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Adsorption Isotherms for Removal of Heavy Metal Ions (Copper and Nickel) from Aqueous Solutions in Single and Binary Adsorption Processes

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Highlights

- Cu(II) and Ni(II) sorption performance of sepiolite were examined in single and binary systems.
- PH=5 was determined as the best point where the sepiolite showed the largest sorption capacity.
- Single metal sorption were quantified by the Langmuir and Freundlich adsorption isotherms.
- Single metal sorption were quantified by Dubinin-Radushkevich and Temkin adsorption isotherms.
- The extended Langmuir and Freundlich equations were applied for the competitive metal sorption.

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Abstract

This study deals with the removal of single and binary heavy metals, which cause great problems in terms of the environment and human health, through very low cost, economical and easily obtainable materials. The purpose of this study is to investigate the single- and binary uptake of Copper (II) and Nickel (II) ions onto the Sepiolite in the terms of a thermodynamic perspective. For mono-component systems, the initial effluent concentration, mixing speed and temperature have been studied as a function of time to determine the conditions where the adsorbents show a great deal of affinity towards the Cu (II) and Ni (II) ions in aqueous solutions. Before the metal adsorption experiments, the Physical properties of Sepiolite were identified via Brunauer–Emmett–Teller (BET) analysis. The single metal ion uptake studies were performed at 20, 25, 30, and 35 °C. At equilibrium, the sorption data were individually shown to correlate well with the non-competitive Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. Among the applied isotherm models, the one-component sorption values do fit the Langmuir isotherm best. The simultaneous and competitive uptake of Cu (II) and Ni (II) was assessed by the extended Langmuir and Freundlich isotherms. Both adsorption equations complied with the two-component sorption data perfectly. Single- and binary-sorption results unclose that the effect of Sepiolite to Cu (II) is greater than that of Sepiolite to Ni (II).

1. INTRODUCTION

The rapid population growth and industrial development have caused environmental pollution and the contamination of clean water resources. The effluents originating from large-scale industrial production are one of the fundamental causes of this pollution. Heavy metals- called cationic pollutants- play a significant role in environmental pollution since a great many sectors such as mining, coating, dye and pigment production, casting, iron steel industry, battery production, and so on frequently use heavy metals in both main production processes and auxiliary processes and dump them into nature. Existing heavy metals in the environment participate in the ecosystem cycle in different ways and result in the contamination of the food chain. These cationic pollutants pose toxic effects even at low concentrations in case they infiltrate any living being at a certain amount [1, 2].

Heavy metals are defined as cations with their concentrations at levels above critical ppm. Notorious heavy metal examples cover Antimony (Sb), Cadmium (Cd), Arsenic (As), Chromium (Cr), Mercury (Hg),

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Copper (Cu), Nickel (Ni), and so on [3]. Among these groups, Ni and Ni-containing allow are commonly used in the rechargeable battery technology, catalyzers, the fabrication of metal coin, and foundry processes because nickel has inherent characteristics such as rigid structure, high electrical and heat conductivity. Annual Ni-containing metarial production exceeds 500,000 tons in the United States [4]. Nickel concentration is increased in the bodies of people and active smokers who consume fruits and vegetables grown in polluted soils. Nickel concentration is increased in the body of people and active smokers who consume fruits and vegetables grown on contaminated soils, not mention to those who drink routine tap water and breathe polluted air [5]. It is natural to take small amounts of nickel into the body, but high quantities could be dangerous for human health. Health problems caused by high doses of nickel can be listed as follows: Lung, nose, larynx, prostate cancer development, dizziness and getting sick when exposed to nickel vapor, lung failure, respiratory failure, shortness of breath, asthma and chronic bronchitis, redness and allergies, especially on the skin caused by the jewelry [6-8].

The removal of heavy metals is of great importance to minimize their adverse effects on the environment and human health. Nowadays, chemical precipitation [9], chemical oxidation and reduction [10], ion exchange [11], filtration [12], and electrochemical treatment [13] are actively used to reduce the contaminant concentrations in effluents, considering the type, amount of heavy metal in the dirty water to be cleaned. However, since the majority of the methods used are expensive due to the high investment and operating costs, it has become essential to develop alternative new techniques that are inexpensive, not difficult to use, and do not pollute the environment. In this context, the adsorption technique is considered as an efficient and productive method that can eliminate the disadvantages of other ways. The adsorption process is a cost-effective water treatment method such that it is employed the removal of organic and inorganic pollutants in wastewaters through diverse physical, chemical and biological processes [14, 15]. The metal sorption phenomenon in aqueous solutions may be correlated linearly or inversely with many parameters such as the surface area, particle size, pore volume of adsorbent, as well as the temperature and concentration of the aqueous phase. By changing the adsorption parameters, it is possible to increase the metal capture capacity and removal efficiency of the adsorbent used.

A suitable adsorbent selection plays a vital role in increasing the efficiency of the adsorption process. Among the conventional adsorbent materials, chitosan, zeolite, clay, sludge, industrial and agricultural wastes, lignin, lignite, peat, citrus peel and sepiolite are potential adsorbent candidates that are commonly used to remove metal ions in drainage waters. Sepiolite - a clay mineral belonging to the phyllosilicate group - has drawn great attention due to its strong affinity towards cationic groups. That could be because three types of active sorption sites exist on the crystal structure of the adsorbent mineral. These active sites are (1) oxygen ions in tetrahedral layers, (2) water molecules coordinated to magnesium ions at the edges of structural chains, and (3) SiOH groups extending along fiber axes.

In an attempt to make the adsorption process more efficient and less costly, many researchers have investigated cheap and sustainable adsorbents. Understanding the nature of the metal uptake process is the most plausible way for cost reduction and effective water treatment. The association between the metal concentration deposited on the adsorbent surface and the remaining metal concentration in the aqueous phase could be explained by adsorption isotherms that were derived for single and binary adsorption systems. The adsorption isotherms generally inform necessary knowledge about adsorption type, energy, and capacity [16]. Experimental equilibrium data from the metal uptake process are not in line with only one isotherm model every time. This is because isotherm equations are derived based on some assumptions to explain the adsorption process.

To sum up, explaining the purification process of a system with more than one mathematical equation would reflect real-like outcomes. In line with this purpose, Langmuir, Freundlich, BET, Temkin, Dubinin-Radushkevich, Redlich-Peterson, Toth, Halsey, and Henderson isotherms are the most common mathematical equations accounting for the metal uptake phenomenon in the single-metal systems [17]. In contrast, the extended Langmuir and Freundlich isotherms were applied to evaluate the competitive sorption in the binary metal systems [18].

For this purpose, numerous studies have been performed regarding the adsorption isotherms to physically and chemically evaluate the equilibrium adsorption process and explain how each sorption parameter affects the process for many years. For instance, Allen et al. used various adsorption isotherms to describe the removal process of basic dye by peat. According to the isotherm models they used, the Redlich-Peterson isotherm was most appropriate for the equilibrium data [19]. In another study, Dada et al. also used the adsorption isotherms derived for the single-component systems for the uptake of Zn^{+2} onto rice husk. Their adsorption data showed that the uptake process of Zn^{+2} onto the rice husk could be explained by the Langmuir isotherm model well [20].

The objective of this study is to (i) evaluate the equilibrium sorption data of Cu (II) and Ni (II) ions adsorbed on Sepiolite by the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms, (ii) examine the effect of temperature on the adsorption phenomena and (iii) evaluate the feasibility of the extended Langmuir and Freundlich equations to the simultaneous sorption of the metal ions in batch systems.

Nomenclature

k_a : Forward rate constant

k_d : Backward rate constant

K : Equilibrium constant of a reaction or ratio of forward rate constant to backward rate constant

q_e : Uptake quantity of single component onto adsorbent at equilibrium instant (mg/g)

Q_o: Maximum uptake quantity of single component onto adsorbent (mg/g)

b : Langmuir isotherm constant (L/ mg)

R_L: Dimensionless separate factor

C_0: Initial concentration of adsorbate in aqueous phase

C_e: Available concentration of adsorbate at equilibrium instant

K_F: Freundlich isotherm constant

n : Adsorption intensity

b_T: Temkin isotherm constant

K_{ad}: Dubinin- Radushkevich constant (mol^2/kj^2)

A_T: Temkin isotherm equilibrium binding constant (L/g)

T : Absolute temperature (K)

q_s: Theoretical saturation capacity of Temkin isotherm (mg/g)

ε : Polanyi Potential (j/mmol)

$q_{eI,II}$: Uptake amount of each component onto adsorbent in simultaneous adsorption (mg/g)

x,y,z: The competitive Freundlich isotherm constants

α,β: The competitive Langmuir isotherm constants

C_{denI}: Equilibrium concentration of first component in binary adsorption (mg/L)

C_{denII}: Equilibrium concentration of second component in binary adsorption (mg/L)

n_I: Individual Freundlich adsorption isotherm constant of each component

b_I, b_2 : Individual Langmuir adsorption isotherm constants of each component (mg/g)

2. MATERIAL METHOD

2.1. Materials and Chemicals

Single and binary sorption experiments were performed with Sepiolite obtained from Manisa-Gürmet region of Turkey. Solid $CuSO_4.5H_2O$ and $Ni(NO_3)_2.6H_2O$ chemicals as starting materials were used in the preparation of the Stock Cu(II) and Ni (II) solutions. All experiments were performed by using beakers of 250 mL capacity containing 1 g/L of adsorbent suspended in copper and nickel solutions. Copper sulfate pentahydrate, nickel(II) nitrate hexahydrate, hydrochloric acid 32% and sodium hydroxide were purchased from Merck. The agents including HCl, NaOH, were all of the analytical grade and all solutions were prepared with distilled water.

2.2. Specific Surface Area

The specific surface area of the Sepiolite was evaluated using N_2 adsorption-desorption (AUTOSORB 1C) at -190 ^{0}C. Before both metal ions is absorbed, the Sepiolite was evacuated until a pressure of 60.1 Pa and ambient temperature was arrived and then heated up to 350 ^{o}C and evacuated until a pressure of 1.3 Pa arrived. This condition was kept overnight [7].

2.3. Determination of Moisture Content in the Adsorbent Structure

To determine the amount of moisture in the adsorbent structure, 1 gram of Sepiolite was put into a crucible, and the crucible was weighted. Then, this crucible was placed in an oven and heated at a constant temperature of 65 ^{o}C for 24 hours. The heated crucible was cooled in a desiccator to prevent moisture from the atmosphere. The crucible was weighed again. This process was repeated until there was a difference of 0.01 g between the initial weight and final weight of the crucible

$$\text{\% Amount of moisture} = \frac{m_1 - m_2}{m_1 - m_3} \tag{1}$$

where m_1 and m_2 are the first weight and final weight of crucible with the adsorbent, respectively, while m_3 stands for the weight of the empty crucible.

2.4. Sorption Experiments

Single and binary adsorption studies were carried out in batch systems. 250 mL flasks with working volumes of 100 mL were utilized as the sorption medium. The mount of flasks was closed to prevent evaporation of the solutions and placed in a water bath running at a constant-shaking rate of 45 rpm and a constant temperature. The experiments were initiated by adding 1 gram of adsorbent to a solution medium containing heavy metal ions. The existing concentrations of both metal ions before and after adsorption were measured with Agilent Technologies Cary 60 UV-Vis Spectrometry.

In the binary adsorption experiments, the adsorption studies of binary metal mixtures including Copper (II) and Nickel (II) ions with Sepiolite were performed at pH=5, where the maximum adsorption of both metal ions was observed. In the studies conducted at the constant pH value (pH=5) at 25 ^{0}C, initial concentrations of Copper (II) were varied in the range of 25-500 mg/L for each experimental set while Nickel (II) ion concentration varying between 25 and 500 mg/L was maintained constant. The effect of the initial concentration of copper (II) ion on the rate, equilibrium of the adsorption, binary adsorption, and adsorption efficiency was investigated in the batch systems. The same experimental procedure was also repeated for Nickel (II) ion.

2.5. The Physical Parameters of The Sepiolite

Some physical parameters of the sepiolite are listed in Table 1. BET analysis revealed that the solid adsorbent possesses a specific surface area of 187 m^2/g, which is compatible with the literature study [21]. The percentage of moisture in Table 1 is an average value, which is due to the humidity in the air.

***Table 1**. Some physical properties of the sepiolite*

Properties	Sepiolite
pH	5.01
% Moisture content	8
Surface area (m^2/g)	187.8

3. THE RESEARCH FINDINGS AND DISCUSSION

3.1. The Single Sorption Studies

The Langmuir isotherm equation is the first adsorption isotherm to be developed theoretically. Most of the adsorption isotherm equations proposed later and suitable for a wide range of experimental results were developed using the Langmuir isotherm model. Thus, the Langmuir equation still occupies an important place in physical and chemical adsorption theories. The US scientist I. Langmuir derived it based on certain assumptions. The most important of these assumptions are; 1) Adsorbents (atoms, molecules or ions) are bound to the active sites in precisely localized regions; 2) Each site contains only one adsorbed substance; 3) The energy level of each adsorbed substance is the same on all parts of the surface, regardless of what is adsorbed in neighboring parts. To sum up, the Langmuir model (also called the localized model) assumes that the surface is smooth and homogeneous, and those lateral interactions between the adsorbed side are negligible.

For the solid-liquid adsorption systems, the Langmuir isotherm is expressed as the following equation [22]

$$q_e = \frac{Q_0 * b * C_e}{1 + b * C_e} \ . \tag{1}$$

The constant “b” in Equation (6) expresses the adsorption affinity. The adsorption affinity indicates how strong the interaction between the adsorbate and adsorbent is. Herein, $\frac{1}{Q_0}$ and $\frac{1}{b * Q_0}$ values can be computed from the slope and intercept of the line in which $\frac{C_e}{q_e}$ values were plotted versus Ce values. It is challenging to clearly explain the equilibrium case through only the Langmuir isotherm equation, especially for heterogeneous adsorption systems in which monolayer adsorption occurs. At this point, a dimensionless separation constant (R_L) formulated through the following equation clues about the essential properties of the Langmuir equation [23]**.** The metal uptake phenomenon by solid adsorbent from the liquid phase in the non-competitive adsorption system with the Langmuir isotherm model is assessed over the dimensionless constant R_L. As can be seen from Table 2, If $R_L>1$, the adsorption isotherm is inappropriate for a non-competitive adsorption system, if $R_L=1$, it is a linear isotherm, if $0 < R_L < 1$, the isotherm model is appropriate, or if $R_L=0$, the isotherm is irreversible

$$R_L = \frac{1}{1 + b * C_0} \ . \tag{2}$$

***Table 2.** Values of R_L constant and types of isotherm*

R_L (Dimensionless separation factor)	**Type of isotherm**
$R_L > 1$	Unsuitable
$R_L = 1$	Linear
$0 < R_L < 1$	Suitable
$R_L = 0$	Irreversible

Considering the R_L values for sorption of both Cu (II) and Ni (II) in Table 3, all values are smaller than one, which indicates that Langmuir adsorption isotherm is convenient. The R^2 values are 0.99, proving that the adsorption data complied with Langmuir's adsorption isotherm well. The adsorption capacity of Sepiolite was observed to increase with increasing temperature, which is further confirmed by the decline in Q^0 values with decreasing temperature. This outcome shows that the nature of the sorption process is an endothermic phenomenon.

Table 3. *Langmuir isotherm constants for the sorption of Cu (II) and Ni (II) at different temperatures*

20 ºC		**20 ºC**		**30 ºC**		**30 ºC**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
Q	256.410	**Q**	222.222	**Q**	294.117	**Q**	250
b	0.005	**b**	0.004	**b**	0.007	**b**	0.004
R_L	0.40	**R_L**	0.496	**R_L**	0.333	**R_L**	0.459
R^2	0.998	**R^2**	0.998	**R^2**	0.999	**R^2**	0.997
25 ºC		**25 ºC**		**35 ºC**		**35 ºC**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
Q	270.270	**Q**	238.095	**Q**	357.142	**Q**	263.158
b	0.006	**b**	0.004	**b**	0.007	**b**	0.005
R_L	0.387	**R_L**	0.491	**R_L**	0.342	**R_L**	0.430
R^2	0.998	**R^2**	0.998	**R^2**	0.995	**R^2**	0.998

Freundlich isotherm is one of the earliest known correlations defined for irreversible and non-ideal adsorption [24]**.** According to Freundlich, the adsorbing area on the surface of an adsorbent is heterogeneous. This empirical relation assumes that interest and heat of adsorption are not equally distributed on the adsorbent surface [25]. This isotherm may be used for multilayer adsorption rather than single-adsorption. Freundlich derived the following equation to describe the adsorption processes in aqueous solutions**;**

$$q_e = K_F * C_e{}^{1/n} \tag{3}$$

K_F and n constants in the Freundlich isotherm equation depend on the temperature and the types of adsorbent and adsorbate. Freundlich isotherm can be reduced to a linear form by taking the logarithm of both sides of the equation. K_F and n constants are found by plotting the change of log q_e versus log C_e. Freundlich model is a realistic model explaining the adsorption mechanism on heterogeneous surfaces [26]**.** The data represented in Table 4 shows that n is higher than one, which indicates a good sorption process. The constant K_F predicts adsorption capacity. As the temperature of the wastewater purification medium increases, the increase in K_F value suggests that the sepiolite has a great adsorption potential for Cu (II) and Ni (II) at elevated temperatures.

Table 4. *Freundlich isotherm constants for adsorption of Cu (II) and Ni (II) at different temperatures*

20 °C		**20 °C**		**30 °C**		**30 °C**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
n	1.654	n	1.505	n	1.709	n	1.493
lnK_F	1.526	lnK_F	2.483	lnK_F	1.898	lnK_F	3.045
K_f	4.600	K_f	11.987	K_f	6.673	K_f	21.010
R^2	0.956	R^2	0.964	R^2	0.951	R^2	0.968
25 °C		**25 °C**		**35 °C**		**35 °C**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
n	1.623	n	1.476	n	1.706	n	1.506
lnK_F	1.577	lnK_F	2.567	lnK_F	2.026	lnK_F	3.515
K_f	4.844	K_f	13.028	K_f	7.590	K_f	33.634
R^2	0.953	R^2	0.969	R^2	0.949	R^2	0.974

Temkin isotherm takes into account the interaction between the adsorbed substances. This isotherm model was developed by taking into account the adsorption enthalpy values of all the molecules in an aqueous phase. This isotherm postulates that the adsorption heat of all molecules in the layer as a function of temperature will decrease linearly with the active attachment sites, ignoring the lower and upper limit concentration sets. The equation expressing Temkin isotherm could be described as [27];

$$q_e = \frac{RT}{b_T} lnA_T C_e \ . \tag{4}$$

The linear form of this equation is;

$$q_e = \frac{RT}{b_T} lnA_T + \left(\frac{RT}{b_T}\right) lnC_e \quad . \tag{5}$$

If the constant coefficients in the above Equation (5) are reduced to a single constant as follows;

$$B = \frac{RT}{b_T} \quad . \tag{6}$$

The final form of the Temkin isotherm is like that;

$$q_e = B \ lnA_T + B \ lnC_e \quad . \tag{7}$$

From the slope and intercept of the Temkin isotherm graph, isotherm constants (A_T and b_T) were calculated for adsorption studies at different temperatures. The results are listed in Table 5. The calculated equation constants reveal that the sorption process for two metal ions is physical adsorption. The R^2 values are higher than that of Dubinin–Radushkevich.

Table 5. *The Temkin isotherm constants for Cu (II) and Ni (II) adsorption at different temperatures*

20 °C		**20 °C**		**30 °C**		**30 °C**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
A_T(L/mg)	0.10	A_T(L/mg)	0.068	A_T(L/mg)	0.130	A_T(L/mg)	0.072
b_T	53.407	b_T	59.564	b_T	47.275	b_T	50.708
B	45.612	B	40.897	B	53.286	B	49.679
R^2	0.972	R^2	0.964	R^2	0.976	R^2	0.966
25 °C		**25 °C**		**35 °C**		**35 °C**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
A_T(L/mg)	0.123	A_T(L/mg)	0.067	A_T(L/mg)	0.144	A_T(L/mg)	0.078
b_T	48.907	b_T	54.425	b_T	43.958	b_T	47.568
B	50.658	B	45.522	B	58.253	B	53.832
R^2	0.972	R^2	0.964	R^2	0.979	R^2	0.967

Dubinin-Radushkevich adsorption isotherm is an empirical equation especially proposed for solving adsorption systems yielding highly rectangular isotherms, giving an idea about the Gaussian energy distribution [28]. The adsorption energy is found from the slope of the linearized isotherm equation, revealing knowledge regarding the adsorption mechanism. The model is generally applied to set apart the heavy metal cations' physical and chemical holding process from their mean free energy.

The mathematical expression of D-R isotherm model is;

$$q_e = (q_s)\exp\left(-K_{ad}\varepsilon^2\right) . \tag{8}$$

The linearized form of the equation is shown as follows;

$$lnq_e = ln(q_s) - (K_{ad}\varepsilon^2) \quad . \tag{9}$$

q_s and K_{ad} values are calculated by plotting lnq_e against ε^2

$$\varepsilon = RTln[1 + \frac{1}{C_e}] \quad . \tag{10}$$

B_{DR} value is a constant used to determine the mean free energy of adsorption in the transfer of each adsorbate molecule from an aqueous phase to the external surface of a solid [29]**.** Herein mean free energy (E) is calculated as noted in Equation (11)

$$E = \frac{1}{\sqrt{2B_{DR}}} \tag{11}$$

where the term "B_{DR}" is an abbreviation that denotes the isotherm constant "K_{ad}" in Equation (8). From the linear form of D-R model, isotherm constants (q_s and K_{ad}) were calculated for the uptake of both metal ions, and the findings are listed in Table 6. The constant parameters in Table 6 indicate that the maximum sorption capacity of Sepiolite increased with increasing temperature for each metal cation. In addition, the mean free energies have suggested that the adsorption mechanism of divalent cations has a physical phenomenon.

Table 6. *The Dubinin Radushkevic isotherm constants for adsorption of Cu(II) and Ni (II) at different temperatures*

20 °C		**20 °C**		**25 °C**		**25 °C**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
qs(mg/g)	147.97	qs(mg/g)	122.339	qs(mg/g)	179.85	qs(mg/g)	148.220
K_{ad}(mol^2/kj^2)	0.011	K_{ad}(mol^2/kj^2)	0.015	K_{ad}(mol^2/kj^2)	0.008	K_{ad}(mol^2/kj^2)	0.014
E(kj/mol)	6.711	E(kj/mol)	5.698	E(kj/mol)	7.580	E(kj/mol)	5.976
R^2	0.903	R^2	0.888	R^2	0.908	R^2	0.885
30 °C		**30 °C**		**35 °C**		**35 °C**	
Copper (II)		**Nickel (II)**		**Copper (II)**		**Nickel (II)**	
qs(mg/g)	160.68	qs(mg/g)	132.462	qs(mg/g)	198.44	qs(mg/g)	160.276
K_{ad}(mol^2/kj^2)	0.010	K_{ad}(mol^2/kj^2)	0.014	K_{ad}(mol^2/kj^2)	0.007	K_{ad}(mol^2/kj^2)	0.012
E(kj/mol)	6.868	E(kj/mol)	5.792	E(kj/mol)	8.006	E(kj/mol)	6.299
R^2	0.889	R^2	0.878	R^2	0.913	R^2	0.885

While the accuracy of an isotherm model often depends on the number of independent parameters, its popularity with respect to process application is an indication of its mathematical simplicity. Figure 1 illustrates four adsorption isotherm models dealing with single copper (II) ion uptake by the Sepiolite in the batch system at 20 °C. The Langmuir, Freundlich, Temkin, and Dubunin–Radushkevich approaches are compatible with the equilibrium data. By all odds, the linear regression parameter (RL) has generally been utilized for evaluating the quality of fit and adsorption efficiency. In the view of the correlation coefficient "R^2", the Langmuir isotherm fits best among others for the non-competitive copper adsorption model.

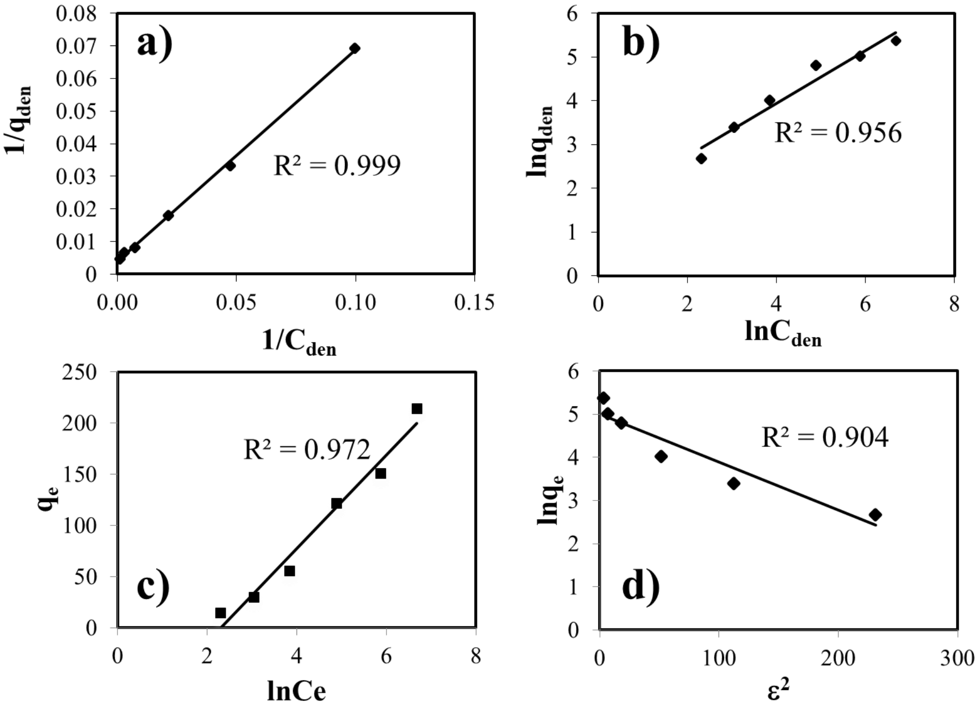

Figure 1*. The linearized form of Langmuir's isotherm (a), Freundlich's isotherm (b), Temkin's isotherm (c), and Dubin-Radushkevic's isotherm (d) for single Cu(II) adsorption at 20 °C*

Figure 2 shows four adsorption isotherm models dealing with single Nickel (II) ion uptake by the Sepiolite in the batch system at 20 °C. The Langmuir, Freundlich, Temkin, and Dubunin–Radushkevich approaches are in agreement with the equilibrium data. In the view of the correlation coefficient "R^2", the Langmuir isotherm fits best among others for the non-competitive copper adsorption model. To sum up, the Langmuir isotherm showed the best fit for both ion adsorption processes carried out in batch systems. This could be attributed to the fact that the Langmuir isotherm is a theoretical equation consisting of two coefficients, whereas the other isotherm models tackled in this study possess three constants. Considering the results, the adsorption capacities of Sepiolite follow the order of $Cu^{2+} > Ni^{2+}$ in the single-component systems, which is compatible with the related literature studies [30,31]. This could be explained by the fact that the ionic radius (0.57nm) of the Cu^{2+} ion is smaller than that (0.69 nm) of the Ni^{2+} ion.

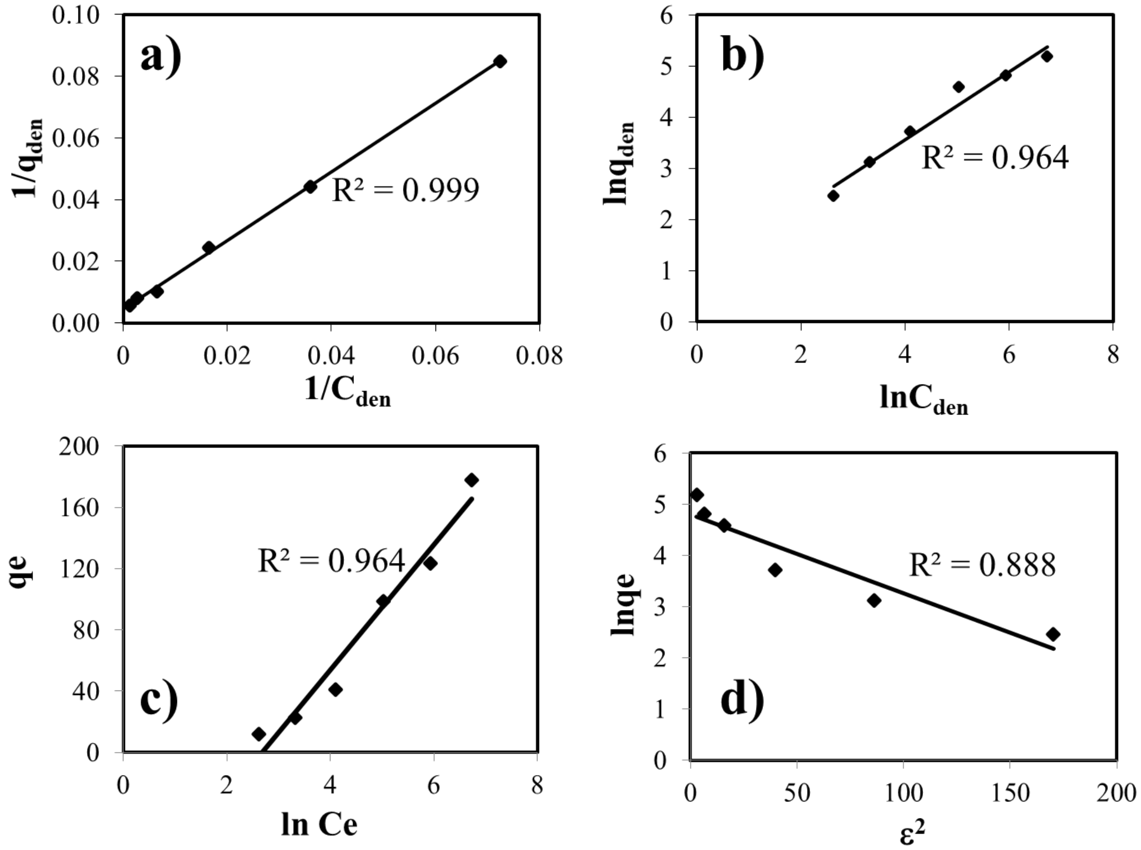

***Figure 2**. The linearized form of Langmuir's isotherm (a), Freundlich's isotherm (b), Temkin's isotherm (c), and Dubin-Radushkevic's isotherm (d) for single Ni(II) adsorption at 20 ^oC*

3.2. The Simultaneous Adsorption Studies

Simplified forms of the Langmuir and the Freundlich isotherms which are derived for multicomponent systems, were used for the binary adsorption experiments. Extended Langmuir isotherm developed by Butler and Ockrent for multicomponent systems assumes that (i) each active sites on the surface have homogeneous adsorption energy, (ii) there is no interaction between adsorbed species, and (iii) adsorbate is available in equal amounts in all the hot spots. The extended Langmuir isotherm can be presented [32, 33] as;

$$q_{denI} = \frac{Q^0{}_1 b_1 \frac{C_{denI}}{\alpha}}{1+b_1\frac{C_{denI}}{\alpha}+b_2\frac{C_{denII}}{\beta}} \quad . \tag{12}$$

The extended Freundlich multicomponent isotherm assumes that each adsorbate ion individually complies with the simple Freundlich isotherm, and an exponential distribution of adsorption energy in multicomponent adsorption is equal to that of the mono-component adsorption system. The Freundlich multicomponent isotherm could be presented [34]as;

$$q_{denII} = \frac{K_{FI}(C_{denI})^{\left(\frac{1}{nI}+x\right)})}{(C_{denI})^x+y((C_{denII})^z} \quad . \tag{13}$$

Binary adsorption data at equilibrium were firstly assessed through the extended Langmuir isotherm model, and the isotherm's parameters were represented in Table 7. The Q values which refer to the maximum sorption capacity of the adsorbent were calculated to be 256.410 for Cu (II) ion and 222.222 for Ni (II). These findings indicate that not only does sepiolite present a stronger sorption affinity towards Cu ion than Ni ion in the competitive sorption medium but also in the non-competitive sorption medium, which is in good agreement with the related literature studies [30, 31]. The deviation between the theoretical and experimental values of Cu (II) was calculated to be 0.917, which is smaller than the deviation value (1.531) found for Ni adsorption. Additionally, the experimental q_{den} values showing the uptake amount of adsorbate were compared with theoretical q_{den} values based on the extended Langmuir and Freundlich isotherms. The findings were plotted in Figure 3 so that they are interpreted geometrically. A great number of the data point for both cations are distributed around the line of 45^o in the low range of concentrations. In contrast, the greater deviations from the line of 45^o were observed in the range of high concentrations because of the competition of the molecules trying to be attached on the surface. To sum up, the magnitude of the predicted aberrations for the copper (II) ion is much lower in the Langmuir multicomponent approach than in the Freundlich multicomponent approach. Thereby, the equilibrium findings suggest that the effect of Sepiolite upon copper (II) was greater than that of Sepiolite upon nickel (II), which supports mono-component adsorption findings.

Table 7. *The adsorption constants of Langmuir and Freundlich's isotherms derived for the binary sorption systems*

Langmuir Constants	**Copper (II)**	**Nickel (II)**
Q	256.410	222.222
b	0.005	0.004
α	1.046	1.509
β	1.063	2.267
% Error	0.917	1.531
Freundlich Constants	**Copper (II)**	**Nickel (II)**
x	0.527	0.721
y	0.445	1.153
z	0.561	0.661
% Error	0.769	2.637

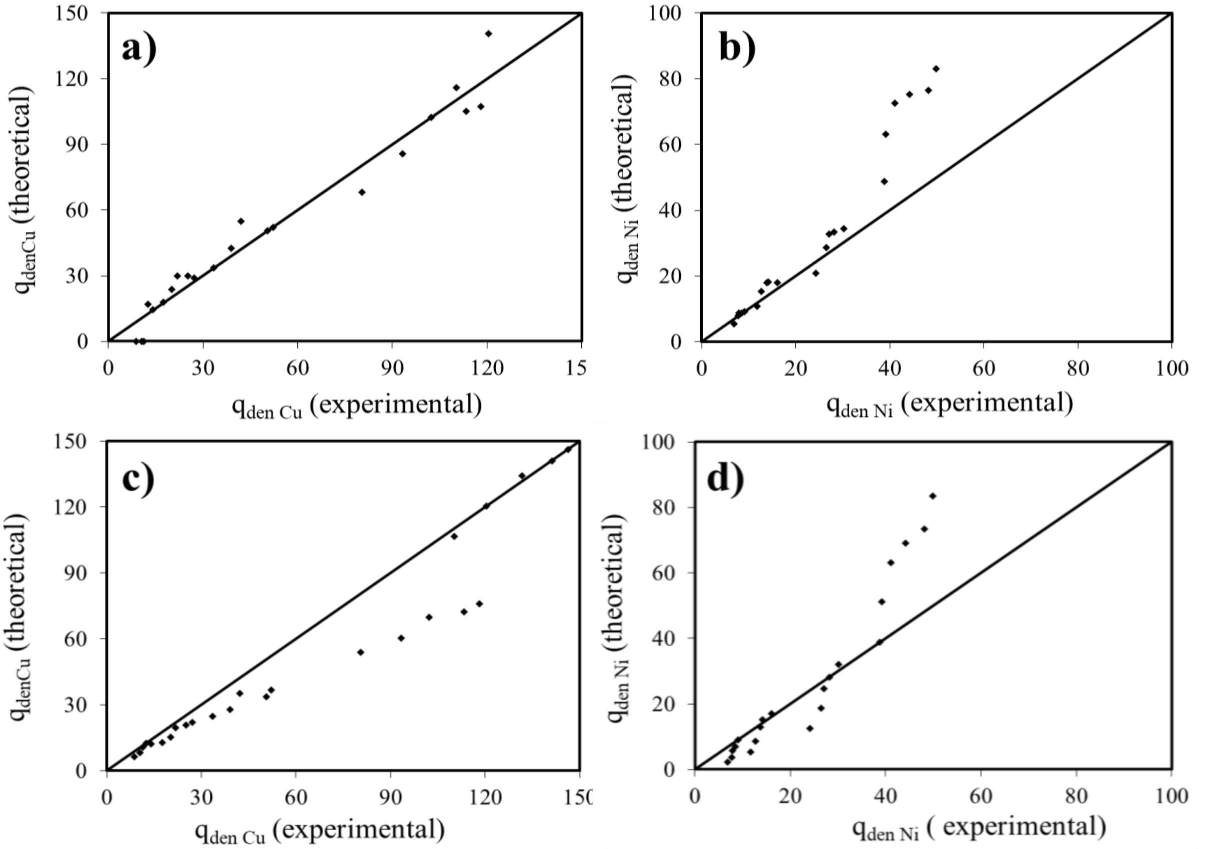

***Figure 3**. Comparison of experimental qden values with its theoretical values predicted with Langmuir (a and b) and Freundlich's isotherm (c and d) derived for the binary sorption systems on the line of 45 °C*

4. RESULTS

This paper deals with the single and binary adsorption of Cu (II) and Ni (II) ions onto Sepiolite procured from Gurmet village of Manisa Province, Turkey. In the single adsorption experiments in which temperature varies between 20 °C and 35 °C, the equilibrium data are in good agreement with the calculated regression values, out of which the equilibrium sorption data fits best with the Langmuir isotherm equation. The metal uptake capacity of the adsorbent increased with increasing temperature in the single adsorption studies.

The simultaneous sorption of Cu (II) and Ni (II) ions on the Sepiolite may be clarified by Langmuir and Freundlich's isotherms that were extended for the multicomponent systems. The equilibrium data obtained from the binary sorption experiments agreed with well the Langmuir isotherm model rather than the Freundlich isotherm model, especially in the adsorption of Cu (II). This outcome indicates that the Cu (II) and Ni (II) ions could be removed individually and simultaneously from the aqueous phase by Sepiolite. On the other hand, deviations were obtained for both competitive two-metal sorption isotherms due to the antagonistic effect between Cu (II) and Ni (II) at high concentrations. This result provides a more realistic description of divalent metal uptake unto the sepiolite.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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