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Isothermic and Thermodynamic Approaches in Cadmium (II) Adsorption with Sivas Province Nanoclay

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Adsorption
Thermodynamics.

Abstract: In this study, the nano clay obtained by grinding clay from Sivas Yıldızeli region, Sivas Nano Clay (SNC), was used as adsorbent for the removal of cadmium from the solution. For the characterization of nano clay; XRD, SEM-EDX, BET and TGA analyses were performed. The surface area of the adsorbent was measured as 153.364 m2/g and the pore size as 3.835 nm. Parameters affecting adsorption such as temperature, adsorbent amount and speed were investigated. The contact time was determined as 180 min. The studies on adsorption equilibrium were applied to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. As a result of the regression on the isotherm models, it was found that the adsorption fit the Temkin model. The adsorption capacity of nano clay was determined as 53.48, 49.50 and 48.54 gmg^{-1} for 298, 308 and 318 K temperatures. Adsorption thermodynamic study, ΔG° values were found to be -26.553, -27.673, -28.796 $kJmol^{-1}$ ΔH° value 6,823 $kJmol^{-1}$ and ΔS° value 0.112 $kJmol^{-1}K^{-1}$ for 298, 308, 318 K, respectively. The positive value of ΔH° indicates that the event is endothermic. The positive value also indicates that the event is chemical. The negative sign of ΔG° indicates that the event is spontaneous

Sivas İli Nanokil İle Kadmiyum (II) Adsorpsiyonunda İzotermik ve Termodinamik Yaklaşımlar

Anahtar Kelimeler
Nanokil,
Adsorpsiyon,
Kadmiyum,
Temkin,
Adsorpsiyon
Termodinamiği.

Öz: Bu çalışmada atık sulardaki ağır metallerin uzaklaştırılması için en uygun yöntemlerden biri olan adsorpsiyon yöntemi tercih edilmiş ve kadmiyumun çözeltiden giderimi için adsorban olarak Sivas Yıldızeli bölgesinden alınan kilin öğütülmesi ile elde edilen nanokil Sivas Nano Clay (SNC) kullanılmıştır. Nanokilin karakterizasyonu için; XRD, SEM-EDX, BET ve TGA analizleri yapılmıştır. Adsorplayıcının yüzey alanı 153.364 m^2g^{-1} olarak,gözenek boyutu 3.835 nm olarak ölçülmüştür. Adsorpsiyonu etkileyen parametrelerden sıcaklık, adsorban miktarı ve hız gibi parametreler incelenmiştir. Temas süresi 180 dk olarak belirlenmiştir. Adsorpsiyon dengesi üzerine yapılan çalışmalar ise, Langmuir, Freundlich, Temkin ve Dubinin-Radushkevich izoterm modellerine uygulanmıştır. İzoterm modelleri ile ilgili yapılan regresyon sonucunda adsorpsiyonun Temkin modeline uyduğu tespit edilmiştir. Nanokilin adsorplama kapasitesi 298, 308 ve 318 K sıcaklıkları için 53.48, 49.50 ve 48.54 gmg^{-1} olarak belirlenmiştir. Adsorpsiyon termodinamiği çalışması ΔG° değerleri 298, 308, 318 K için sırasıyla -26.553, -27.673, -28.796 $kJmol^{-1}$ ΔH° değeri 6,823 $kJmol^{-1}$ ve ΔS° değeri 0.112 $kJmol^{-1}K^{-1}$ olarak bulunmuştur. ΔH°'ın pozitif değerli oluşu olayın endotermik olduğunu göstermektedir. Pozitif değer ayrıca olayın kimyasal olduğunu göstermektedir. ve ΔG°'ın negatif işarete sahip olması olayın kendiliğinden yürüdüğünü göstermektedir.

1. INTRODUCTION

One of the most important environmental pollution types is water pollution. Water pollution, which is a problem all over the world, will start to decrease the amount of water due to the unconscious and irresponsible use of water and may bring water wars as an inevitable end. In this context, it has become a necessity to reduce water pollution and to raise awareness of people on this issue [1]. Among the studies on this subject, adsorption is one of the effective and cheap methods. Adsorption is the accumulation of ions or molecules in solution on the appropriate contact surface or interface between two phases. These phases can be liquid-liquid, solid-liquid or gas-liquid, or gas-solid combination [2].

The substance deposited on the contacted surface is called adsorbed (adsorbate) and the adsorber is called adsorbent. It is possible to talk about three types of adsorptions: physical, ion exchange and chemical adsorption. In physical adsorption, there is an adsorption based on Van der Waals attraction force, which is a weak interaction force between molecules [2]. The main reason why an ion is selectively retained on the surface of a solid is due to electrostatic attraction. The reversible exchange of ions between some solids and the electrolyte solution is referred to as ion exchange. However, although the ion exchange process is much more complex than adsorption, the data obtained with general techniques are quite similar[3]. In chemical adsorption, both covalent and ionic bond interactions take place between the molecules of the adsorbate and the molecules on the surface of the absorber. In this process, a single layer is formed on the surface of the adsorbate. The factor that causes this is the chemical interaction between the adsorber and the adsorbate. In chemical adsorption, the process is irreversible[4]. While applying this method, the most efficient isotherm analysis should be performed. For this reason, among the models in which chemical adsorption is applied, the most commonly used ones are Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkins-Jura [5]. The recognition of adsorption phenomenon dates back to ancient times. However, its scientific use and the development of its application areas has been mostly in the twentieth century. It has almost reached its peak, especially in wastewater treatment. This is due to its easy availability and low cost [1,6].

1.1. Clay

Clays are key elements not only in geological and environmental processes but also in many human activities. In the description of the clay research organization known as the Association Internationale Pour L'etude des Argiles (AIPEA), the most important element that distinguishes clay from other soils is its plasticity. This is also emphasized as a distinctive feature. However, there is no reliable criteria for plasticity. This makes particle size criteria common. Clay research disciplines have different understandings about the definition of clay. Geologists consider it to be 2μm and colloidal, sedimentologists consider it to be < 4μm in particle size (equivalent spherical diameter), and chemists consider it to be only 1 μm. [7].

Zeolite, clay diatomite, wheat straw, activated carbon, montmorrillonite, waste biomass and many natural adsorbents have been used. [8]. Canpolat and his friends was used Midyat stone as an adsorbent. [9].

1.1.1. Nanoclay

The literal meaning of nano is expressed as one billionth of a physical size. Nanometer means a length equal to one billionth of a meter. To understand how small the nanometer is, it would be enough to think that the diameter of a human hair is around 100 000 nm. If 100 to 1000 atoms of the atoms that make up an object come together, the nano size is formed. Nano technology or nanoscience is certain to be the most used and brightest field of the 21st century and beyond. Because many countries in the world are making investments and research on this subject [10].

Towards the end of the 20th century, scientists discovered the scanning tunneling microscope which can directly image atoms and its derivative, the atomic force microscope. With these discoveries, they brought different perspectives to physics and chemistry at the nanometer scale. In this way, by observing chemical reactions, a wide range of processes and their interactions, it has become possible to obtain artificial materials by moving atoms one by one to the desired locations in a controlled manner [11] . By reducing the material at the nano-size level, its properties change too. For example, when the size of the ceramic particle, which is fragile, is reduced to the nanometer level, it can be deformed and shaped. In other words, it is defined as the processing, creation and manipulation of tools, materials and structures at the molecular level. Due to the decline in profits in manufacturing sectors similar to the automotive sector, economists in the US recognized these opportunities and accepted nanotechnology as a priority area by elucidating the situation to then President Clinton. After that, it spread rapidly all over the world [12].

1.2. Heavy Metals

Heavy metals are naturally occurring elements with high atomic weights and a density almost five times that of water. Today, there are many different definitions. They are defined according to their atomic weight, density, chemical properties or toxicity. In reality, they are defined as metals with a density greater than $5g/cm^3$. In medicine, however, the situation is different. Regardless of the atomic weights of the elements, they are described as metals with all toxic properties [13].

Heavy metals, which are used in a wide range of applications, are preferred especially in industry, technology, domestic, agricultural, and medical fields. Their excessive use adversely affects human health and the environment and raises concerns. Because depending on the toxicity dose of heavy metals, many factors such as age, gender, genetics, exposure pattern and even nutritional status of the individuals exposed to them are important. Elements such as lead, arsenic, mercury, cadmium and chromium, which have extreme toxicity, are among the most important metals in terms of public health. Since exposure to even low doses of these elements can cause multiple organ failure, they are classified as human carcinogens (known or probable) by both the International Agency for Research on Cancer and the US Environmental Protection Agency [14]. Many studies on the adsorption of heavy metals have taken their place in the literature [15,17].

1.2.1. Cadmium (Cd)

Cadmium, which is in group II B of the periodic table, is a silver-white metal element. In nature, it is usually found in the form of CdS (cadmium sulfide) and among zinc ores. Cadmium, which is a by-product of zinc production, is between zinc and mercury in terms of chemical properties. Most of its compounds are used as red and yellow pigments in paints. It is mostly coated on iron, zinc, steel, and copper, making them resistant to corrosion. Accumulators with cadmium electrodes last much longer than lead batteries [17]. Cadmium, which is used extensively in industry and is among the important environmental pollutants, can cause life-threatening hazards due to exposure in daily life. Cd, which has a long half-life, is known to cause direct or indirect toxicity in cardiovascular, respiratory, nervous system, urinary, gastrointestinal and bones. In addition, if it accumulates in the body in excess, it can cause many diseases such as anemia, osteoporosis, anosmia, eosinophilia, and chronic rhinitis [18].

1.2.2. Adsorption Isotherm Models

Adsorption isotherms are concerned with the behavior of adsorbents in equilibrium at constant temperature. Depending on the interaction between the adsorbent and the absorber, adsorption processes can be either physisorption or chemisorption [5,19].The following table provides the most commonly used adsorption isotherm models.

Table 1. Table of adsorption ısotherm models

Isotherm Model	Formulas	Remarks
Freundlich Isotherm Model	$q_e = K_F C_e^{\frac{1}{n}}$ Eq. (1) (Non-Linear) $\log q_e = \log K_F + \frac{1}{n} \log C_e$ Eq. (2) (Linear Form)	• The linear state of the equation of the Freundlich model, which is an experimental (empirical) model, is obtained by taking the logarithm of the two sides of the equation in the first part. Here; Ce; represents concentration in equilibrium state (mgL^{-1}), q_e; the amount of adsorbed substance in equilibrium (mgg-1), K_F; The Freundlich constant (mgg^{-1}), n; the adsorption intensity values. k – constant indicating the relative adsorption capacity of the adsorbent (mgg^{-1})(Lm^1)1/n; 1/n – constant for the intensity of the adsorption, 0 < 1/n<1; Ce – equilibrium concentration of the solute in the solution (mgL^{-1}), equation (1 and 2). [5,21].
Langmuir Isotherm Model	$q_e = \frac{Q_0 K_L C_e^{\theta}}{1 + K_L C_e}$ (Non-Linear) Eq. (3) $\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{K_L}$ Eq.(4) (Linear Form)	• In the Langmuir isotherm model, it is stated that the distribution of reactive groups on the surface of particles is homogeneous. This model was developed based on gas theory and is widely used to describe gas adsorption on solids. qmax - maximum adsorption capacity (mgg^{-1}); b – constant related to the free energy of adsorption (Lmg^{-1}), equation (3 and 4). [21,22].
Temkin Isotherm Model	$q_e = BlnA_T + BlnC_e$ Eq. (5) (Linear Form)	• According to this model, the heat of adsorption in a linear order is due to the interaction between the adsorbent and the adsorbate. The decrease in adsorption energy is linear, not exponential [5]. Here the b value is the constant related to the adsorption heat ($J.mol^{-1}$) and is expressed as B=RT/bT. bT is the Temkin isotherm constant. A_T is the equilibrium binding constant ($L\ g^{-1}$). T is the absolute temperature (K). R is the ideal gas constant ($J\ mol^{-1}\ K^{-1}$). The values B and A_T are calculated from the slope and cut-off point of the linear plot plotted by ln Ce versus qe respectively, equation (5).
Dubinin-Radushkevich (D-R) Isotherm	$lnq_e = lnq_m - K_{DR}\varepsilon^2$ Eq. (6) $\mathcal{E} = RTln(1 + \frac{1}{C_e})$	• The D-R isotherm model refers to the potential change that occurs on a heterogeneous surface. Here, E represents the average adsorption energy and allows us to find out the mechanism of adsorption. As for $K_{DR,}$ it is the isotherm constant in the adsorption energy[22]. • Ɛ: shows Polanyi's potential and q_m : shows adsorption capacity (molg-1), equation (6 and 7) [24] . (Saloğlu, 2019)

Halsey Isotherm Model	$E = \frac{1}{\sqrt{2K_{DR}}}$ Eq. (7) $lnq_e = \left[\left(\frac{1}{n}\right) lnK\right] - \left(\frac{1}{n}\right) lnC_e$ Eq.(8)	• The Halsey isotherm model can be used in case of the presence of multi-layered and irregular porous structures, equation (8) [24].
Jovanovich Isotherm Model	$q_e = q_{max}(1 - e^{k_j C_e})$ Eq. (9) (Non-Linear) $lnq_e = lnq_m - K_j C_e$ Eq.(10) (Linear Form)	• It is a mathematical concept derived from the mechanism of adsorption on homogeneous solid surfaces according to the Jovanovich isotherm model. This model assumes that the adsorption event is non-specific, without side interactions and that the solid surface where the adsorption function takes place is covered by a monolayer mechanism. The second equation on the left-hand side gives its linear form. Kj – Jovanovic constant (Lmg^{-1}). equation (9 and 10). [20,23,]

1.4. Thermodynamic Definitions

Enthalpy; It refers to the total energy change of a substance at constant pressure. Its unit is $Jmol^{-1}$, its symbol is ΔH. ΔH provides information about whether a reaction is exothermic or endothermic. If the sign of ΔH is positive, the reaction is endothermic and if it is negative, the reaction is exothermic. While physical adsorption is only exothermic, chemical adsorption can be endothermic or exothermic. ΔG, called Gibbs free energy, determines whether a reaction is spontaneous or not. Its unit is $Jmol^{-1}$. A negative sign of ΔG indicates that the event occurred spontaneously, while a positive sign indicates that it is not possible for the event to occur, but that an event in the opposite direction can only occur by 'expending energy'. ΔG is a valuable concept of very critical value for the science of chemistry, which tries to understand the behavior of matter by linking it to its structure. ΔS is called entropy. It is a measure of the irregularity of matter. Its unit is entropy of the system decreases. The Gibbs equation connects these concepts [25].

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

2. MATERIAL AND METHOD

In this study, nanoclay obtained from Yıldızeli district of Sivas province was used to remove cadmium element from aqueous media. The clay was centrifuged at a speed of 14000 rpm in a Thermo- SL-16R model device. The colloidal part was taken into a container and kept for 15 days, and the upper non-collapsing clayey part was centrifuged again in the same device. Then the colloidal liquid part was filtered through 2 layers of filter paper. The filtrate was dried in an oven at 110 °C and beaten in a porcelain pestle. Then it was ground in a Retsch Brand ball grinder and tried to be brought to nano size. The sample obtained was teste in the SEM device and it was determined to be approximately 336.8 nm in size. This value is due to the fact that the dry clay could not be refined too much in the ball grinder.

Figure 1. The obtained nanoclay milled in a ball grinder and SEM analysis image

2.1. Characterization

The characterization of the prepared sample was performed on SEM -EDX (Quanta FEG 250)), BET (Quantachrome Nova Win) branded device. Multipoint surface area and pore size determination analysis was performed by applying vacuum process at 105°C for 20 hours. XRF analysis was performed using UQ program of Thermo ARL XRF device. for XRD, Bruker -D8-advance, FT-IR analysis was performed on Perkin Elmer device and Shimadzu-DTG-60H was used for TGA. For the analysis results, Agilent 200 Series AA device was used.

3. RESULTS

3.1. SEM Analysis

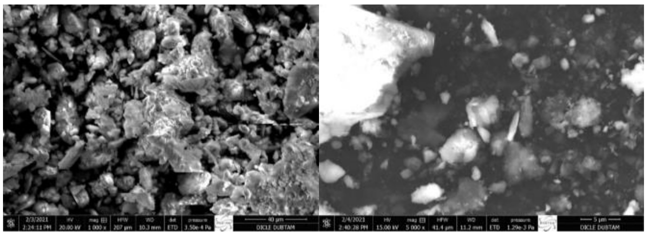
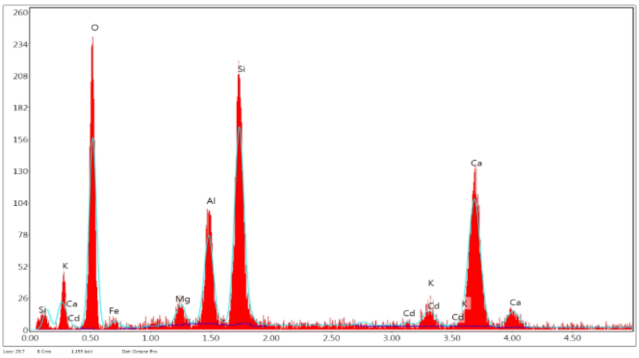


Figure 2. Natural and Cd-treated SEM images of the nanoclay.

Figure 2 clearly shows the peaks of Cd ion in the FE-SEM image of the nanocomposite used in the study. In the EDX diagram, the ratio of Cd retained is given.



Element	Wt %	Atomic %	Error %	Net Int.	Net Error %	K Ratio	Z	R	A	F
O K	53.56	70.74	11.22	82.08	2.65	0.1302	1.0590	0.9650	0.2296	1.0000
Mg K	1.90	1.65	22.35	9.92	15.99	0.0086	0.9802	0.9995	0.4569	1.0077
Al K	6.88	5.39	9.92	45.28	4.89	0.0389	0.9442	1.0068	0.5930	1.0103
Si K	14.41	10.84	7.10	105.68	2.78	0.0930	0.9652	1.0137	0.6638	1.0074
Cd L	0.59	0.11	59.18	1.91	57.01	0.0048	0.7074	1.2351	1.0855	1.0606
K K	1.39	0.75	23.28	8.72	21.28	0.0124	0.8958	1.0429	0.9334	1.0621
Ca K	16.61	8.76	5.29	86.16	3.67	0.1472	0.9123	1.0477	0.9530	1.0193
Fe K	4.66	1.76	21.55	11.86	19.83	0.0399	0.8140	1.0690	0.9895	1.0640

Figure 3. EDX diagram obtained as a result of interaction of nano clay with metal.

When the data in this diagram are examined, it is understood that cadmium element is adsorbed by nanoclay.

Table 2. Classification values of the sample according to SiO_2 ratios

SiO_2 Ratio (%)	Type
>63	Acidic
63-52	Medium
52-45	Basic
<45	Ultrabasic

When the data in this table are evaluated, it is understood that the clay has a moderate SiO_2 ratio [5].

3.2. XRF Analysis

XRF analysis of clay was performed and the results obtained are given in the table below.

Table 3. Clay XRF Results

Sample Sign %	Sivas Nanoclay
LOI	10.50
Al_2O_3	14.7
CaO	3.7
Fe_2O_3	7.5
K_2O	1.0
MgO	4.3
MnO	0.1
Na_2O	0.1
P_2O_5	<0.1
SiO_2	57.1
TiO_2	0.6

When the data in Figure 3 and Table 3 are analyzed, it is understood that there is a consistency between the SEM-EDX and XRF results and the microscopic and macroscopic data and that they support each other

3.3. XRD Analysis

The structure of the obtained nanoclay was determined by X-ray powder diffraction (XRD) method. These measurements were performed with a Brucer D8 Discover X-ray diffractometer. The diffractogram of the composite is given in Figure 4

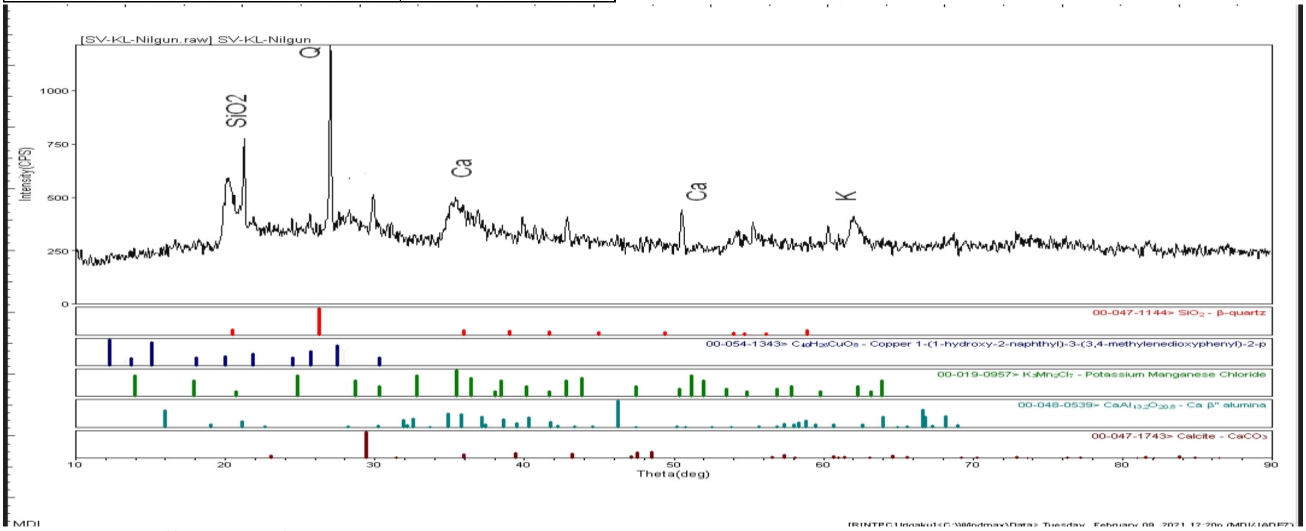


Figure 4. XRD diffractogram of nanoclay.

On the diffractogram, quartz peak is striking.

3.4. TGA Analysis

The amount of volatile matter in the sample was determined by thermal gravimetric analysis. Looking at the TGA peak (25-800°C), there is a decrease around 100°C due to humidity, while the situation is relatively stable between 100-600°C. The % decrease between 600-800 °C is due to the thermal decomposition of $CaCO_3$, the main ingredient of calcite, turns into limestone (CaO) by releasing CO_2 or dehydration of the Al-OH bond. As a result of the analysis, it was determined that the mass had approximately 25% volatile matter.

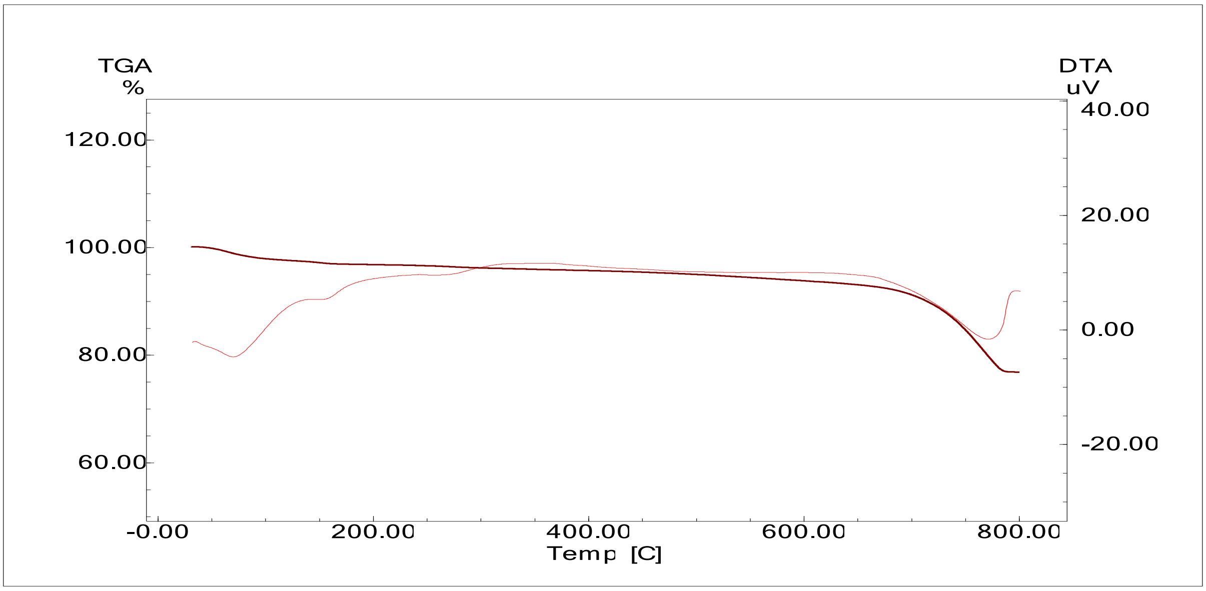


Figure 5. TGA diagram of the nanoclay

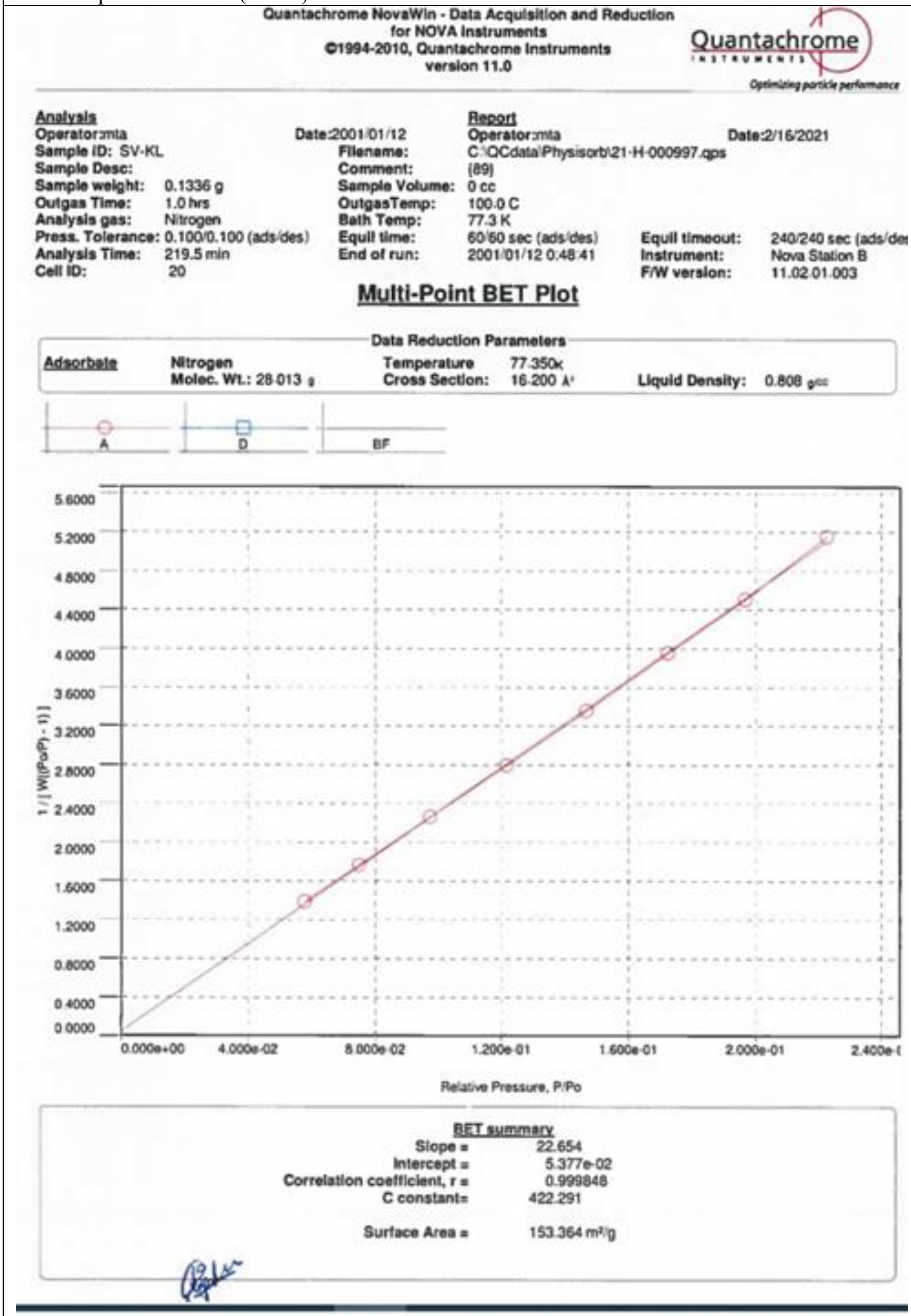
3.5. BET Analysis.

At 77.3 K temperature and low pressure, BET (Braun Emmet Teller) method was applied with nitrogen gas adsorption and the surface area was measured as 153.364 m^2/g. BET detail table is given below.

Table 4. BET detail data table

Surface Area Data
Multi Point BET……………………………………………………………1.534e+02 m^2/g BJH method cumulative adsorption surface area…………………………...3.897e+01 m^2/g BJH method cumulative desorption surface area …………………………7.257e+01 m^2/g DH method cumulative adsorption surface area……………………………3.957e+01 m^2/g DH method cumulative desorption surface area……………………………7.400e+01 m^2/g t- method external surface area……………………………………………..9.391e+01 m^2/g t- method micropore surface area……………………………………......5.945e+01 m^2/g NLDFT cumulative surface area…………………………………………1.148e+02 m^2/g …………………………………………3.794e+00 nm
Pore Volume Data Total pore volüme for pores with Diameter Less than 131.14 nm at P/Po=0.985135……………………………………1.470e-01 cc/g BJH method cumulative adsorption pore volume…………………………...8.512e-02 cc/g BJH method cumulative desorption pore volume.. …………………………9.910e-02 cc/g DH method cumulative adsorption pore volume ……………………………8.406e-02 cc/g DH method cumulative desorption pore volume ……………………………9.713e-02 cc/g t- method micropore volume ………………………………………………2.714e+01 cc/g HK method cumulative pore volume ……………………………………...8.543e+01cc/g SF method cumulative pore volume ……………………………………...8.565e+01cc/g NLDFT method cumulative pore volume …………………………………1.322e+01cc/g

Pore Size Data
Average pore Diametter……………………………………………………...3.835e+00 nm
BJH method adsorption pore Diameter (Mode Dv (d))……………………...3.146e+00 nm
BJH method desorption pore Diameter (Mode Dv (d))……………………...3.709e+00 nm
DH method adsorption pore Diameter (Mode Dv (d)) ……………………..3.146e+00 nm
DH method desorption pore Diameter (Mode Dv (d)) ……………………...3.709e+00 nm
HK method pore Diameter (Mode)…………………………………………..4.315e+01 nm
SF method pore Diameter (Mode) …………………………………………3.508e+01 nm
NLDFT pore Diameter (Mode) ….



AREA-Volume Summary
Data Reduction Parameters Data

Adsorbate: Nitrogen Temparature: 77.350 K
Molec. Wt. 28.013 g Cross Section 16.200 A° Liquid Density:0.808 g/cc

3.6. Adsorption Models

3.6.1. Isotherm Studies

The experimental and instrumental studies of the adsorption isotherm followed a similar path to the kinetic studies. The adsorption of cadmium ion was carried out at 3 temperatures of 298, 308 and 318 K. Adsorption was carried out at different concentrations until equilibrium was reached. The solutions obtained as a result of the process were analyzed in AAS device and data were obtained. These data were applied to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Halsey and Jovanovich isotherm models.

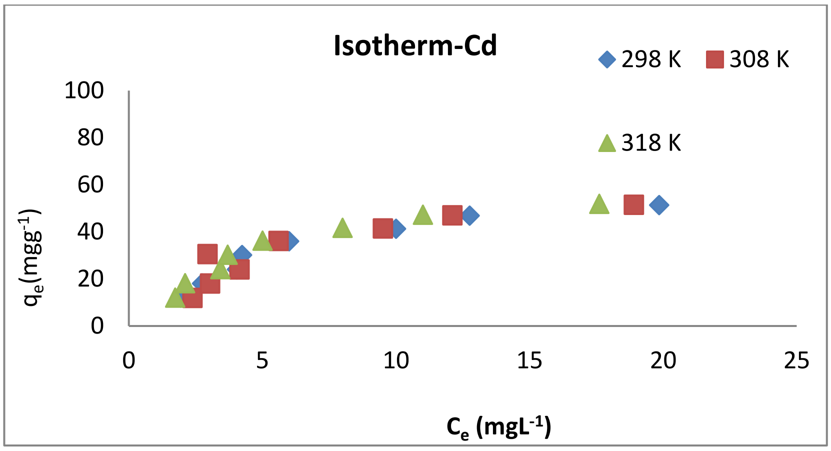


Figure 6. Isotherm plots of Cd (II) at 298,308 and 318

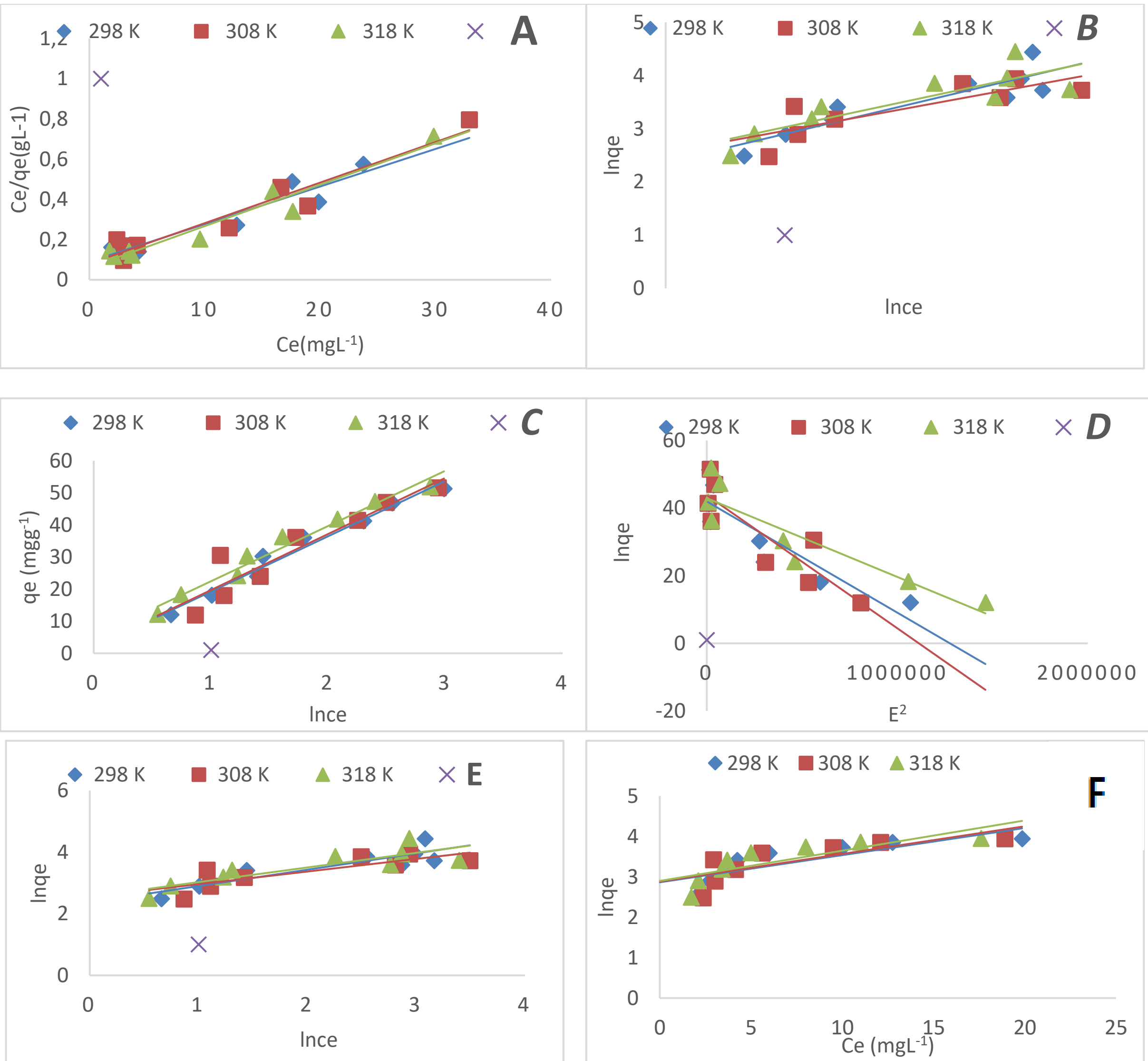


Figure 7. (**a**) Langmuir, (**b**) Freundlich, (**c**) Temkin, (**d**) Dubinin-Radushkevich, (e) Halsey, (f) Jovanovich plots of Cd (II) at 298,308 and 318 K

Thus, Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Halsey and Jovanovich isotherm linear plots were obtained. The necessary parameters of these models were obtained from these plots. These parameters are given in table.7.

Table 5. Constants achieved from Adsorption Isotherm Experiment

Langmuir Isotherm				Freundlich Isotherm			Temkin Isotherm			Dubinin-Radushkevich Isotherm		
T (K)	K_L(L/mg)	q_{max} (mg/g)	R^2	K_F	n	R^2	B	K_{TM}	R^2	K_{DR} (L/mg)	E (kJ/mol)	R^2
298	0.208	53.476	0.915	234.423	1.885	0.8041	17.242	1.123	0.9745	$3E.10^{-5}$	129	0.7932
308	0.253	49.50	0.928	356.396	2.438	0.6811	17.490	1.134	0.8829	$4E.10^{-5}$	111.8	0.7778
318	0.338	48.54	0.946	357.026	2.101	0.7366	17.227	1.354	0.9728	$2E.10^{-5}$	158.1	0.8216
Halsey Isotherm							Jovanovich Isotherm					
T	K_H		n		R^2		K_J		q_{max}		R^2	
298	-4.468		-1.885		0.804		-0.0672		17.544		0.677	
308	-6.223		-2.438		0.681		-0.0684		17.849		0.616	
318	-5.364	-2.101	0.737	-0.0748	18.143	0.654	-0.0748	18.143	0.654			

3.6.2. Thermodynamic studies

ΔH and ΔS values can be found from the formula $\ln Kd^o = -\Delta H/R + \Delta S/R$. For this, it is essential to find the lnKd° value. Therefore, the plot given in figure 10 was created and lnKd° values were found for each temperature from the shift of the plot.

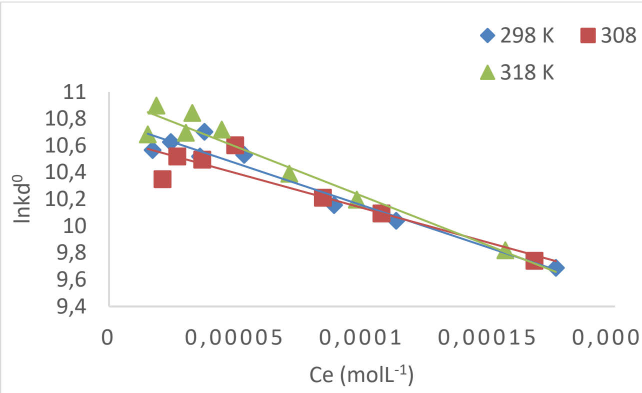


Figure 8. lnKd plot of different concentration values of Cd (II)

The lnKd° values found were plotted with corresponding 1/T values and the Van't Hoff plot given in figure 11 was obtained.

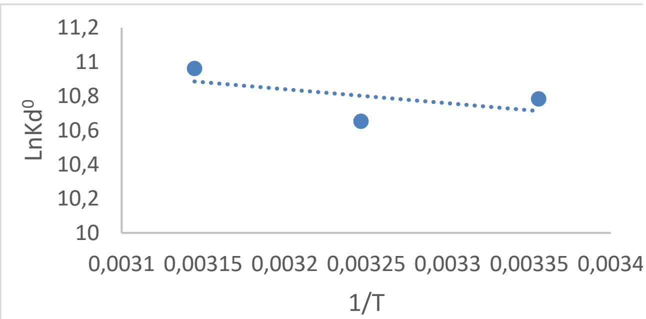


Figure 9. Van't Hoff plot of Cd (II)

The equation obtained from the plot is applied to Gibbs' equation: The obtained ΔG, ΔH and ΔS values are given in table.7.

Table 6. Thermodynamic parameters related to the adsorption of Cd (II) on nanoclay.

T (K)	ln K°	ΔG ($kJmol^{-1}$)	ΔH ($kJmol^{-1}$)	ΔS($kJmol^{-1}K^{-1}$)
298	10.784	-26.553	6.823	0.112
308	10.654	-27.673		
318	10.962	-28.796		

Figure. 10 shows the Gibbs equation in its Onursal notation. The shift of the equation of the plot directly gives ΔH and the negative value of the slope directly gives the entropy.

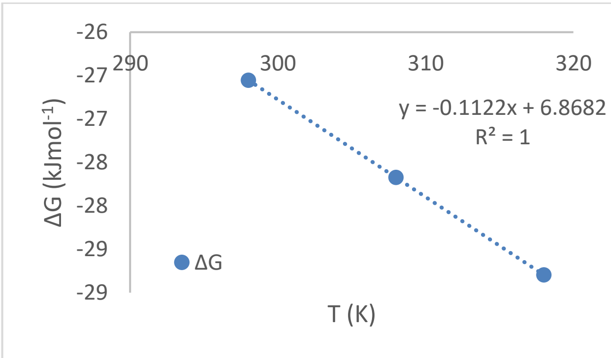


Figure. 10. Onursal representation of the Gibbs formula.

3.6.3. Adsorbent Quantity

In figure 11, the variation of the amount of adsorbed material with the amount of adsorbent is plotted. As can be seen, although the amount of adsorbent is inversely proportional to q_e, it converges to a base value. This has two meanings. The first is that as adsorbent concentration rises, efficiency falls. The second meaning is that q_e does not increase after a certain point, regardless of how much the amount of adsorbent increases.

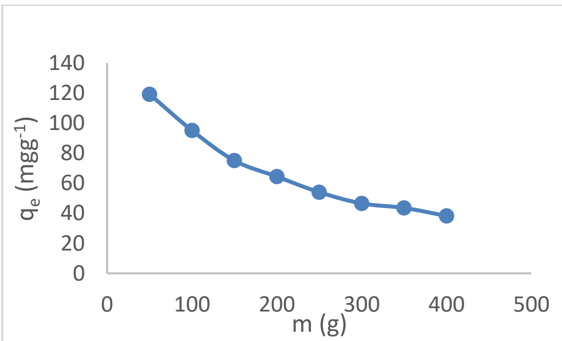


Figure 11. Quantity plot of Cd (II)

4. DISCUSSION AND CONCLUSION

The purpose of this study was to investigate the adsorption method for removing cadmium and to look at the variables that affect adsorption.

According to the results of the analysis, it was understood that it contains the materials that make up the clay. Both vesicular appearance, SEM images and XRF analysis results showed that the material is natural clay. Especially the SiO_2 value is proof of this. SEM_EDX results show that the clay adsorbs Cd (II). Instrumental analysis methods such as XRD, XRF, BET and SEM-EDX were also used to characterize the adsorber. The adsorber pore size was measured as 3.835 nm and the surface area was measured as 153.364 m^2g^{-1}. In kinetic studies, 180 min was determined as the working time and the equilibration time was measured as 45 min on average.

In the studies on adsorption equilibrium, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich, Halsey and Jovanovich isotherm models were applied. As a result of the regression on the isotherm models, it was found that the adsorption complied with the Temkin model. The adsorption capacity of SNC was determined as 53.48, 49.50 and 48.54 mgg^{-1} for 298, 308 and 318 K temperatures.

As a result of the adsorption thermodynamic study, ΔG° values were found to be -26.553, -27.673, -28.796 $kJmol^{-1}$, ΔH° value 6.823 $kJmol^{-1}$ and ΔS° value 0.112 $kJmol^{-1}K^{-1}$ for 298, 308, 318 K, respectively. The positive value of ΔH° indicates that the event is endothermic. The positive value also indicates that the event is chemical. The negative sign of ΔG° indicates that the event is spontaneous.

As a result, it was determined that SNC can be used as an effective adsorbent due to its high capacity and rapid equilibration.

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