Removal of Zn^{+2} and Pb^{+2} from Wastewater by using Natural Nano Montmorillonites

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ABSTRACT---*In this study, nano montmorillonite which is an economic and naturally abundant material was investigated in terms of its adsorption capability to remove lead and zinc ions from aqueous solutions. A series of experiments were performed at various temperatures such as 25^0C, 35^0C, 45^0C. The experimental results of potential adsorption belonging to lead and zinc ions were evaluated by using Langmuir, Freundlich and Temkin isotherm models. According to the data obtained, adsorption of both metal ions was well fitted with Langmuir isotherm model. In the adsorption of lead and zinc ions by nano montmorillonite, effects of adsorbent dosage, stirring speed, pH, reaction time, temperature and initial concentration were investigated. According to the results, the highest removal efficiency for lead ions was achieved with 0.25 g nano montmorillonite, 200 rpm stirring speed, pH 5, 200 mg/L initial concentration, 120 minutes and 84% removal efficiency was obtained. For zinc ions, 81% removal efficiency was obtained with 0.3 g nano montmorillonite, 200 rpm stirring speed, pH 5, 200 mg/L initial concentration and 180 minutes. For both metal ions, thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 were calculated and it was determined that adsorption process was spontaneous and endothermic. Moreover, adsorption kinetics was considered and this process was fitted well with pseudo-second order kinetic model. In accordance with the results of this study, it can be concluded that adsorption capability of nano montmorillonite for the removal of heavy metals from aqueous solutions is quite high.*

Keywords- Zinc and lead adsorption, isotherm, kinetics, nano-montmorillonite, thermodynamic.

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1. INTRODUCTION

Industrial wastewater having high heavy metal content is one of the most important sources of pollution for receiving water environment [1]. Heavy metals are resulted from industrial applications such as dye industry, photography, surface treatment, metal coating, battery production, etc. [2]. The most important characteristics of heavy metals are that they are not biodegradable, are resistant to decomposition, accumulate in living things and transfer to other living things via food chain. For this reason, removal of heavy metals from water and wastewater which become a threat for humans and the environment is of vital importance. Methods such as ion exchange, chemical precipitation, reverse osmosis, oxidation and ultrafiltration are used for the removal of heavy metals from industrial wastewater. Ion exchange and chemical precipitation are commonly used among other methods [3, 4]. Experimental studies are performed in two phases. In the first phase, the optimum $MnSO_4$ dose for removal of Cr(VI) was determined. In the second phase, the optimum pH was studied. About 96% removal of chromium was launched with 530 mg l^{-1} $MnSO_4$ dose at pH value 9 in the wastewater sample [5] [6] demonstrated that the adsorption process was spontaneous and endothermic under natural conditions. The maximum removal efficiencies were 93% for Cu(II) at pH 4, 82% for Ni(II) at pH 8, and 84% for Cr(VI) at pH 3.

When compared to other methods, adsorption is the method which is widely used for the removal of pollutants from wastewater. This method is more preferable due to its high efficiency especially in the removal of heavy metals [7]. Adsorption is a process in which atom, ion or a molecule is adsorbed on the surface of the solid. In adsorption process, the substances adsorbed are called adsorbates. Adsorbates can be one or more than one. The substance on the surface of

which adsorption is occurred is the adsorbent. The main feature of a good adsorbent is to have wide surface area per unit mass.

Many different substances such as peat [8], almond shell [9], fly ash [10], silicon antimonate ion exchanger [11], grafted silica [12], sewerage sludge ash [13] woody plants [14], natural zeolite [15], bones [16], Sphaeroplea algae [17] chitosan [18], ash of thermal power plant [19] are effectively used as adsorbent.

Clay which is a natural adsorbent has three well known kinds such as smectites (e.g. montmorillonite), kaolin and mica. Montmorillonite has high cation exchange capacity. Its marketing price is 20 times less than that of activated carbon. For this reason, clays including especially montmorillonite are effectively used for the removal of metal ions such as Zn^{+2}, Pb^{+2} from aqueous solutions [20]. There are many studies in the literature which were aimed to reveal the capacity of montmorillonite in heavy metal removal. Montmorillonite and kaolin were used for the removal of lead and cadmium and it was presented that adsorption capacity of montmorillonite was higher than that of kaolin [21]. Also montmorillointe was evaluated in the removal of zinc and cadmium and more zinc ions were absorbed by montmorillonite than cadmium ions [22]. In other studies, acid-treated montmorillonite was used for the removal of lead [23] and modified montmorillonite was used for copper and zinc removal [24].

2. EXPERIMENTAL STUDIES

2.1. Chemicals

The chemicals used in the experiments were all analytical grade and $ZnCl_2$ salt was used for Zn^{2+} solution and $PbCl_2$ salt was used to prepare Pb^{2+} solution. 1000 mg/L stock solutions of zinc and lead were prepared. Then, required concentrations of metal ion solutions were prepared by diluting the stock solution. For pH adjustments, 1M HCl and 1M NaOH solutions were prepared.

2.2. Adsorbent

Nano montmorillonite, a natural clay mineral, was used as an adsorbent. This adsorbent was provided from Erzurum domain which was then processed by ANKA Nanotechnology Construction Geotechnique Informatic Food Commerce Marketing Co. Ltd., XRD analysis was carried out in order to determine the mineralogical properties of nano montmorillonite (Figure 2). According to the results of XRD analysis, it was observed that our sample constituted of montmorillonite mineral. In Table 1., chemical components of nano montmorillonite are given. SEM images show lamellar structure and surface shape of nano montmorillonite. In Figure 3. SEM images of the adsorbent are given. It was observed that mined montmorillonite was yellow in color. In order to determine the concentrations of metals during experiments, GBC trade HG393AA model Atomic Absorption Spectrometer was used. Adsorption experiments performed with ZHWY-200B Incubator Shaker. For weighing of the amounts, SARTORIUS TE214S analytical balance was used. HACH HQ40d MULTI trade pH meter was used for pH analysis. Moreover, BINDER trade incubator and ELEKTRO-MAK EM 4808 P and centrifuge were used. The glass materials and balance are calibrated and certificated.

DTA -TG analysis of Montmorillonite: In the DTA-TG analysis of nano montmorillonite samples, it was observed that they were dehydrated at around 80-100^{0}C (Figure 1). Nano montmorillonite samples dehydrated their crystal water content between montmorillonite layers at 100-300ºC [25] and dehydroxylation occurred in nano montmorillonite samples due to endothermic reactions above 300ºC [26] and the samples dehydrated their water content as a result of dehydroxylation [27]. In Figure 1. dehydroxylation peaks of Yellow montmorillonite samples can be observed at 404ºC in illite mineral and at 653ºC in montmorillonite mineral.
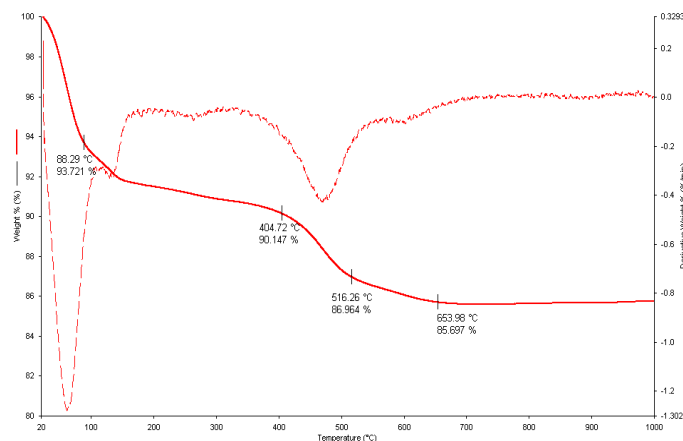

Figure 1 DTA-TG analysis of nano montmorillonite; a) Green mont. b)Red mont. c)Yellow mont.

ZP Measurements: Zeta Potential, -22.5 mV, EC: 10.6 μS/cm, pH: 7.59, Density of particles: 2.55086 gr/cm^3, Surface area: 12.36210 m^2/g, Pore space: 0,020325 cm^3/gr.

Table 1. Chemical components of natural montmorillonite mineral.

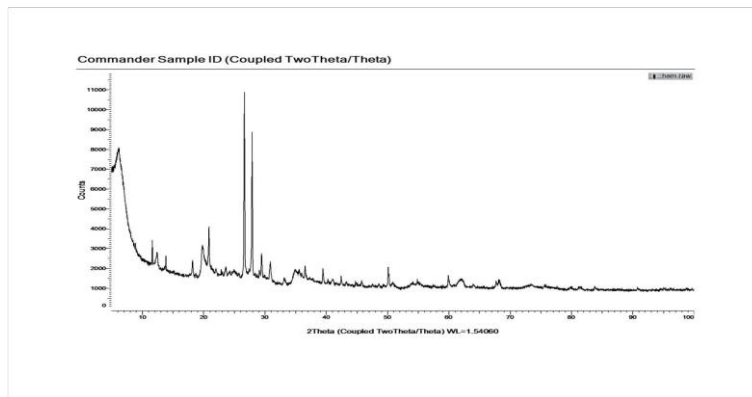| Symbol	Components
Na_2O	0.02
MgO	2.82
Al_2O_3	20.67
SiO_2	53.28
K_2O	0.82
CaO	6.13
TiO_2	0.63
Fe_2O_3	6.13

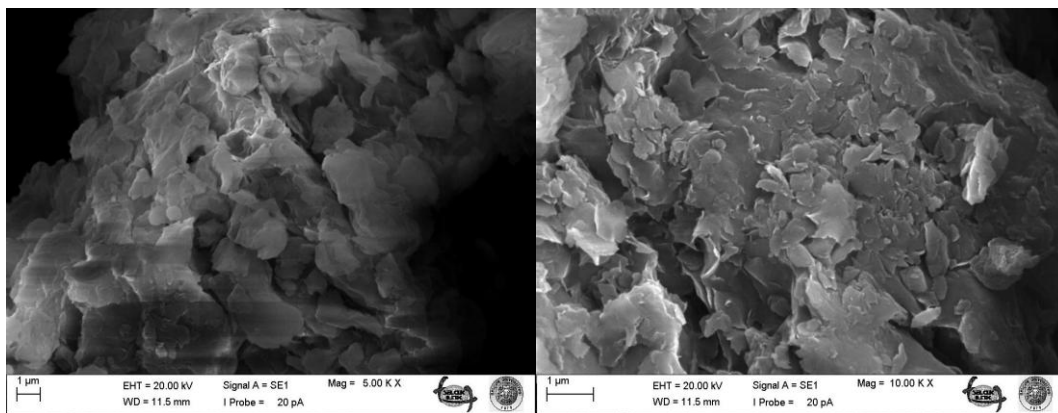**Figure 2.** XRD analysis of nano montmorillonite.

Figure 3. SEM images of nano montmorillonite.

Table 2. Contact angle values of nano montmorillonite samples

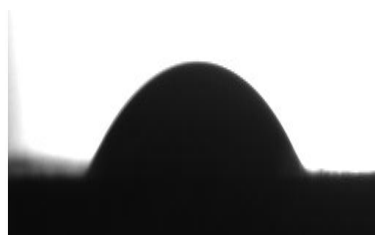| Additive (%)	Yellow montmorillonite TA (^{0})
Natural	35

Figure 4. Contact angle of Natural Yellow montmorillonite samples (35°)

2.3. Adsorption experiments

Optimum values of parameters affecting adsorption were determined. First of all, effect of contact time on adsorption was investigated and experiments performed in time periods varying between 1 and 300 minutes. In order to determine adsorbent dosage, the amount of adsorbent was varied between 50 and 400 mg. Effect of stirring speed was investigated by an optimization study within the range of 100 – 300 rpm. The pH experiments were carried out by changing the pH values between 2 and 9. Moreover, the effect of temperature on adsorption was investigated by performing the experiments at 25, 35, 45 ^{0}C temperatures. Langmuir, Freundlich and Temkin isotherm models were applied to the results of experiments performed under optimum conditions. Isotherm constants were calculated by using linearized forms of these isotherm equations. Moreover as well as kinetic studies thermodynamic parameters were calculated from classical thermodynamic equations.

3. RESULTS AND EVALUATIONS

3.1. Optimization Studies

3.1.1. Determination of Optimum Time

250 mg nano montmorillonite was added into 200 mL of solutions including 200 mg/L Pb^{2+} and Zn^{2+} ions and they were mixed. The samples were taken from shaker within 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 210, 240, 270 and 300 minutes, respectively and then they were measured with AAS after separation by filter paper. Removal efficiencies with time are given in Figure 5.a and Figure 5.b. First, adsorption increased with time and reached to equilibrium after having a plateau value. Adsorption of Pb^{2+} ions reached to equilibrium in 120 minutes (Figure 3.1.a) and significant removal efficiency was not observed after 120th minute. It was observed that adsorption of Zn^{2+} ions, on the other hand, reached to equilibrium in 180 minutes (Figure 3.1.b).
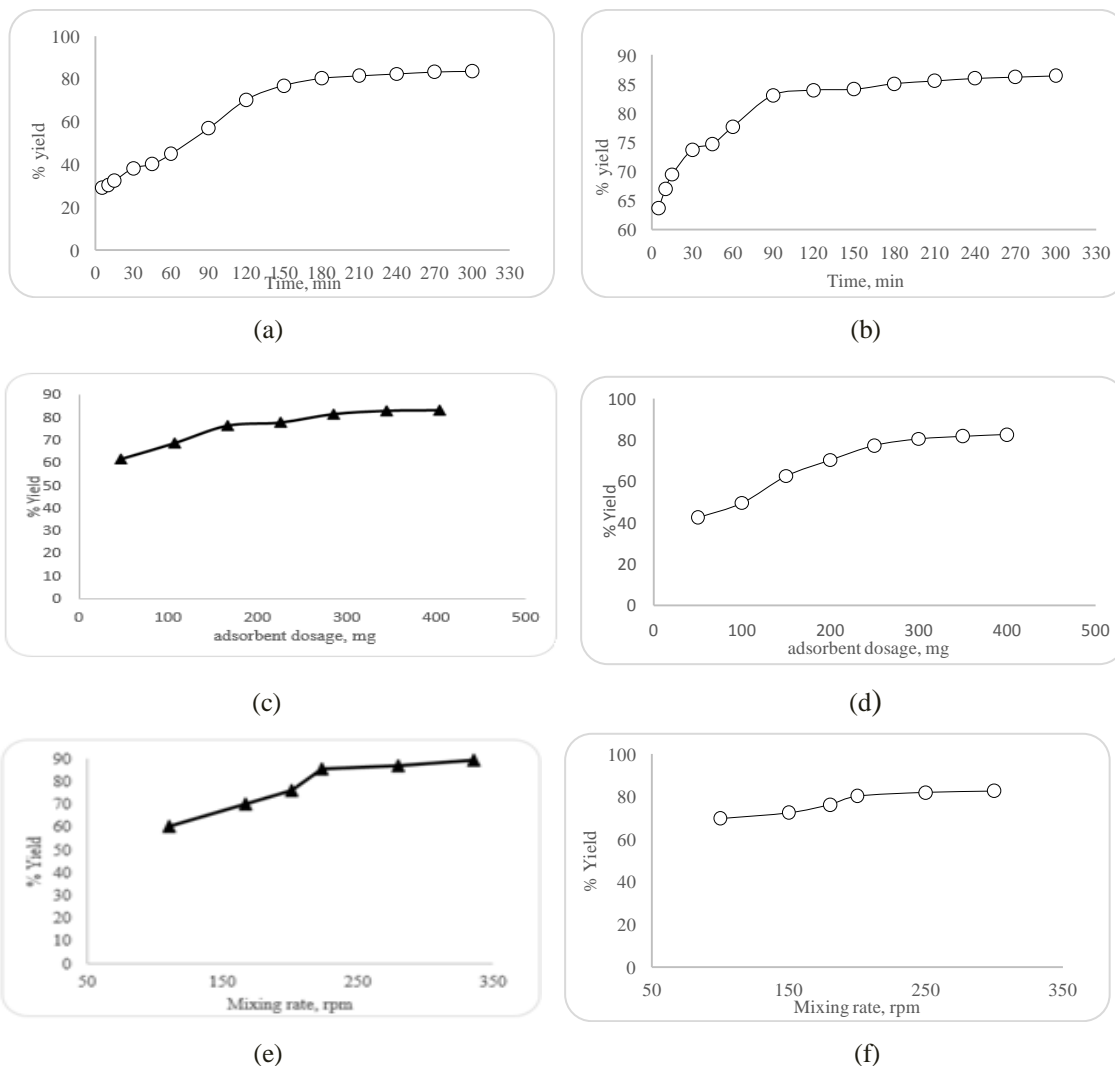

(a)

(b)

(c)

(d)

(e)

(f)

Figure 5. Removal efficiency of Pb (II) (a,c,e) and Zn (II) (b,d,f) with respect to time (a,b), adsorbent dosage (c,d) and stirring speed (e,f).

3.1.2. *Determination of Optimum Adsorbent Dosage*

In this part of the study, the effect of adsorbent dosage on the adsorption of Pb^{2+} and Zn^{2+} ions was investigated and the results are given in Figure 5.c and Figure 5.d. For Pb^{2+} metal ion, the experiments were performed with 50, 100, 150, 200, 250, 300, 350 mg adsorbent dosages in 200 mL sample solution of 200 mg/L initial concentration in 120 minute-equilibrium time. It was observed that increase in adsorbent dosage resulted in increase in removal efficiency however a significant change was not determined after 250 mg. In the adsorption of Pb^{2+} metal ion, optimum adsorbent dosage was determined as 250 mg (Figure 5.c). For Zn^{2+} metal ion, the experiments were performed with 50, 100, 150, 200, 250, 300, 350, 400 mg adsorbent dosages in 200 mL sample solution of 200 mg/L initial concentration in 180 minute-equilibrium time. Optimum adsorbent dosage was determined as 300 mg (Figure 5.d).

3.1.3. *Determination of Optimum Stirring Speed*

A set of experiments was carried out with different stirring speeds at predetermined optimum adsorbent dosage and equilibrium time of adsorption. For Pb^{2+} metal ion; the experiments were performed with 100,150, 180, 200,250,300 rpm stirring speeds in the solution of 200 mg/L initial concentration having 250 mg adsorbent dosage in 120 minute-equilibrium time. Effect of different stirring speeds on adsorption was investigated and the results are given in Figure 5.e. When Figure 5.e was considered, it was observed that removal efficiency increased as the stirring speed was increased and considerable increase in removal efficiency was not observed after a point. The optimum stirring speed was determined as 200 rpm. For Zn^{2+} metal ion; effect of stirring speed on adsorption was investigated with 100, 150, 180, 200, 250, 300 rpm in the solution of 200 mg/L initial concentration having 300 mg adsorbent dosage in 180 minute-equilibrium time and the results are given in Figure 5.f. When the results are considered, adsorption efficiency increased as the stirring speed was increased and remained constant after a point. Therefore, optimum stirring speed was determined as 200 rpm.

3.1.4. *Determination of Optimum pH*

The effect of pH on the adsorption of Pb^{2+} and Zn^{2+} metal ions was investigated and the results are given in Figure 6.a and Figure 6.b. When pH values of synthetic wastewater prepared for the experiments were considered, it was observed that they varied between 5.0 and 5.5. pH values of the samples including 200 mg/L Pb^{2+} and Zn^{2+} metal ions were adjusted to 2, 3, 4, 5, 7, 9 with HCI and NaOH solutions. 250 mg adsorbent was added to solutions including 200 mg/L Pb^{2+} ions and the experiments were performed with 200 rpm stirring speed in 120 minute-equilibrium time. As pH increased, the efficiency decreased. It was concluded that pH of the solution should be 5 when initial pH of the water and chemical material usage in terms of economics were considered. Moreover, 300 mg adsorbent was added to solutions including 200 mg/L Zn^{2+} ions and the experiments were carried out with 200 rpm stirring speed in 180 minute-equilibrium time. pH of Zn^{2+} solutions was also selected as 5 due to the reasons mentioned above.

3.1.5. *Determination of Optimum Temperature*

In this part of the study, effect of temperature on the adsorption of Pb^{2+} and Zn^{2+} ions and the results are given in Figure 6.c and Figure 6.d. For Pb^{2+} metal ions; the experiments were performed at 25, 35, 45 ^{0}C temperatures with 200 mg/L initial concentration, 250 mg adsorbent dosage, 200 rpm stirring speed, at pH 5 in 120 minute-contact time and as it can be seen in Figure 6.c, as temperature increased, the removal efficiency also increased. For Zn^{2+} metal ion; the experiments were performed at 25, 35, 45 ^{0}C temperatures with 200 mg/L initial concentration, 300 mg adsorbent dosage, 200 rpm stirring speed, at pH 5 in 180 minute-contact time. As it can be seen from the results in Figure 6.d, efficiency of adsorption is directly proportional to the increase in temperature.
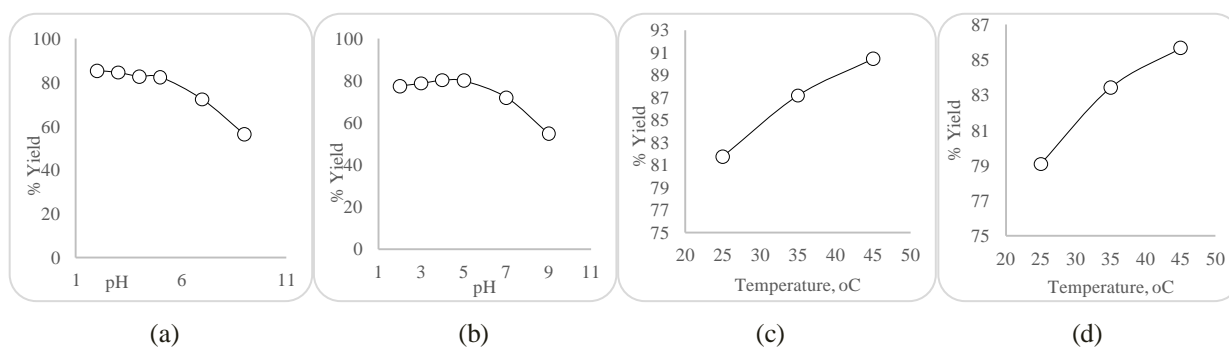

Figure 6. Removal efficiency of Pb(II) (a,c) and Zn (II) (b,d) with respect to pH (a,b) and temperature (c,d)

3.2. Adsorption Isotherms

The amount and concentration of heavy metal adsorbed by nano montmorollonite were calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)}{M} xV \tag{1}$$

where q_e (mgg^{-1}); the amount of substance adsorbed per unit mass of nano montmorillonite, Co (mgL^{-1}); initial concentration of the substance that will be adsorbed, C_e(mgL^{-1}) concentration of substance in the solution left as unadsorbed, V (L); volume of solution, M (g); amount of adsorbent. Adsorption isotherms of lead and zinc on nano - montmorillonite were investigated as temperature controlled. At different temperatures, q_e and C_e isotherm graphs are given in Figure 7.a for lead ion and in Figure 7.b for zinc.
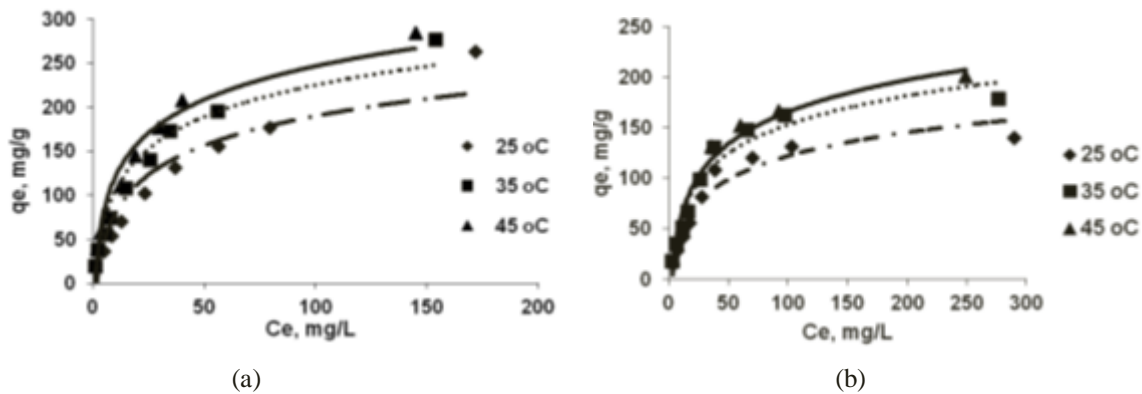

(a)   (b)

Figure 7. q_e vs. C_e graphs of Pb (II) (a) and Zn (II) (b).

In Langmuir isotherm, adsorption energy has a uniform distribution. Langmuir isotherm is expressed as in Equation 2:

$$C_e / q_e = (1/Q^0 b) + (1/Q^0) C_e \tag{2}$$

where, C_e (mg L^{-1}); concentration of the substance left in the solution after adsorption, q_e (mg g^{-1}); the amount of substance adsorbed per unit mass of the adsorbent, b (L g^{-1}); a constant related with adsorptivity of the adsorbent, Q^0 (mg g^{-1}); maximum adsorption capacity of adsorbent.

The slope and intercept of the line obtained from C_e/q_e vs., C_e graph (Figure 8.a and Figure 8.b) resulted in Q^0 and b constants, respectively. This isotherm ca nnot explain clearly the equilibrium in heterogeneous adsorption systems occurred especially as single-layer adsorption. In order to determine convenience of the adsorption, dimensionless R_L (dispersion) constant is calculated (Equation 3) and convenience is provided if the value of this constant is between 0 and 1 [28].

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

Here, b (L mg^{-1}); Langmuir constant, C_0 (mg L^{-1}) initial concentration of the substance in the solution. Freundlich isotherm explains equilibrium on heterogeneous surfaces and does not assume single-layer capacity since amount of adsorbed substance increases with the increase in solution concentration [29]. Freundlich equation is given as follows;

$$\log q_e = \log K_F + n \log C_e \tag{4}$$

where K_F (L g^{-1}) and n (untiless) are Freundlich constants being adsorbent capacity and heterogeneity factor, respectively. The slope of the line obtained from log q_e vs. log C_e graph (Figure 8.c, Figure 8.d) results in 1/n and its intercept results in log K_F. If the value of "n" is less than 1, it is indicated that adsorption process in convenient [30].
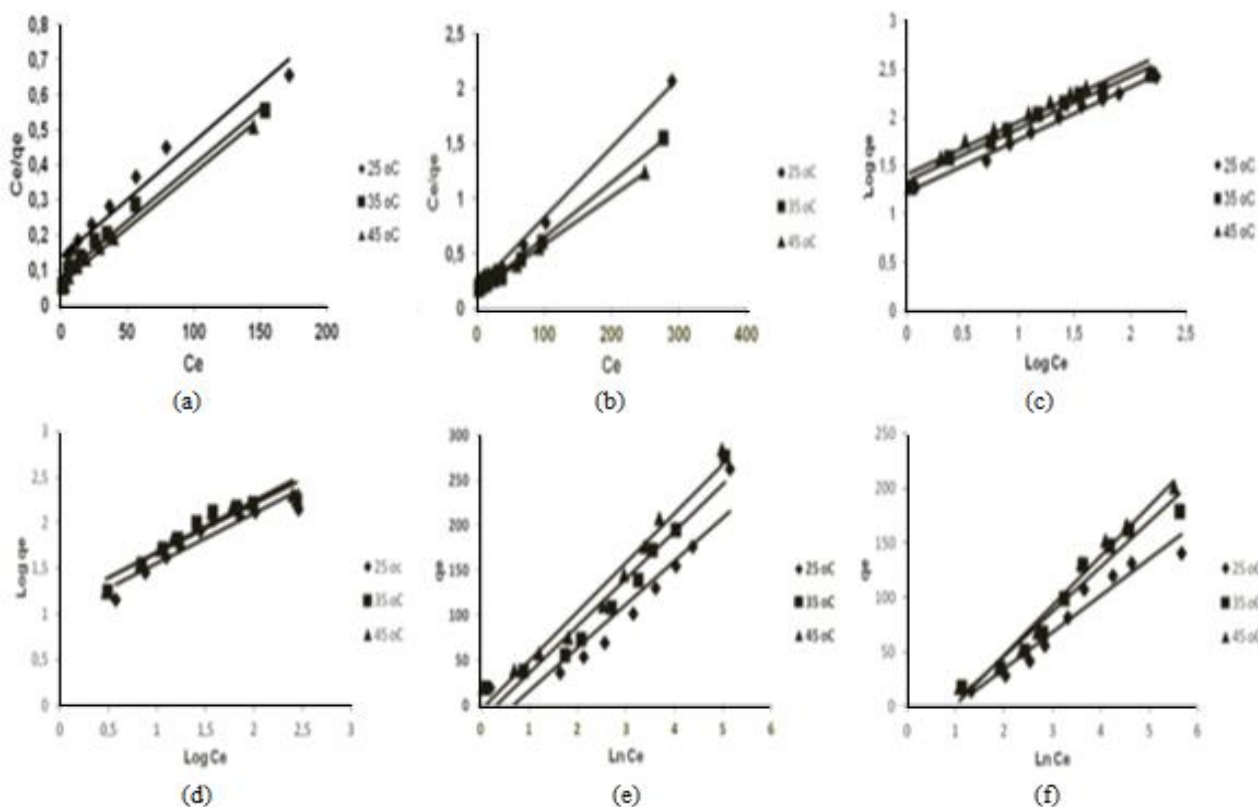
Figure 8. a) Langmuir isotherm graph for Pb (II) adsorption at different temperatures, b) Langmuir isotherm graph for Zn (II) adsorption at different temperatures, c) Freundlich isotherm graph for Pb (II) adsorption at different temperatures d) Freundlich isotherm graph for Zn (II) adsorption at different temperatures, e) Temkin isotherm graph for Pb (II) adsorption at different temperatures, f) Temkin isotherm graph for Zn (II) adsorption at different temperatures.

Temkin adsorption isotherm is the one which expresses the indirect effects of adsorbate-adsorbent interactions on adsorption. According to Temkin isotherm, adsorption heat of all molecules in the layer decreases linearly. Temkin isotherm is generally given as Equation (5) [31].

$$q_e = \frac{RT}{b}\ln(A) + \frac{RT}{b}\ln(AC_e) \tag{5}$$

"B" is written instead of RT/b and A together with B are called Temkin constants. Here R is gas constant (J mol^{-1}K^{-1}), T is the temperature of the medium (K). Temkin isotherm graphs are given in Figure 8.e and Figure 8.f. Isotherm constants and R^2 values obtained in the adsorption of both metal ions at different temperatures are given in Table 3.

When R^2 values were considered, it was determined that Langmuir adsorption isotherm was well fitted for the adsorption of both metal ions.

Table 3. Isotherm constant obtained at different temperatures

Temperature	T	Lead			Zinc		
		25 ^{0}C	**35 ^{0}C**	**45 ^{0}C**	**25 ^{0}C**	**35 ^{0}C**	**45 ^{0}C**
Langmuir Adsorption Isotherm	Q^0	30.30	31.25	32.26	15.63	20.00	22.73
	b	0.1372	0.0815	0.0606	0.1829	0.1422	0.1485
	R^2	0.948	0.984	0.994	0.9932	0.9963	0.9983
	R$_L$	0.23 – 0.014	0.33 – 0.024	0.062 – 0.032	0.18 – 0.011	0.22 – 0.012	0.21 – 0.013
Freundlich Adsorption Isotherm	K$_F$	16.79	22.17	25.92	10.22	13.31	12.97
	n	1.83	1.84	1.85	1.83	1.85	1.77
	R^2	0.993	0.977	0.956	0.8748	0.8981	0.9239
Temkin Adsorption Isotherm	B	48.15	52.32	54.72	33.65	41.29	45.66
	A	31.94	15.83	5.40	33.21	37.17	44.90
	R^2	0.890	0.946	0.969	0.942	0.956	0.976

3.3. Adsorption Kinetics

Adsorption kinetics was investigated in terms of pseudo-first order and pseudo-second order kinetics models as well as intraparticle diffusion model. Pseudo-first order kinetics model is expressed as follows [32];

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{6}$$

q_e (mg g^{-1}) and q_t (mg g^{-1}) are amount of adsorbed substance at equilibrium and at any time t, respectively, k_1 (min^{-1}) is rate constant for pseudo-first order.

The slope and the intercept of the line belonging to the graph of log (q_e – q_t) vs. t (Figure 9.a and Figure 9.b) are used to determine adsorption density at equilibrium q_e and pseudo-first order rate constant k_1, respectively [33]. Pseudo-second order adsorption kinetics is given in the following equation [34];

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \tag{7}$$

k_2 (g mg^{-1}min^{-1}) is the rate constant of pseudo-second order. Rate constant of pseudo-second order adsorption kinetics (k_2) and amount of adsorbed heavy metal at equilibrium (q_e cal.) were determined from the slope and intercept of t vs. t/q_t graph (Figure 9.c and Figure 9.d), respectively [35]. Intraparticle diffusion equation is the one which was presented to explain the rate change in fractional equilibrium systems. Intraparticle diffusion model is given as follows [36];

$$q_t = k_{int} t^{1/2} \tag{8}$$

k_{int} (mg g^{-1} min$^{-1/2}$) is the rate constant of intraparticle diffusion model. The graph of $t^{1/2}$ versus q_t was drawn (Figure 9.e and Figure 9.f). The values of k_{int} were calculated from the slope of the graph. The constants and parameters calculated for adsorption kinetics are given in Table 4. When the results in Table 4. were considered and R^2 values were investigated, it was determined that the adsorption of both metal ions on nano montmorillonite was in accordance with pseudo-second order kinetics model. According to the results, the adsorption capacities of the adsorbent for lead and zinc were calculated as 138.8 g. and 143.8 g, respectively.

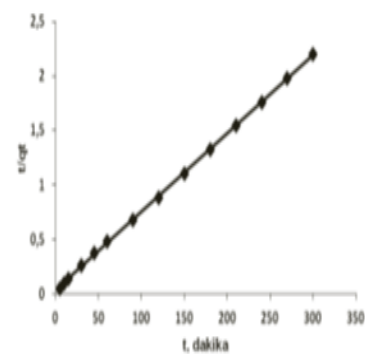**Table 4.** Kinetik parameters and correlation coefficients

	q_e experimental	Pseudo first order kinetic model			Pseudo second order kinetic model			Intraparticle diffusion model	
		k_1	q_{ehes}	R^2	$k_2 \times 10^3$	q_{ehes}	R^2	k_{int}	R^2
Pb^{2+}	136.72	0.0087	30.77	0.947	1.7	138.88	0.999	2.26	0.865
Zn^{2+}	111.33	0.0108	143.81	0.954	0.21	126.58	0.978	5.78	0.944

(a)   (b)   (c)

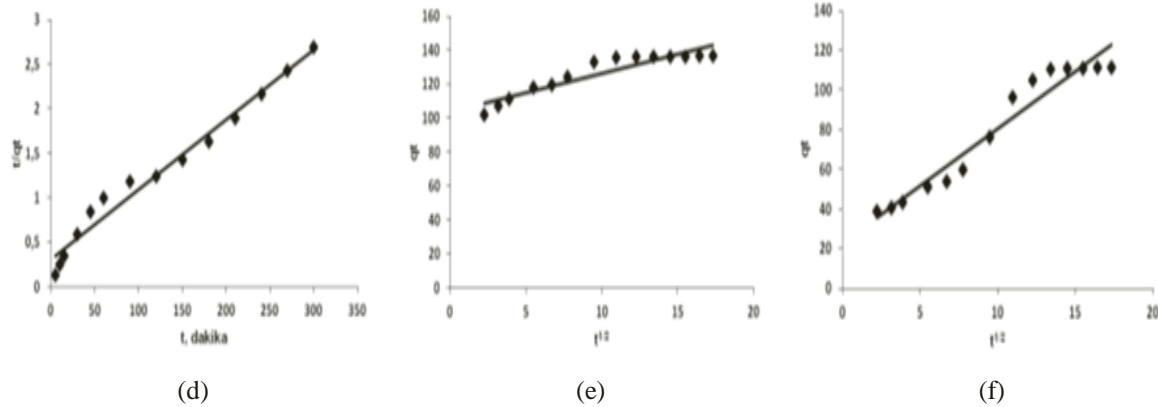|		
(d)	(e)	(f)
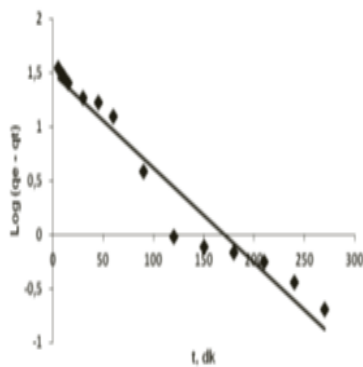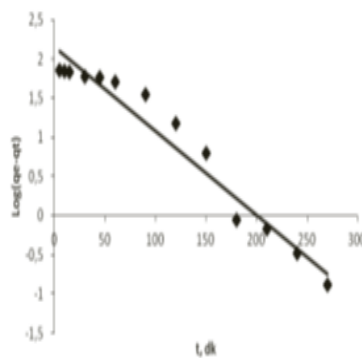
Figure 9. a) Pb(II) Pseudo-first order kinetic model b) Zn(II) Pseudo-first order kinetic model c) Pb(II) Pseudo-second order kinetic model d) Zn(II) Pseudo-second order kinetic model e) Pb(II) Intraparticle diffusion model f) Zn(II) Intraparticle diffusion model

3.4. Adsorption Thermodynamics

Investigation of thermodynamic parameters such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) is important in terms of deciding its feasibility for the adsorption of Zn and Pb heavy metal ions on nano-montmorillonite and its spontaneous nature. The value of ΔG^o can be calculated as follows [24];

$$\Delta G^0 = -RT \ln K_c \tag{9}$$

Where R (8.314 J mol^{-1}K^{-1}) is gas constant, T (Kelvin) is temperature, K_c is distribution coefficient and is calculated as follows:

$$K_c = q_e / C_e \tag{10}$$

The following equations are used to calculate enthalpy (ΔH^o) and entropy;

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{11}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{12}$$

Generally a system is in a tendency of having the lowest energy and the highest entropy. Therefore, a reaction having negative $\Delta H°$(exothermic) and positive $\Delta S°$ (entropy increases) values proceeds forward in the formation of products. If $\Delta H°$ value is positive and $\Delta S°$ value is positive, it can be said that the reaction is spontaneous. If $\Delta H°$ value is positive and $\Delta S°$ value is negative, then the reaction is non spontaneous. If $\Delta H°$ is positive, the reaction is endothermic and if $\Delta H°$ is negative, then the reaction is exothermic. The driving force of a reaction is expressed with Gibbs free energy $\Delta G°$. Negative $\Delta G°$ values indicate that the process is possible and the reaction occurs spontaneously [37]. The thermodynamic parameters ΔH^o and ΔS^o values were calculated from the slope and intercept of the graph of 1/T versus ln K_c (Figure 10.a and Figure 10.b), respectively and are given in Table 5.
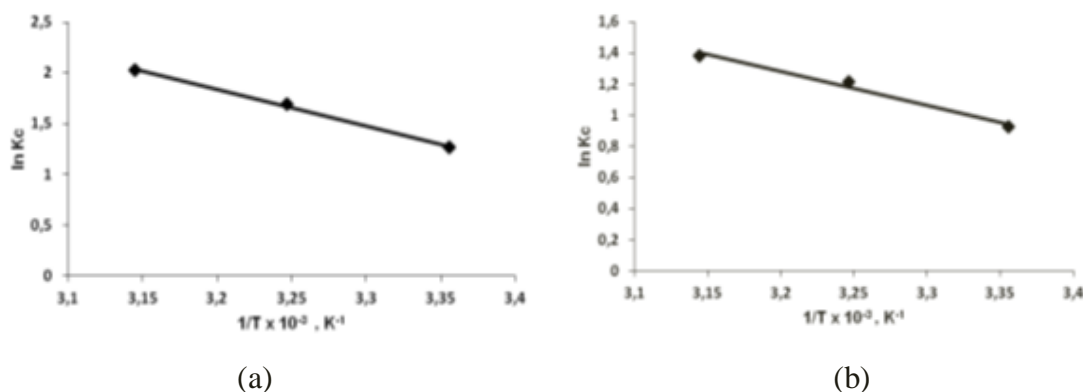

(a)	(b)

Figure 10. a) 1/T–ln K_c graph for thermodynamic parameters of Pb(II) adsorption b) 1/T–ln K_c graph for thermodynamic parameters of Zn(II) adsorption.

Table 5. Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) values of metal ions at different temperatures

Temperature	Lead			Zinc		
	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0
298 ^{0}K	-3.13			-2.29		
308 ^{0}K	-4.34	29.87	110.86	-3.10	18.12	68.64
318 ^{0}K	-5.35			-3.66		

When the results are investigated, ΔG^0 values for both metal ions were calculated as negative. Negative values of ΔG^0 express the spontaneous nature of the process. If the change in enthalpy (ΔH^0) is positive, it means that the adsorption process is endothermic and if the change in free entropy (ΔS^0) is positive, then it means that the disorder on the interface of solid and the solution increases.

4. RESULTS

In this study, the possibility for the treatment of lead and zinc heavy metal ions from aqueous solutions by nano montmorillonite adsorption was investigated. In the optimization studies, the optimum values of the parameters were determined. The isotherm constants were calculated by using the linearized forms of Langmuir, Freundlich and Temkin isotherm equations within a temperature range of 25 ºC, 35 ºC and 45 ºC. When regression coefficients (R^2) calculated in the adsorption of lead and zinc ions were investigated, it was determined that adsorption was well fitted with Langmuir isotherm. Maximum adsorption capacities for lead at 25 ºC, 35 ºC and 45 ºC temperatures were calculated as 30.30, 31.25, 32.26 mg g^{-1}, respectively and for zinc at 25 ºC, 35 ºC and 45 ºC temperatures were found as 15.63, 20.00, 22.73 mg g^{-1}, respectively. As a result of kinetic studies, it was observed that adsorption kinetics was in accordance with pseudo-second order kinetics model. As a result of thermodynamic calculations, $\Delta H°$ and $\Delta S°$ values for the adsorption of lead and zinc ions on nano montmorillonite were positive and were calculated as 29.87 kJ/mol and 110.86 J/mol.K for lead and as 18.12 kJ/mol and 68.64 J/mol.K for zinc, respectively. This reaction was endothermic. The values of $\Delta G°$ for lead were -3.13, -4.34, -5.35 kJ/mol and -2.29, -3.10, -3.66 kJ/mol for zinc. It was observed that removal of lead and zinc was better at high temperatures. Positive $\Delta H°$ value is a factor which explains that the heat of adsorption is endothermic. $\Delta G°$ values were calculated as negative for the adsorption of both metal ions. Negative values of $\Delta G°$ indicated that the process was spontaneous.

Consequently, it was revealed that natural nano montmorillonite mineral can be effectively used as an adsorbent for the removal of Pb^{2+} and Zn^{2+} ions after providing appropriate processes and optimum conditions. Moreover, using nano montmorillonite as its natural form without any physical and chemical pretreatment in adsorption experiments will reduce the cost of process.

5. ACKNOWLEDGMENT

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