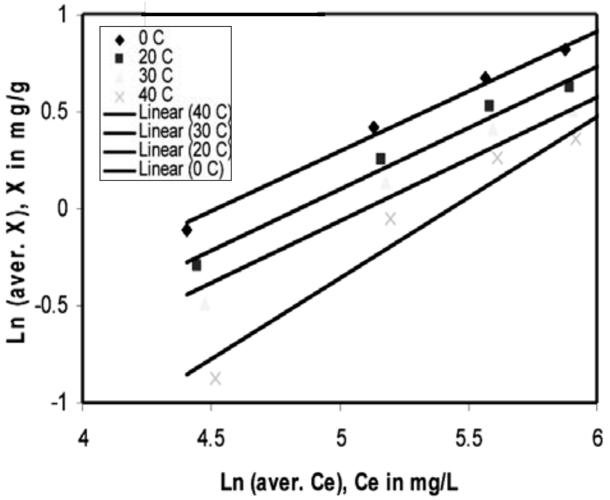

Figure 5. Frendlich lines, ℓn(average X) against ℓn (average Ce), for the adsorption of Cd(II) at 0, 20, 30 and 40 °C.

Freundlich plots for all of the trials at all temperatures were obtained. Freundlich constants "a" and "n" (based on equation 3) and the linear correlation coefficient values delivered from these plots are shown in Table 1. These correlation coefficient values indicate good linear relationships which support the Freundlich behavior for the adsorption of cadmium ion onto tripoli

It is noticed from Figure 3 that the average adsorption capacity is higher at lower temperatures, this relationship between adsorption capacity and temperature is noticed by many workers,[11,14,17,18] even though an opposite behavior is noticed in some other cases.[19–21] The constant "a" in Freundlich equation is a measure of the affinity of the adsorbent towards the adsorbate,[21] where higher affinity is indicated by a higher "a" value. It is noticed that the affinity of tripoli towards adsorption of cadmium ion is lower at higher temperature as the value of "a" is decreasing with the increase in temperature for all trials. The "n" values are low which indicates relatively low adsorption, where low adsorption is indicated by an "n" value lower than 2.[23]

For each temperature and for all trials, the values of the equilibrium constants and ionic strengths of the reaction mixtures were calculated at different equilibrium concentrations. The equilibrium constant K is calculated based on equation (4), and the equilibrium concentrations were employed in order to calculate the ionic strength in each case. A plot which is based on the average values of the equilibrium constants for the different trials at different temperatures against ionic strength is shown in Figure 6. Calculations of ionic strength is based on the average equilibrium concentrations.

Semilogarithmic plots of ℓn (equilibrium constant K) against the ionic strength for trials A, B and C at all of

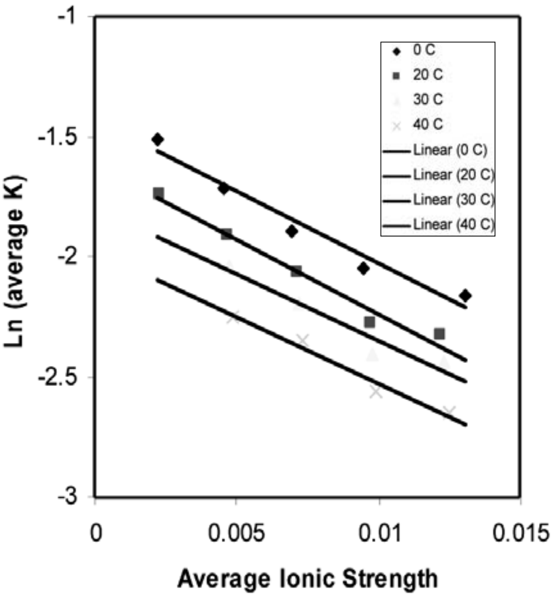

Figure 6. Semilogarithmic plot of ℓn(average K) against the ionic strength of the average concentration at 0, 20, 30 and 40 °C

Table 1. Freundlich constants, "a" and "n", as obtained from the linear plots of ℓnX vs ℓnCe for different trials at different temperatures.

	273 K		293 K		303 K		313 K	
Trial A	$r^2 = 0.9979$		$r^2 = 0.9807$		$r^2 = 0.9844$		$r^2 = 0.9715$	
	a	n	a	n	a	n	a	n
	0.04042	1.463	0.03086	1.420	0.02723	1.422	0.01586	1.300
Trial B	$r^2 = 0.9846$		$r^2 = 0.9918$		$r^2 = 0.9895$		$r^2 = 0.9968$	
	a	n	a	n	a	n	a	n
	0.08411	1.7743	0.05196	1.6239	0.03404	1.497	0.009324	1.1618
Trial C	$r^2 = 0.9928$		$r^2 = 0.9972$		$r^2 = 0.9881$		$r^2 = 0.9732$	
	a	n	a	n	a	n	a	n
	0.06492	1.635	0.05212	1.626	0.02620	1.4004	0.008192	1.138
Average	0.06315 ± 0.02190	1.624 ± 0.1558	0.04498 ±0 .01223	1.557 ± 0.1178	0.02916 ± 0.00426	1.440 ± 0.0507	0.01113 ± 0.004142	1.200 ± 0.0874

Table 2. Correlation coefficients (r) for the linear plots of ℓnK against ionic strength, Intercepts (I) and thermodynamic equilibrium constants (K°) for different trials at different temperatures.

	273 K		293 K		303 K		313 K	
Trial A	r^2 = 0.9964		r^2 = 0.9727		r^2 = 0.9968		r^2 = 0.9780	
	I	K°	I	K°	I	K°	I	K°
	–1.532	0.2160	–1.672	0.1879	–1.829	0.1569	–1.896	0.1569
Trial B	r^2 = 0.9846		r^2 = 0.9918		r^2 = 0.9895		r^2 = 0.9968	
	I	K°	I	K°	I	K°	I	K°
	–1.322	0.2666	–1.596	0.2027	–1.772	0.1699	–1.993	0.1362
Trial C	r^2 = 0.9942		r^2 = 0.9837		r^2 = 0.9729		r^2 = 0.9346	
	I	K°	I	K°	I	K°	I	K°
	–1.363	0.2559	–1.592	0.2035	–1.846	0.1579	–2.038	0.1303
Average K°	0.2462 ± 0.02667		0.1989 ± 0.008802		0.1616 ± 0.007221		0.1389 ± 0.0106	

the indicated temperatures were obtained. The values of the thermodynamic equilibrium constants K° at each temperature were obtained from the intercept. K° is the equilibrium constant at limit of zero ionic strength. The correlation coefficient values indicate good linear relationship between ℓnK and the ionic strength "I". These values, together with K° values obtained at different temperatures are shown in Table 2.

Based on equation (10)[19], the enthalpy change, ΔH°, and the entropy change, ΔS° for the adsorption equilibrium are calculated from the slope and intercept of a plot of ℓnK° against reciprocal of temperature respectively. This type of calculations assumes that ΔH° and ΔS° are independent on temperature in the studied temperature range.[14] An average plot , Figure 7, is obtained by plotting of logarithm of the average value of the equilibrium constant at infinite dilution, K°, for all of the trials against reciprocal of the temperature.

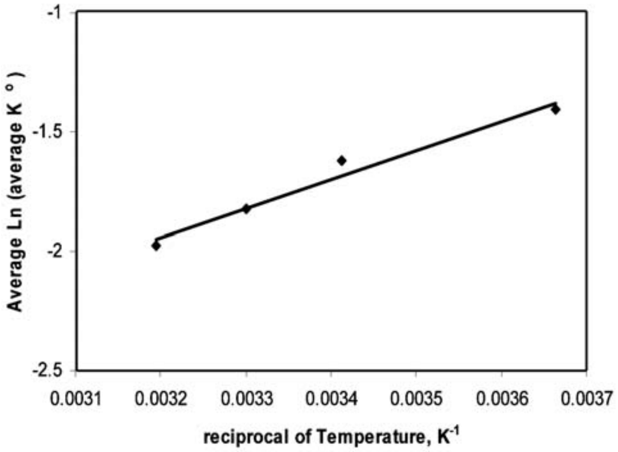

Figure 7. Average ℓnK° against reciprocal of temperature, T (K^{-1}).

The linear correlation coefficient value (r = 0.9930) indicates good linearity. The values of ΔH° and ΔS° obtained were used to calculate the free energy ΔG° at the required temperatures assuming that the difference between the standard pressure (1 bar) and the room pressure has negligible effect in the case of liquids, the results are shown in Table 3.

Table 3. Summary of the data obtained from plots of ℓn K° against reciprocal of temperature for the different trials. I = Intercept, S = Slope; ΔH = –SxR , ΔS = IxR.

Trial	**r^2 (Correl. Coeff.)**	**I (unitless)**	**S (K)**
A	0.9755	–4.503	814.8
B	0.9878	–6.406	1396
C	0.9776	–6.577	1434
Average (from Fig 7)	0.9852	–5.828 ± 1.151	1215 ± 347.1

The results of the calculations of the enthalpy change and entropy change obtained from the three trials, and the free energy change calculated based on equation (9) at 25 °C are shown in Table 4.

Table 4. Thermodynamic parameters for the adsorption of cadmium ion onto tripoli.

Trial	**ΔS° (kJ/mol K)**	**ΔH° (kJ/mol)**	**ΔG° (kJ/mol)**
A	–0.03744	–6.775	4.381
B	–0.05326	–11.60	4.267
C	–0.05480	–11.93	4.368
Average ± s	–0.04727 ± 0.01174	–10.10 ± 2.886	4.339 ± 0.06240

The enthalpy of adsorption here is negative but small in magnitude (ΔH° = –10.10 ± 2.886 kJ mol^{-1}), which means that the bonds of attraction between cadmium ion and the active sites on the tripoli surface are weak, and as well the enthalpy change is not even enough to compensate the large decrease in entropy (ΔS° = –0.04727 ± 0.01 kJ mol^{-1}) in order to make the adsorption process spontaneous. Usually in adsorption processes ΔS° is negative because ions in solution have more freedom of motion than the ones attached to a surface.[24] The value of adsorption enthalpy may be used to distinguish between chemical and physical adsorptions, the adsorption enthalpy of later type is from 0 to 20 kJ/mol,[25] this indicates that the adsorption of Cd(II) onto tripoli in this case is physical.

The ΔG^o values at 0, 20, 30 and 40 °C are 4.860, 5.956, 6.60 and 7.052 kJ/mol respectively. The increase in the free energy with the increase in temperature indicates that the adsorption process becomes energetically less favorable because the free energy becomes more positive at higher temperature. This again can be shown from figure 3 where the adsorption capacity becomes lower with the increase in temperature.

The pH of the medium is an important factor in determination of the adsorption capacity. In the case of adsorption of metal ions the pH has an upper limit that is governed by the precipitation of the metal ion from the solution as hydroxide, from the solubility product constant value of $Cd(OH)_2$,[26] this limit is 8.7 and 8.5 for cadmium ion concentrations of 100 ppm and 500 ppm respectively, the pH of solutions in this work was in the range of 5 to 6 where formation of $Cd(OH)_2$ precipitate is not possible in this pH rang.

4. Acknowledgment

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Povzetek

Raziskovali smo adsorpcijo Cd(II) na mineralu tripoli v temperaturnem območju med 0 in 40 °C pri pH = 5 – 6. Določili smo termodinamsko ravnotežno konstanto adsorpcije ter ostale termodinamske parametre (ΔH°, ΔS°, ΔG°). Ugotovili smo, da adsorpcijo lahko opišemo s Freundlichovo adsorpcijsko izotermo in da je proces adsorpcijekot običajno ugodnejši pri nižji temperaturi.