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RESEARCH ARTICLE

The Evaluation of Affection of *Methylobacterium extorquens* - Modified Silica Fume for Adsorption Cadmium (II) Ions from Aqueous Solutions Affection

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Summary

In this present study, it was investigated for adsorbtive removal of cadmium (Cd) ions from aqueous solutions using *Methylobacterium extorquens* - modified silica fume waste material. Batch adsorption experiments have been performed as a function of pH, contact time, temperature and adsorbent dosage. The optimum results were obtained at pH 5.0, contact time of 60 min, temperature of 25°C and an adsorbent dose of 1 mg/mL. The adsorption data was correlated with Langmuir and Freundlich adsorption models. The maximum adsorption capacity obtained from Langmuir adsorption model was 166.67 mg/g. The results show that the bacteria - modified silica fume could be used for the treatment of aqueous solutions containing Cd as an alternative low cost adsorbent.

Keywords: *Wastewater, Bacteria modified silica fume, Cadmium pollution, Environmental pollution, Adsorption kinetics*

Sulu Çözeltilerden Cadmiyum (II) İyonlarının Adsorpsiyonu için *Methylobacterium extorquens - Modifiye Silis Dumanı* Etkinliğinin Değerlendirilmesi

Özet

Bu çalışmada, *Methylobacterium extorquens* ile modifiye edilmiş atık malzeme silis dumanı kullanılarak sulu çözeltilerden kadmiyumun uzaklaştırılması araştırılmıştır. Adsorpsiyon deneyleri pH, temas süresi, sıcaklık ve adsorban dozajının bir fonksiyonu olarak yapılmıştır. Optimum sonuçlar pH 5.0'de, 60 dk temas süresinde, 25°C sıcaklıkta ve 1 mg/mL adsorban dozunda elde edilmiştir. Adsorpsiyon verileri Langmuir ve Freundlich adsorpsiyon modelleri ile korelasyonu göstermektedir. Langmuir adsorpsiyon modelinden elde edilen maksimum adsorpsiyon kapasitesi 166.67 mg/g'dır. Elde edilen sonuçlar bakteri modifiye - silis dumanının Cd (II) içeren sulu çözeltilerin iyileştirilmesinde alternatif düşük maliyetli adsorban olarak kullanılabileceğini göstermektedir.

Anahtar sözcükler: *Atık su, Bakteri modifiye silis dumanı, Kadmiyum kirliliği, Çevre kirliliği, Adsorpsiyon kinetikleri*

INTRODUCTION

Heavy metals pollutions are considered to be a serious threat, non-biodegradable and have great environmental, public health and economic impacts. The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life. They accumulate in living tissues throughout the food chain which has humans at its top [1-3].

One such heavy metal, cadmium, along with its compounds, is widely used in pigments, as heat stabilizers for plastics, for corrosion resistance of steel and cast iron, metal plating, phosphate fertilizer, mining, pigments, alloy industries, in soldering and brazing and in the battery industry (Ni-Cd batteries). Cadmium is highly toxic and there is some evidence that it is carcinogenic [3]. Cadmium

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poisoning may occur that cadmium or cadmium compounds enters the body through the digestive or respiratory [4-6].

Removal, separation and enrichment of heavy metal ions in aqueous solutions play an important role for the environmental remediation of wastewater. Different treatment techniques such as chemical precipitation, chemical reduction, ion exchange, membrane separation, evaporation and adsorption, etc, have been developed to remove metal ions from industrial wastewater [7]. However, these methods often incur high operational costs [8-10]. As an alternative low-cost absorbent material, solid wastes are generally used as adsorbent for the removal of heavy metal from wastewater. Silica fume is a by-product of silicon material or silicon alloy metal factories [2,9,10].

Methylobacterium extorquens is a major model of methylotrophic bacteria. This facultative methylotroph is able to grow on C_1- but also on multicarbon (C_2-C_4) compounds. *M. extorquens* plays an important role in metabolic pathway of plant-derived methanol [11,12]. *Methylobacterium extorquens* is not toxic and it has also been used for improving the taste of some fruits like strawberries [13]. This paper describes the use of *M. extorquens*-modified silica fume to remove cadmium from aqueous solutions. The adsorption of cadmium ions has been investigated as a function of contact time, pH, temperature and adsorbent dose. The cadmium ions have been absorbed by bacteria-modified silica fume from polluted river water and $Cd(NO_3)_2$ solution and the results have been shown on the adsorption behavior of cadmium on *M. extorquens*-modified silica fume. Equilibrium and kinetic studies have been performed to describe the adsorption process.

MATERIAL and METHODS

Adsorbent

Silica fume, also known as microsilica, is a by product of the reduction of higy-purity quartz with coal inelectric furnaces in the production of silicon and ferrosilicon alloys. It is also collected as a by product in the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium and calcium silicon. Silica fume has been obtained from Ferro-Chromate Factory in Antalya [14].

Adsorbent Preparation

The silica fume was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200 mesh screen. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered, and the residual solid was then dried at 105°C, ground in a mortar, and sieved through a 200 mesh sieve. The product was used in the study. Its chemical and index properties are summarized in *Table 1*.

Table 1. *Chemical compositions and engineering properties of silica fume used in the study*

Tablo 1. *Bu çalışmada kullanılan silis dumanının kimyasal kompozisyonu ve mühendislik özellikleri*

Chemical Composition		Engineering Properties	
Property Compound	Silica Fume	Property Density	Silica Fume
SiO_2, %	85-95	Density, (mg/m³)	2-2.5
Al_2O_3, %	1-3	**Grain size**	
Fe_2O_3	0.5-1.0	Gravel (>2000 µm), %	-
CaO, %	0.8-1.2	Sand (2000-75 µm), %	-
MgO, %	1-2	Silt, (2-75 µm), %	20
TiO_2, %	-	Clay (< 2 µm), %	80
Heat loss, %	0.5-1	*Specific surface area* Specific surface area, m²/g	20.12

1 g of silica fume sample was shaken with 10 mL, 10^8 CFU/mL *M. extorquens* solution for approximately 1 h, and then the separated particles were stored [15].

Adsorbent Characterization

The pH values were determined with a pH meter. The scanning electron microscope (SEM) was used to examine the surface of the adsorbent. Images of native adsorbent and metal loaded adsorbent were magnified 5.000 times by SEM modeled JEOL JSM-6400 SEM. Before SEM examinations, the sample surfaces were coated with a thin layer (20 nm) of gold to obtain a conductive surface and to avoid electro-static charging during examination. The same machine was also used for the energy dispersive X-ray (EDX) spectra analysis to know the elemental composition of the silica fume.

Adsorption Procedure

The amount of Cd was determined with dithizone at 228 nm by using spectrophotometer according to calibration curve *(Fig. 1)* [16].

The adsorption capacity of adsorbent (q_t) was calculated using Eq. 1.

$$qe = \frac{(C_o - C_t) * V}{m} \quad (1)$$

where, q_t is the adsorption capacity of the adsorbent at time t (mg adsorbate/g adsorbent); C_o is the initial concentration of metal (mg/L); C_t is the residual concentration of metal after adsorption had taken place over a period of time t (mg/L); *V* is volume of metal solution in shake flask (L) and m is mass of adsorbent (g). The metal removal percentage (*R* %) was calculated using Eq. 2.

$$R(\%) = \frac{(C_o - C_t) * 100}{C_o} \quad (2)$$

where (R %) is the ratio of difference in metal concentration before and after adsorption; C_o is the initial concentration of metal (mg/L); C_t is the residual concentration of metal after adsorption had taken place over a period of time t (mg/L).

RESULTS

Linear regression is one of the most frequently used analyses in calibration. From the calibration curve in the *Fig. 1*, it was observed that there is an approximate linear relationship between absorbance and cadmium concentration in the aqueous solutions. It is observed that the regression coefficient (R^2) is quite high, and its value is 0.9881.

In order to find the optimal pH value for the sorption process, the removal of cadmium ions in the pH range 3-7 was investigated and the data were illustrated in the *Fig. 2*. The effect of temperature influencing the adsorption has been studied in the range of 10-80°C. The effect of temperature on the adsorption capacity of bacteria-modified silica fume is shown in *Fig. 3*.

Fig. 4 illustrates the effect of contact time on the adsorption process. It clearly shows that the equilibrium is attained just after only 60 min. The effect of the adsorbent dosage was studied by varying the adsorbent amounts from 0.5 to 3.0 mg/mL. The effect of bacteria-modified silica fume dosage on amount of cadmium adsorbed was shown in *Fig. 5*. The cadmium concentration of polluted river water and $Cd(NO_3)_2$ solutions treated with bacteria-modified silica fume indicate that bacteria-modified silica fume enhances adsorption capacity *(Fig. 6)*.

Images of native adsorbent and metal loaded adsorbent were magnified 20.000 times by SEM was used to examine the surface of the adsorbent. The SEM photographs showed that the progressive changes occurred in the surface of native adsorbent *(Fig. 7A)* after its surface loaded by cadmium ions *(Fig. 7B)*. The EDX measurements were recorded for qualitative analysis of the element constitution of the adsorbents in *Table 2* and the EDX spectra of native

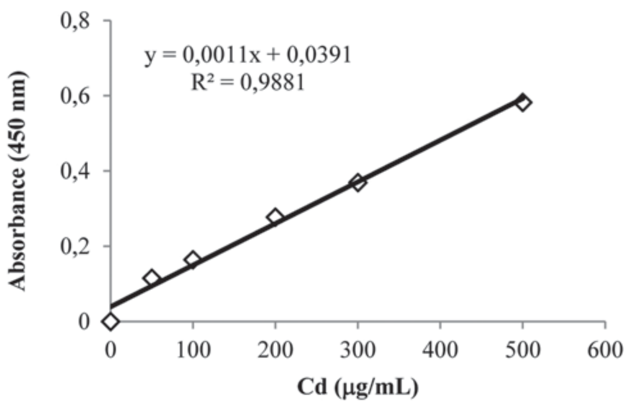

Fig 1. Calibration curve of cadmium adsorbtion

Şekil 1. Kadmiyumun adsorbsiyonu için kalibrasyon grafiği

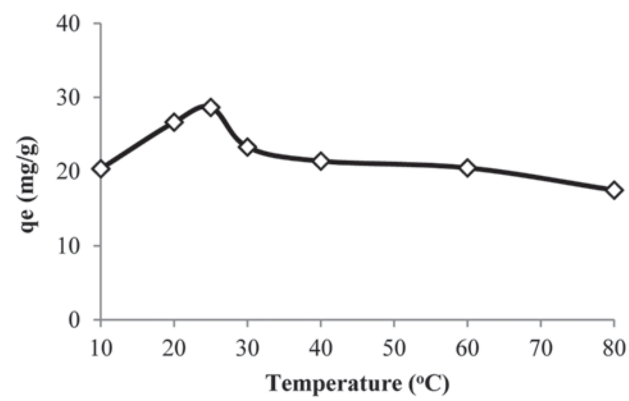

Fig 3. Effect of cadmium as a function of temperature (pH:5.0, initial cadmium concentration: 1 mg/mL, silica fume dose: 1 g/50 mL, agitation speed: 500 rpm, contact time 60 min)

Şekil 3. Kadmiyum iyonu adsorpsiyonu üzerine sıcaklık değişiminin etkisi (pH: 5.0, ilk kadmiyumun konsantrasyonu 1 mg/mL, silis dumanı doz: 1 g/50 mL, çalkalama hızı: 500 rpm ve temas süresi 60 dak)

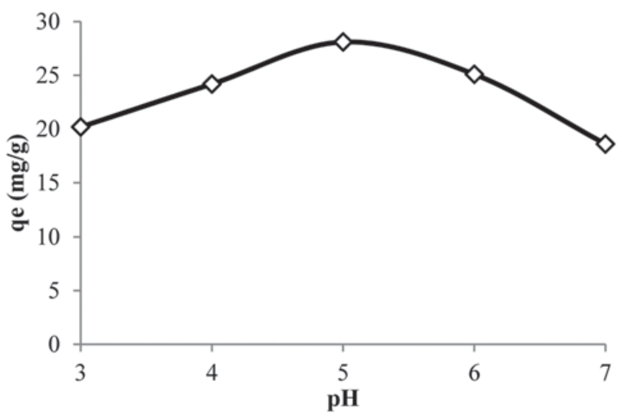

Fig 2. Effect of cadmium as a function of pH (initial cadmium concentration: 1 mg/mL, silica fume dose: 1 g/50 mL, agitation speed: 500 rpm and temperature: 25±1°C)

Şekil 2. Kadmiyum iyonu adsorpsiyonu üzerine pH değişiminin etkisi (ilk kadmiyumun konsantrasyonu 1 mg/mL, silis dumanı doz: 1 g/50 mL, çalkalama hızı: 500 rpm ve sıcaklık: 25±1°C)

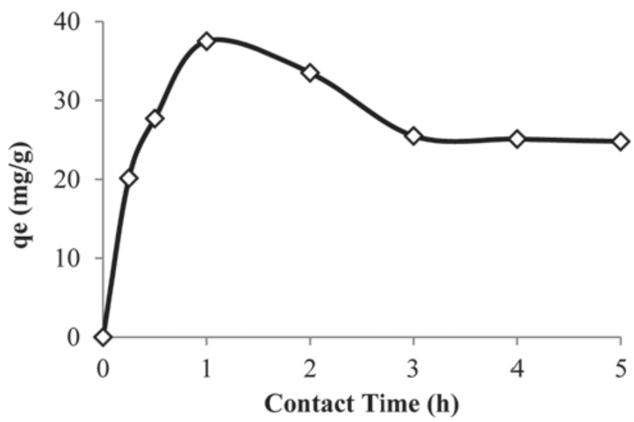

Fig 4. Removal of cadmium as a function of equilibrium time (pH:5.0, initial cadmium concentration: 1 mg/mL, silica fume dose: 1 g/50 mL, agitation speed: 500 rpm and temperature: 25±1°C)

Şekil 4. Kadmiyum'un giderilmesinde denge zamanı (pH: 5.0, ilk kadmiyumun konsantrasyonu 1 mg/mL, silis dumanı doz: 1 g/50 mL, çalkalama hızı: 500 rpm ve sıcaklık 25±1°C)

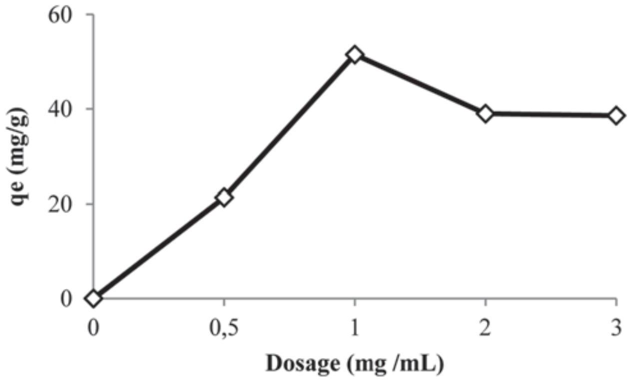

Fig 5. Effect of silica fume dosage on adsorption of cadmium (pH 5.0, initial cadmium concentration: 1 mg/mL, agitation speed: 500 rpm, contact time 60 min)

Şekil 5. Kadmiyumun adsorpsiyonu üzerine silis dumanı miktarının etkisi (pH: 5.0, ilk kadmiyumun konsantrasyonu 1 mg/mL, silis dumanı doz: 1 g/50 mL, çalkalama hızı: 500 rpm ve temas süresi 60 dak)

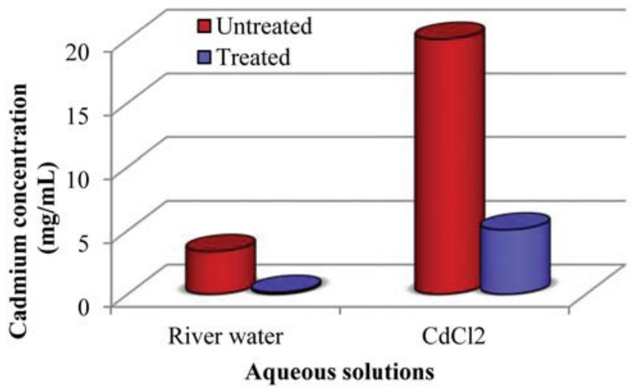

Fig 6. Variation of cadmium concentration after silica fume treating with river water and $Cu(NO_3)_2$

Şekil 6. Nehir suyu ve $Cu(NO_3)_2$ ile silis dumanının muamelesinden sonra kadmiyum konsantrasyonunun değişimi

***Table 2.** Results of EDX spectrum*

***Tablo 2.** EDX spektrumun sonuçları*

Elements	Native Adsorbent		Cadmium Ion Loaded Adsorbent	
	Weight (%)	**Atom (%)**	**Weight (%)**	**Atom (%)**
Mg	2.11	2.62	3.40	4.35
Si	77.65	83.68	74.70	82.85
K	9.21	7.13	6.21	4.95
Ca	2.19	1.66	1.09	0.85
Cr	3.11	1.81	4.27	2.56
Fe	1.17	0.64	1.47	0.82
Cu	1.88	0.89	2.53	1.24
Zn	1.82	0.84	2.56	1.22
Cd	-	-	3.64	1.01

***Table 3.** Values of the Langmuir and Freundlich constant for adsorption of cadmium*

***Tablo 3.** Kadmiyumun adsorbsiyonu için Langmuir and Freundlich sabitlerinin değerleri*

Adsorption Isotherm	Value
Langmuir constants	
Q_o(mg/g)	166.67
b(L/mg)	0.022
R^2	0.996
Freundlich constants	
K_F	0.181
N	0.824
R^2	0.993

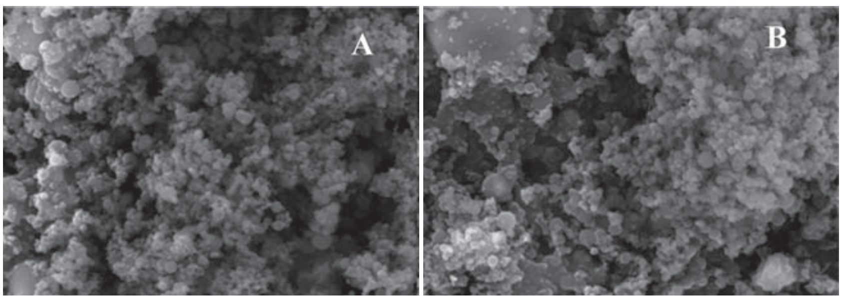

Fig 7. SEM images of native adsorbent (A) and cadmium loaded adsorbent (B)

Şekil 7. Doğal adsorbent (A) ve kadmiyum yüklenmiş adsorbent (B)'in SEM görüntüleri

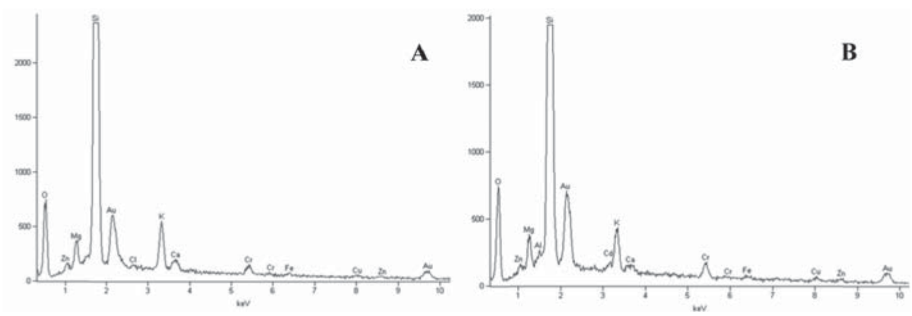

Fig 8. EDX spectra of native adsorbent (A) and cadmium loaded adsorbent (B)

Şekil 8. Doğal adsorbent (A) ve kadmiyum yüklenmiş adsorbent (B)'in EDX spektrumları

Table 4. *Thermodynamic parameters for the adsorption of cadmium onto silica fume adsorbent*

Tablo 4. *Silis dumanı üzerine kadmiyumun adsorbsiyonu için termodinamik parametreler*

Adsorbent	$\Delta H_{ads}°$ (kJmol^{-1})	$\Delta S_{ads}°$ (Jmol^{-1})	$\Delta G_{ads}°$ (kJmol^{-1})		
			298 K	303 K	313 K
Silica fume	10.634	-36.374	-205.45	-387.32	-751.06

adsorbent and cadmium ion loaded adsorbent were illustrated in the *Fig. 8A* and *8B*.

Freundlich and Langmuir adsorption isotherms model were applied to evaluate the experimental data and results are shown in *Table 3*. A comparison of the correlation coefficients results shown in *Table 3*.

Thermodynamic parameters were determined such as change in free energy *(ΔG°)* kJ/mol, enthalpy *(ΔH°)* kJ/mol, and entropy *(ΔS°)* J/Kmol from 298 to 313 K *(Table 4)*.

DISCUSSION

The uptake and percentage removal of metals from the aqueous solution are strongly affected by the pH of the solution [17,18]. The optimal pH was investigated the removal of cadmium ions in the pH range 3-7. It shows the effect of pH variation on adsorption of cadmium ions on the silica fume particle surface. It was shown that the absorption amount of cadmium increases with increasing pH and maximum adsorption of cadmium ions were obtained at pH 5.0. The uptake of cadmium increased from 24.19 to 28.1 mg/g when the pH of solution was increased from 4 to 5 *(Fig. 2)*. This is due to the surface complexation reactions, which are mostly influenced by the electrostatic force of attraction between cadmium and the surface of the silica fume [2,19,20].

Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate [21,22]. The effect of temperature on the adsorption has been determined in the range of 10-80°C *(Fig. 3)*. It is observed that the degree of adsorption increases with increasing temperature and maximum adsorption of cadmium ions are obtained at 25°C which is the temperature of the solution for the bacteria-modified silica fume [23]. The increase of the temperature can change the pore sizes which become wider, and can induce a certain activation of the surface of the solid support [24].

The contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption [24]. Therefore, it is important to study its effect on the capacity of retention of cadmium by bacteria-modified silica fume. The effect of contact time on the adsorption process was determined as 60 minutes *(Fig. 4)*. The increase in contact time has increased the cadmium uptake and this can be explained by the affinity of the support towards cadmium. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [3,25,26].

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate [2]. The adsorbent dosage was studied by varying the adsorbent amounts from 0.5 to 3.0 mg/mL by using bacteria-modified silica fume as a adsorbent *(Fig. 5)*. A trend of increase in adsorption capacity with increase in adsorbent dosage was observed from 0.5 mg/mL to 1 mg/mL. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. The amount of maximum cadmium removal was 51.5 mg/g at 1 mg/mL of adsorbent dose. Some trends were reported similar with the present study [27,28].

Without the addition of the bacteria-modified silica fume, the leachate cadmium concentration is approximately 3.345 and 20 mg/mL for polluted river water and $Cd(NO_3)_2$ solutions, respectively. The addition of bacteria-modified silica fume strongly inhibits the leaching of cadmium in the polluted river water and $Cd(NO_3)_2$ solutions *(Fig. 6)*. The increase in the adsorption capacity of aqueous solutions treated by bacteria-modified silica fume is attributed to the pH values and active components of bacteria-modified silica fume [2].

The SEM enables the direct observation of the surface microstructures of different adsorbents [27]. Images of native silica fume and metal loaded *M. extorquens*-modified silica fume were magnified 20.000 times by SEM was used to examine the surface of the adsorbent. After modified-silica fume's surface loaded by cadmium ions, the SEM photographs showed that the some changes occurred in the surface of native silica fume *(Fig. 7A* and *7B)*. From the EDX spectra, the cadmium ions were sorbed onto the adsorbent. The EDX analysis provided direct evidence for the adsorption of cadmium onto adsorbent [27]. It is shown from EDX spectra that after cadmium adsorption, cadmium concentration increased in the cadmium loaded adsorbent *(Fig. 8A* and *8B*; *Table 2)*.

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of an adsorption system. In an adsorption isotherm study, several equilibrium models have been developed to describe adsorption isotherm relationships [29]. The Freundlich [30] and Langmuir [31] equations are the world-widely used models because of their simplicity [32]. The Langmuir adsorption isotherm model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules [27]. Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of an adsorbent and it is given as;

$$q_e = \frac{q_m * K_L * C_e}{1 + K_L * C_e} \quad (3)$$

where q_e (mg/g) is the adsorption amount of adsorbent at equilibrium, q_m (mg/g) is the maximum adsorption amount of metal ions, C_e (mg/L) is the equilibrium concentration of adsorbate in solution and K_L (L/mg) is the equilibrium adsorption constant which is related to the affinity of the binding sites. The Langmuir constants K_L and q_m are calculated with the following equation;

$$\frac{C_e}{q_e} = \frac{1}{K_L * q_m} + \frac{q_e}{q_m} \quad (4)$$

where C_e (mg/L) is the equilibrium concentration of adsorbate in solution, *qe* (mg/g) is the adsorption amount of adsorbent at equilibrium, q_m (mg/g) is the maximum adsorption amount of metal ions and K_L (L/mg) is the equilibrium adsorption constant which is related to the affinity of the binding sites. The Freundlich isotherm is based on the assumption that adsorption is on a heterogeneous surface and exponential distribution of sites and their energies [32], which can be expressed by the following equation;

$$q_m = K_F + C_e^{1/n} \quad (5)$$

where q_m (mg/g) is the maximum adsorption amount of metal ions, C_e (mg/L) is the equilibrium concentration of adsorbate in solution. K_F (mg/g) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively. They can be calculated in the following linear form;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where q_e (mg/g) is the adsorption amount of adsorbent at equilibrium, C_e (mg/L) is the equilibrium concentration of adsorbate in solution, K_F (mg/g) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption. The Langmuir and Freundlich isotherms were obtained from the experiments.

The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane [25,33]. The Langmuir characteristics parameters and the degree of correlation of the adsorption data with respect to this equation are given in *Table 3*. The parameters K_F and n for cadmium calculated from experimental data and results obtained are given in *Table 3*. The magnitude of exponent n gives an indication of favorability and capacity adsorbent/adsorbate. The n value is 0.824 L/mg *(Table 3)* and it is located to range 1-10 represent good adsorption characteristic [25].

The sorption capacity of natural and bacteria-modified clay adsorbent increased with increase in the temperature of the system from 298-313 K. Thermodynamic parameters such as change in free energy (ΔG^o) kJ/mol, enthalpy (ΔH^o) kJ/ mol, and entropy (ΔS^o) J/Kmol were determined using the following equations [34]:

$$K_L = \frac{C_s}{C_e} \quad (7)$$

$$\Delta G^o = -RT \ln K_L \quad (8)$$

$$\ln K_L = \left(\frac{\Delta S^o}{R}\right) - \left(\frac{\Delta H^o}{RT}\right) \quad (9)$$

where K_L is the equilibrium constant, C_s is the solid phase concentration at equilibrium (mg/L), C_e is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant.

From the temperature variation from 298 to 313 K on the sorption, ΔH^o and ΔS^o were obtained. The ΔH_{ads}^o and ΔS_{ads}^o values obtained from the slope and intercept of Van't Hoff plots is presented in *Table 4*. Gibbs free energy (ΔG) was calculated as:

$$\Delta G^o = \Delta H^o - T\Delta S \quad (10)$$

The values of thermodynamic parameters for the sorption of cadmium on bacteria-modified silica fume adsorbent are given in *Table 4*. The Gibbs free energy change *(ΔG^o)* was calculated to be -205.45, -387.32 and -751.06 $kJmol^{-1}$ on bacteria-modified silica fume for cadmium adsorption at 298, 303, 313 K, respectively. Negative ΔG^o values indicated the feasibility of the process and spontaneous nature of the adsorption, were obtained for cadmium at each of the temperatures studied. The $\Delta H°$ parameter was found to be 10.634 kJ/mol for cadmium adsorption on bacteria-modified silica fume. The positive values of $\Delta H°$ further confirmed the endothermic nature of adsorption process. The heat of adsorption value between 10 and 400 kJ/mol indicates the chemisorptions process [35].

The $\Delta S°$ parameter was found to be -36.374 (kJ/mol K) for cadmium adsorption on bacteria-modified silica fume. The negative value of $\Delta S°$ corresponds to a decrease in degree of freedom of the adsorbed species. During the adsorption process, the coordinated water molecules were displaced by metal cations, resulting in increased randomness in the adsorbent-adsorbate system [36,37].

In this study, *Methylobacterium extorquens*-modified silica fume was converted into an adsorbent, and the suitability of the *Methylobacterium extorquens*-modified silica fume for adsorption of cadmium from the polluted river water and $Cd(NO_3)_2$ solutions was investigated by adsorption experiments. This study shows clearly that sawdust which is a cheap and abundant material can be used as an effective adsorbent for removal of cadmium from wastewater.

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