Original Research

Bacteria-Modified Red Mud for Adsorption of Cadmium Ions from Aqueous Solutions

Ekrem Kalkan[1], Hayrunnisa Nadaroglu[2]*, Neslihan Dikbaş[3], Esen Taşgın[4], Neslihan Çelebi[2]

[1]Geological Engineering Department, Oltu Earth Sciences Faculty, Ataturk University, 25400 Oltu-Erzurum, Turkey
[2]Department of Food Technology, Erzurum Vocational School, Ataturk University, 25240 Erzurum, Turkey
[3]Department of Biotechnology, Agriculture Faculty, Ataturk University, 25240 Erzurum, Turkey
[4]Primary Department, Bayburt Education Faculty, Bayburt University, 69000 Bayburt, Turkey

Abstract

Cadmium is a toxic metal widely used in industry and it enters the environment from electroplating, smelting, alloy manufacturing, pigments, plastics, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations, and refining industries. Considering the harmful effects of cadmium, it is necessary to remove cadmium from liquid wastes at least to the limit accepted by regulations. The present study describes removal of cadmium from aqueous solutions using bacteria-modified red mud 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 4.0, contact time of 60 min, temperature of 30ºC, 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 83.034 mg/g. The kinetic processes of cadmium adsorption on bacteria-modified red mud were described by applying pseudo-first-order and pseudo-second-order rate equations. The kinetic data for the adsorption process obeyed pseudo-second-order rate equations. Various thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ were calculated and the negative value of $\Delta G°$ obtained indicate that the process was spontaneous, and the positive value of $\Delta H°$ confirms the reaction to be endothermic, and the positive value of $\Delta S°$ shows that the decrease in the degree of freedom of the adsorbed species.

The bacteria-modified red mud investigated in this study exhibited a high potential for the removal of cadmium from aqueous solutions.

Keywords: wastewater, bacteria-modified red mud, cadmium removal, adsorption isotherm, adsorption kinetic, adsorption thermodynamic

Introduction

Heavy metals pollution has become a serious threat and of great environmental concern as heavy metals are non-biodegradable and thus persistent. The presence of heavy metals in the environment a major concerns because of their toxicity and threat to human life. They accumulate in living tissues throughout the food chain, with humans at the top [1-4]. Heavy metal species are some of the most common pollutants that are found in industrial wastewater. Because of their toxicity, these species can have a serious impact if released into the environment as a result of bioaccumulation, and they may be extremely toxic even in trace quantities [5-11]. High concentrations of heavy metals in

*e-mail: hnisa25@atauni.edu.tr

the environment can be detrimental to a variety of living species. Heavy metal ions can be accumulated through the food chain even at lower concentrations, leading to reduced mental and central nervous functions, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs [12-14].

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 [9]. Toxicological studies have shown that long-term effects from cadmium poisoning include kidney damage and changes to the constitution of the bone, liver, and blood. Short-term effects include nausea, vomiting, diarrhea, and cramps. So, minimizing production of hazardous waste and heavy metals became one of the most important environmental challenges that the world faces today [15].

Several conventional methods exist for the removal of heavy metal pollutants from wastewater. These methods include precipitation, electroplating, chemical coagulation, ion-exchange, membrane separation, and electro kinetics. However, these methods often incur high operational costs [3, 16-26].

The most commonly used methods for the removal of cadmium ions from aqueous solution include chemical precipitation [27, 28], ion exchange [29], solvent extraction [30, 31], dialysis/electro-dialysis [32], reverse osmosis [33], supported liquid membrane [34], and adsorption [35-37]. Among them, chemical precipitation, ion exchange and solvent extraction are not economically viable to remove cadmium to low concentrations from aqueous solutions. Adsorption is one of the most effective approaches to cadmium removal over a wider range of pH values and at lower concentrations [38]. The adsorption of cadmium by a number of materials such as clays [39-41], minerals such as hydroxyapatite [42] and calcite [43-45], calcareous soils [46], some industrial by-products and waste materials such as slags and sludges [47], modified asphaltite ashes [48], chitosan, dead biomass, modified wool, moss, peat, seaweed, sesquioxides (iron, aluminum, or manganese oxides) [49], and others [50, 51] have been reported in the literature.

As an alternative low-cost absorbent material, solid wastes are generally used as adsorbent for the removal of heavy metals from wastewater. One type of solid waste material, red mud, is largely produced from the alumina industry. Red mud emerges as a by-product of the caustic leaching of bauxite to produce alumina. Its major constituents are Fe_2O_3, Al_2O_3, SiO_2, Na_2O, and CaO. It contains little amounts of Zr, Y, Th, and U elements, and trace amounts of rare earth elements. This waste material has a reddish-brown color and a superfine particle size distribution. Alkalis, iron oxides and hydroxides, aluminum hydroxides, calcium carbonate, titanium, and silica form its chemical composition. Red mud is principally composed of fine particles of silica, aluminum, iron, calcium, and titanium oxides and hydroxides, which are responsible for its

high surface reactivity [52-54]. Because of these characteristics, red mud has been the subject of many investigations, including some on the removal of toxic heavy metals from wastewater and acid mine drainage, or on reducing the leaching of soil nutrients [14, 55-61]. It has been noted in the literature that red mud could be used for decontaminating mining sites and other contaminated areas, which generate acidic leachates and produce high concentrations of hazardous heavy metal ions [62]. From earlier research, researchers have shown that red mud shows adsorption toward anionic pollutants such as phosphate [63] and chromate [64].

Staphylococcus cohnii GC subgroup A is a bacteria that has the capability to eliminate Ca ions from the environment. It was thought that it can reduce metals on the surface of red mud particles and contribute to remove Cd ions from the environment by connecting them to the surfaces of red mud particles. Therefore, *Staphylococcus cohnii GC subgroup A* bacteria has been selected to modify red mud to obtain more effective adsorbency for cadmium removal from aqueous solutions.

This paper describes the use of bacteria-modified red mud 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 red mud from polluted river water and $Cd(NO_3)_2$ solution, and the results have been shown on the adsorption behavior of cadmium on bacteria-modified red mud. Adsorption isotherm, kinetic, and thermodynamic studies have been performed to describe the adsorption process.

Experimental Procedure

Adsorbent

Red mud has been obtained as bauxite waste in the manufacture of alumina and emerges as unwanted by-products during alkaline-leaching of bauxite in the Bayer process. The alkaline red mud-water pump has been dumped annually into specially constructed dams around the Seydisehir Aluminum Plant (Konya, Turkey). Red mud used in this experimental study has been obtained from this plant. Its physical properties, chemical composition and mineralogical composition are given in Table 1.

Adsorbent Preparation

The red mud was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200 mesh screen. A little amount of the suspension remained on the sieve and was discarded. 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 105ºC, ground in a mortar, and sieved through a 200 mesh sieve. 1 g of red mud sample was shaken with 10 mL, 10^8 CFU/mL *Staphylococcus cohnii GC subgroup*

Table 1. Physical property, chemical constituent, and mineralogical composition of red mud.

	Value
Property	
Density (Mg/m³)	28.50
Specific gravity	3.05
pH	12-13
Constituents	
Al_2O_3	20.20
Fe_2O_3	35.04
CaO	5.30
MgO	0.33
TiO_2	4.00
Na_2O	9.40
SiO_2	17.29
Ignition	8.44
Mineral (%)	
Sodalite ($Na_2O \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.73H_2O$)	32.20
Cancrinite ($3NaAlSiO_4 \cdot NaOH$)	4.60
Hematite (Fe_2O_3)	34.70
Diaspore (AlO(OH)	2.60
Rutile (TiO_2)	1.60
Calcite ($CaCO_3$)	1.30

A solution for approximately 1 h, and then the separated particles were stored. The red mud was used for the study of cadmium removal from aqueous solution after its modification by using bacteria called *Staphylococcus cohnii GC subgroup A*.

Adsorbent Characterization

The pH values were determined with a pH meter (Thermo Scientific Orion 5 star plus multifunction). A 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 model 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 electrostatic charging during examination. The same machine also was used for the energy dispersive X-ray (EDX) spectra analysis to know the elemental composition of the red mud. In addition, the Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out to identify functional groups and molecular structure in the bacteria-modified red mud and cadmium-loaded bacteria-modified red mud. FTIR spectra were recorded on the Perkin-a

Perkin-Elmer GX2000 FTIR spectrometer. The spectrum of the adsorbent was measured within the range of 4,000-700 cm⁻¹ wave number.

Adsorption Procedure

For studying metal adsorption, a 10 mL sample solution was pipetted into a 100 mL erlenmeyer flask, and 5 mL 1 mM dithizone was added as a complexing agent. The pH was adjusted to 8 (optimum value) with 1 mM NaOH or 1 mM HCl. The aqueous phase was diluted to 40 mL, and 0.15 g naphthalene was added as a solid solvent. Then, this solution was heated in a water bath to about 85ºC and stirred (800 rpm) for 2 min to dissolve the complex in the molten naphthalene, and allowed to stand for 15 min at room temperature to form micro crystalline naphthalene containing Cd-dithizone complex. After filtration with fritted glass, this microcrystalline naphthalene was washed with deionized water and dissolved in a 2 mL volumetric flask with acetone. The absorbance of the solutions was measured at 228.8 nm with spectrophotometer. A calibration curve was prepared in the range 0-40 ng mL⁻¹ of cadmium according to the general procedure.

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

$$q_e = \frac{(C_o - C_t) * V}{m} \qquad (1)$$

...where, q_e 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.

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

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

Results and Discussion

Calibration Curve

Linear regression is one of the most frequently used analyses in calibration. Once the relationship between the input value and the response value assumed to be represented by a straight line is established, the calibration curve is used in the evaluation of accuracy of the result. 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 0.9994.

Effect of pH

The pH of the aqueous solution is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent, and the degree of ionization of the adsorbate during reaction [65]. In other words, the uptake and percentage removal of metals from the aqueous solution are strongly affected by the pH of the solution [43, 66-68]. In order to find the optimal pH value for the sorption process, the removal of cadmium ions in the pH range 3-6 was investigated and the data were illustrated in Fig. 1. It shows the effect of pH variation on adsorption of cadmium ions on the red mud 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 4.0. The uptake of cadmium increased from 27.70 to 33.37 mg/g when the pH of solution was increased from 3 to 4. 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 red mud. The acidity of the medium can affect the metal ions' uptake amount of the adsorbent because hydrogen ions in the solution could compete with cadmium for active sites on the adsorbent surface [14, 69].

Red mud is a metal oxide adsorbent containing different metal oxides in the structure. Hydroxylated surfaces of these oxides developed a charge on the surface of the water. This can be due to the interaction between cadmium ion and metal oxide. The removal of cadmium pollutant from aqueous solution by adsorption is highly dependent on pH of the media affecting the surface charge of the solid particles and degree of ionization and speciation of adsorbate [70-73].

Effect of Contact Time

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption [74]. Therefore, it is important to study its effect on the capacity of retention

Fig. 2. Removal of cadmium as a function of equilibrium time (pH: 4, initial cadmium concentration: 1 mg/mL, bacteria-modified red mud dose: 1 mg/mL, agitation speed: 500 rpm and temperature: 30±1ºC).

of cadmium by bacteria-modified red mud. Fig. 2 illustrates the effect of contact time on the adsorption process. It clearly shows that the equilibrium is attained after only 60 minutes. The increase in contact time has increased cadmium uptake, and this can be explained by the affinity of the support toward cadmium. It is clearly shown that the amount of cadmium removal is higher at the beginning. This is probably due to the larger surface area of the bacteria-modified red mud being available at the beginning for the adsorption of cadmium ions. 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 [13, 75]. This result is important, as equilibrium time is one of the important parameters for selecting a wastewater treatment system, when the time consumed for wastewater disposal should be considered. This rapid removal of the adsorbate has significant practical importance since it will facilitate smaller reactor volumes, ensuring efficiency and economy [76-78].

Effect of Temperature

Temperature is known to have a profound effect on various chemical processes. Temperature affects the adsorption rate by altering molecular interactions and the solubility of the adsorbate [79, 80]. The effect of temperature influencing adsorption has been studied in the range of 20-80ºC. The effect of temperature on the adsorption capacity of bacteria-modified red mud is shown in Fig. 3. It has been observed that the degree of adsorption increases with increasing temperature, and maximum adsorption of cadmium ions are obtained at 30ºC, which is the temperature of the solution for the bacteria-modified red mud. An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. These result in the enhancement of the sorptive capacity of the adsorbent [81]. The increase in adsorption capacity with temperature suggested that the active surface sites available for adsorption have increased with temperature. The increase of the temperature encourages the process of agglomeration in a very determined sense, until a certain
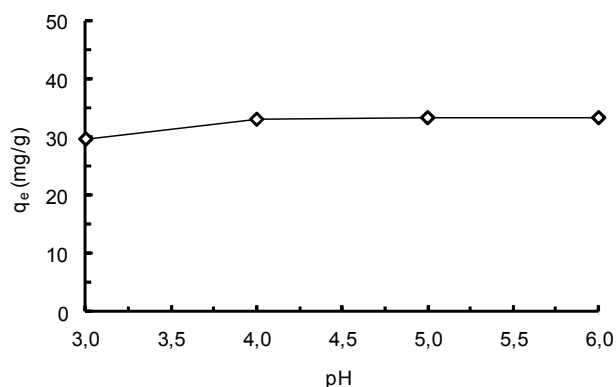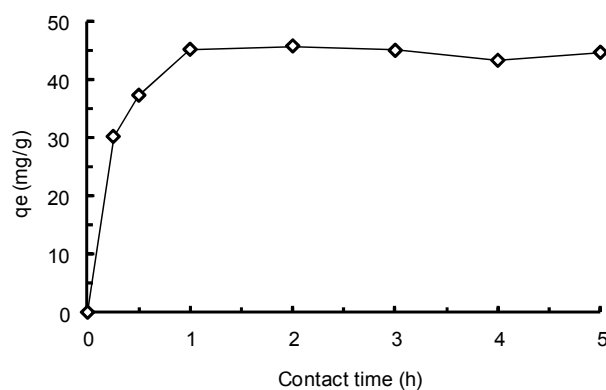

Fig. 1. Effect of cadmium as a function of pH (initial cadmium concentration: 1 mg/mL, bacteria-modified red mud dose: 1 mg/mL, agitation speed: 500 rpm and temperature: 30±1ºC).
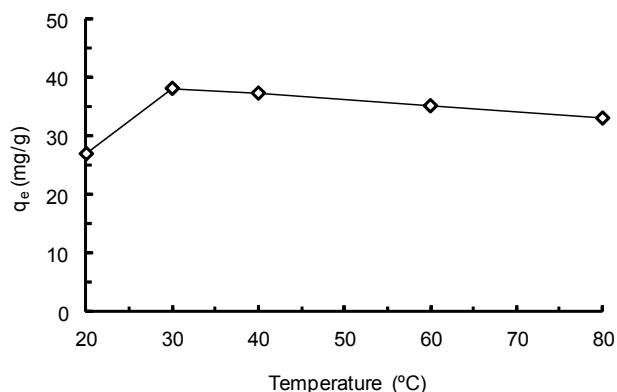
Fig. 3. Effect of cadmium as a function of temperature (pH: 4, initial cadmium concentration: 1 mg/mL, bacteria-modified red mud dose: 1 mg/mL, agitation speed: 500 rpm).

temperature limit, beyond which desorption becomes more important and hence reducing the rate of adsorption, as time goes on. Also, 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 [74].

Effect of the Adsorbent Dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate [14]. 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 red mud dosage on the amount of cadmium adsorbed was shown in Fig. 4. 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 43.62 mg/g at 1 mg/mL of adsorbent dose. The phenomenon of increase in the amount of cadmium removal with an increase in adsorbent dosage may be explained as with the increase in the adsorbent dosage, more and more surface becomes available for metal ion to adsorb and this

increase the adsorption rate [82, 83]. The same trends have been reported in literature [68, 84, 85].

The cadmium concentration of polluted river water and $Cd(NO_3)_2$ solutions treated with bacteria-modified red mud indicate that bacteria-modified red mud enhances adsorption capacity. Without the addition of the bacteria-modified red mud, the leachate cadmium concentration is approximately 2.162 and 20 mg/mL for polluted river water and $Cd(NO_3)_2$ solutions, respectively. The addition of bacteria-modified red mud strongly inhibits the leaching of cadmium in the polluted river water and $Cd(NO_3)_2$ solutions. When the bacteria-modified red mud is added to the cadmium-contaminated aqueous solutions, the cadmium concentration in the leachate is drastically reduced, whereas the adsorption capacity increases. The cadmium concentration of the leachates treated by bacteria-modified red mud decreases from 2.162 to 0.373 mg/mL and from 20.000 to 2.130 mg/mL for the polluted river water and $Cd(NO_3)_2$ solutions, respectively (Fig. 5). The increase in the adsorption capacity of aqueous solutions treated by bacteria-modified red mud is attributed to the pH values and active components of bacteria-modified red mud [14, 86].

Image Analysis

The SEM enables the direct observation of the surface microstructures of different adsorbents [82]. Images of native adsorbent and metal-loaded adsorbent were magnified 20,000 times by SEM, which 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. 6a) after its surface was loaded by cadmium ions (Fig. 6b). The SEM of exhausted adsorbents clearly indicates the presence of new shiny bulky particles and layer over the surface of metal-loaded adsorbents which are absent from the native adsorbent before metal loading [13]. It is shown in Fig. 6a that large continuous pores among the adsorbent particles provide a large portion of the total void ratio, while small connected pores exist among the cadmium-laden adsorbent particles. The cadmium ions cover the surrounding adsorbent particles and fill the voids (Fig. 6b).
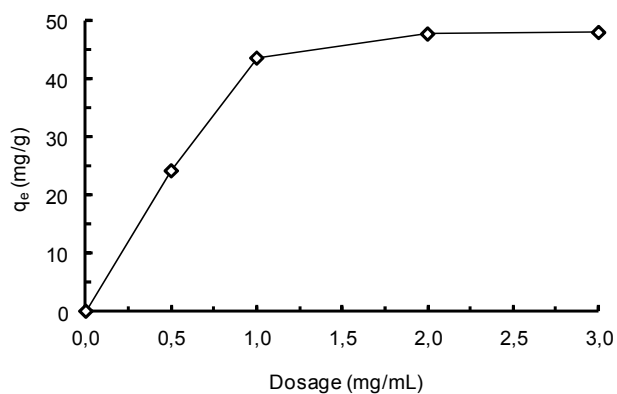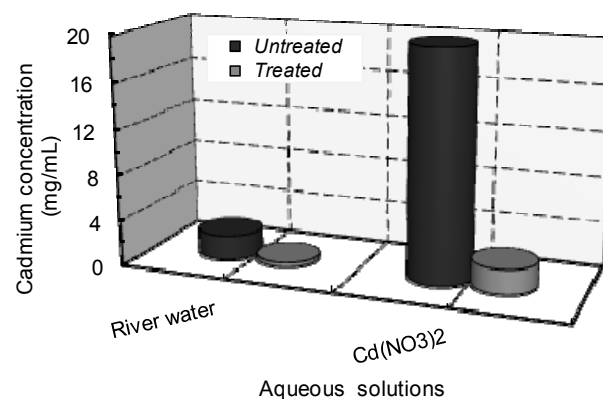

Fig. 4. Effect of bacteria-modified red mud dosage on adsorption of cadmium (pH: 4, initial cadmium concentration: 1 mg/mL, agitation speed: 500 rpm).

Fig. 5. Variation of cadmium concentration with bacteria-modified red mud on river water and $Cd(NO_3)_2$.

Table 2. Results of EDX spectrum.

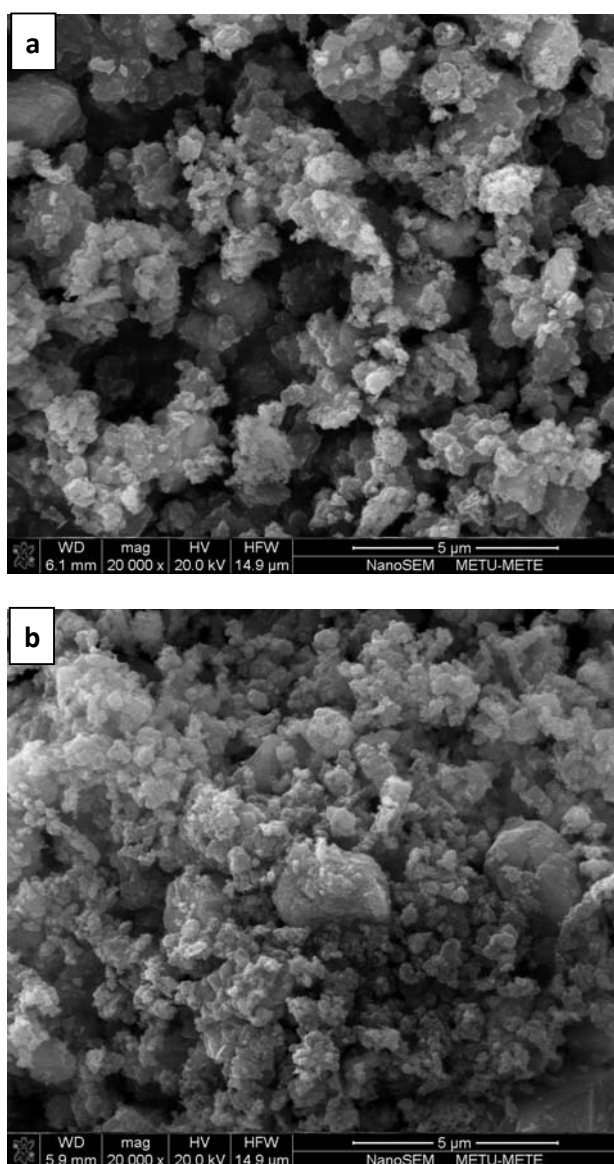| Elements	Native adsorbent		Cadmium loaded adsorbent	
	Weight (%)	Atom (%)	Weight (%)	Atom (%)
Na	14.00	21.49	11.85	18.92
Al	20.02	26.19	19.65	26.72
Si	15.58	19.59	14.67	19.17
K	0.66	0.60	0.42	0.39
Ca	1.00	0.88	1.19	1.09
Ti	5.21	3.84	5.33	4.08
Fe	42.29	26.73	43.34	28.47
Cu	1.24	0.69	-	-
Cd	-	-	3.55	1.16

Fig. 6. SEM images of native adsorbent (a) and cadmium loaded adsorbent (b).

The EDX measurements were recorded for qualitative analysis of the element constitution of the adsorbents, and the EDX spectra of native adsorbent and cadmium ion loaded adsorbent are illustrated in Figs. 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 [82]. It is shown from EDX spectra that after cadmium adsorption, cadmium concentration increased in the cadmium loaded adsorbent (Figs. 7a and 7b, Table 2).

FT-IR Analysis

The FT-IR technique can be used to analyze organic materials and some inorganic materials. It measures the absorption of various infrared radiation by the target material, producing an IR spectrum that can be used to identify functional groups and molecular structures in the sample. Figs. 8a and 8b illustrate the functional groups and surface properties of the adsorbent after adsorption by FT-IR spectra. At 3262-3269 cm^{-1}, a strong band was present in the hydroxyl stretching region in the spectra. This was likely due to the presence of H_2O in the red mud [87, 88]. At 1,644 cm^{-1}, a band was detected. This was attributed to the water molecules occluded inside the aluminosilicate structure [89]. The absorption band of carbonates incorporated in the main channel of cancrinite [90], appeared within the 1,410-1,470 cm^{-1} region in the samples. The peak recorded at 1,410 cm^{-1} in the samples could be attributed to NO_3^- present in both cancrinite and sodalite. The band at 964-970 cm^{-1} observed in samples could be assigned to the stretching vibrations of Si(Al)-O. This band is sensitive to the content of structural Si and Al [91]. To evaluate, using the FTIR technique, the interaction mechanisms between the Cd^{2+} ions and RM, we focused our attention on a part of the midinfrared region, 687-862 cm^{-1}, where bands associated with various Cd-O(H) stretching vibrations were found [92-95]. It is shown that there is no significant change in the functional biomass groups of clay soil after adsorption of cadmium ions on the red mud when cadmium ions were
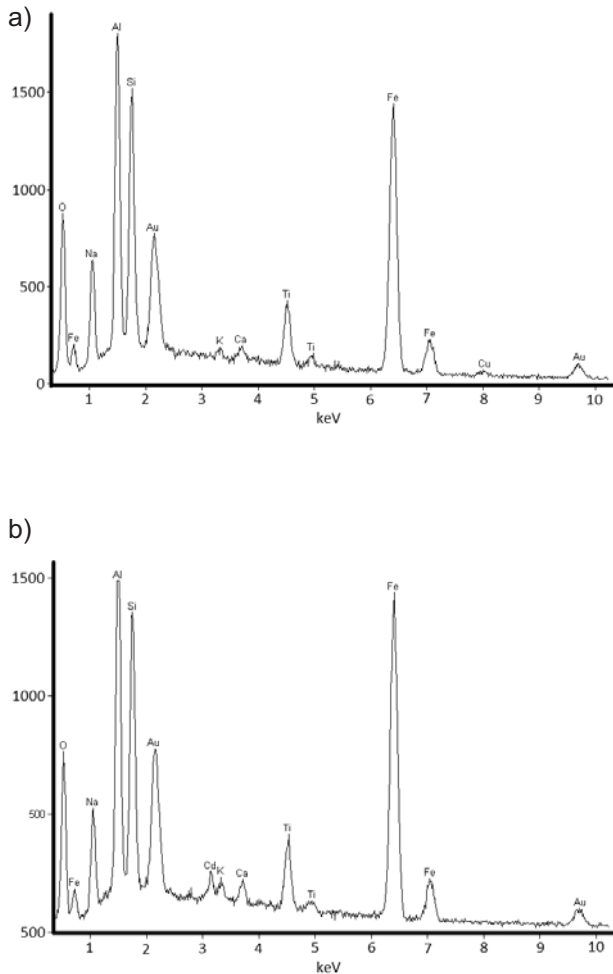
a)

b)

Fig. 7. EDX spectra of native adsorbent (a) and cadmium-loaded adsorbent (b).

treated with red mud. It was concluded that cadmium ions did not damage functional groups on the adsorbent.

Adsorption Isotherms

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 [69, 96]. The Freundlich [97] and Langmuir [98] equations are the most widely used models because of their simplicity [99]. 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 [82]. The Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of an adsorbent and it is given as:

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

...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 related to the affinity of the binding sites. The Langmuir constants K_L and q_m are calculated with the following equation:

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

...where C_e (mg/L) is the equilibrium concentration of adsorbate in solution, q_e (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 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 [99], which can be expressed by the following equation:

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

...where q_m (mg/g) is the maximum adsorption amount of metal ions and C_e (mg/L) is the equilibrium concentration of adsorbate in solution. K_F (mg/g) and n are the Freundlich
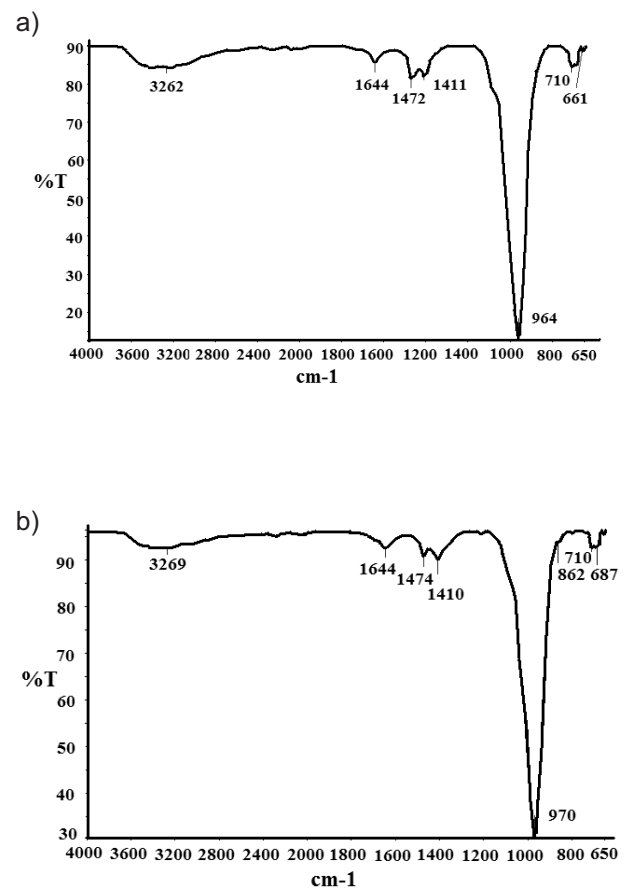
a)

b)

Fig. 8. FT-IR spectrum of adsorbent (a) and adsorbent loaded with cadmium ions (b).

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

Adsorption isotherm	Value
Langmuir constants	
Q_o (mg/g)	83.034
K_L (L/mg)	0.0803
R^2	0.9998
Freundlich constants	
K_F	20.1929
n	3.4129
R^2	0.9994

Fig. 10. The Freundlich isotherm for the adsorption of cadmium by bacteria-modified red mud.

constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively. They can be calculated in the following linear form:

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

...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, and 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 [51, 100]. Fig. 9 shows the straight line obtained plotting C_e versus C_e/q_e for cadmium on bacteria-modified red mud samples. The Langmuir characteristics parameters and the degree of correlation of the adsorption data with respect to this equation are given in Table 3.

Fig. 10 shows a linear relationship $\log q_e$ versus $\log C_e$. The parameters K_F and n for cadmium calculated from
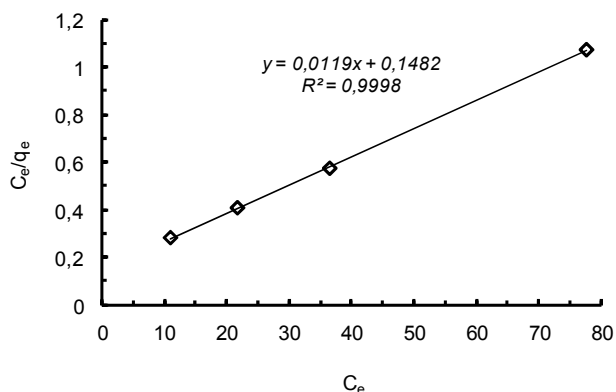

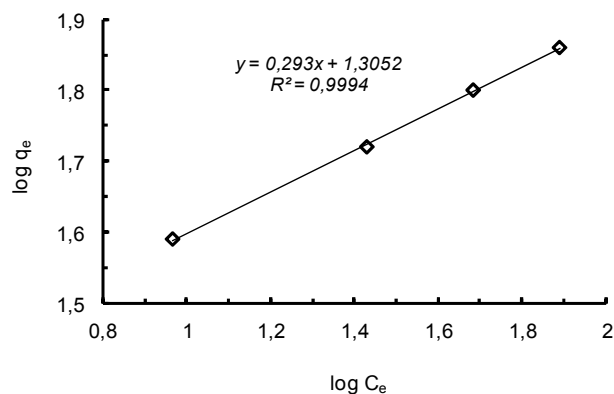Fig. 9. The Langmuir isotherm for the adsorption of cadmium by bacteria-modified red mud.

experimental data and results obtained are given in Table 3. The magnitude of exponent n gives an indication of favorability and capacity adsorbent/adsorbate. It is generally stated that the value of n in the range 1-10 represents good adsorption. The magnitude of the exponent n gives an indication of the favorability of the adsorption. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics [101]. The n value is 3.4129 L/mg (Table 1) and it is located to range 2-10 represent good adsorption characteristic [82]. Based on the correlation coefficient values, it has been deduced that the Freundlich model better fit the experimental data. The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of cadmium ions.

Adsorption Kinetics

Experimental data generated from cadmium adsorption tests using the bacteria-modified red mud were evaluated by using pseudo-first-order kinetic and pseudo-second-order kinetic models to understand the mechanisms and dynamics of the adsorption process. The pseudo-first-order kinetic model, also known as the Lagergren kinetic equation as expressed in the following equation, is widely employed to understand the kinetic behavior of the adsorption reactions [102].

$$1/q_t = k_1/q_e t + 1/q_e \qquad (7)$$

...where q_e and q_t are the amounts of cadmium adsorbed at equilibrium and at time t (mg·g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}). This equation was applied to the present study of cadmium adsorption. k_1 and the correlation coefficients for cadmium adsorption at different concentrations ranging from 5 to 100 mg/L were calculated from the linear plots of $\log (q_e - q_t)$ versus t (Fig. 11), and were listed in Table 4. The correlation coefficients for the pseudo-first-order kinetic model were high, ranging from 0.9064 and 0.9978. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment

and calculation was observed, indicating a high pseudo first-order fit to the experimental data. These results confirm the better sorption capacity of the bacteria-modified red mud.

The adsorption kinetics also can be described by a pseudo-second order reaction [75]. The pseudo-second-order kinetic model is based on the assumption that the limiting rate step may be chemisorption, which involves valence forces by sharing or electron exchange between the adsorbent and the adsorbate [103]. The pseudo-second-order kinetic model is given by the following equation:

$$1/q_t = k_2/q_e^2 + t/q_e \qquad (8)$$

...where: k_2 is the equilibrium rate constant of pseudo-second-order model (g·mol^{-1}·min^{-1}). This equation was applied to the present study of cadmium adsorption. The k_1, q_e and the correlation coefficients for cadmium adsorption at different concentrations ranging from 5 to 100 mg/L were calculated from the linear plots of t/q_t versus t (Fig. 12), and were listed in Table 4. At all initial cadmium concentrations studied, straight lines with high correlation coefficients (>0.9532) were obtained. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetics.

The pseudo second-order kinetic analysis reveals that k_2 decreases with an increase in initial cadmium concentrations. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentrations. At higher concentrations, the competition for the surface active sites is high and, consequently, lower sorption rates are obtained. The equilibrium adsorption capacity (q_e), however, increased with an increase in initial cadmium concentration because a large number of cadmium ions are adsorbed at the available adsorption sites [75].

Adsorption Thermodynamics

The experiments also were performed in order to understand the kinetics of cadmium removal by bacteria-modified red mud. It is an established fact that the adsorption of cadmium ions in an aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface and two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation are the kinetics and the equilibrium [75].

The sorption capacity of natural and bacteria-modified clay adsorbent increased with increase in the temperature of the system from 293-303 K. Thermodynamic parameters such as change in free energy ($\Delta G°$) kJ/mol, enthalpy ($\Delta H°$) kJ/mol, and entropy ($\Delta S°$) J/Kmol were determined using the following equations [104]:

$$K_L = \frac{C_s}{C_e} \qquad (9)$$

$$\Delta G^o = -RT \ln K_L \qquad (10)$$

$$\ln K_L = \left(\frac{\Delta S^o}{R}\right) - \left(\frac{\Delta H^o}{RT}\right) \qquad (11)$$

...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 293 to 313 K on the sorption, ΔH^o and ΔS^o were obtained (Fig. 13). The $\Delta H_{ads}°$ and $\Delta S_{ads}°$ values obtained from the slope and inter-
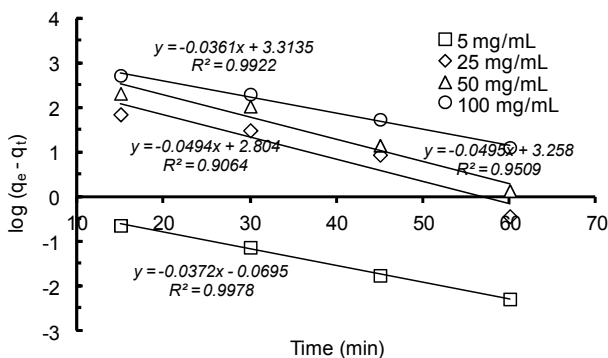

Fig. 11. Pseudo first-order reaction for cadmium adsorbed onto bacteria-modified red mud adsorbent at different concentrations.

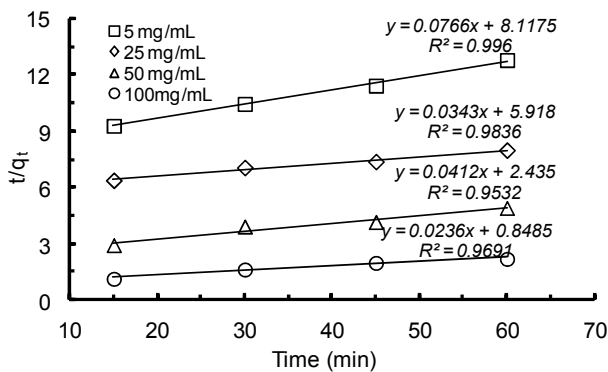Fig. 12. Pseudo second-order reaction for cadmium adsorbed onto bacteria-modified red mud adsorbent at different concentrations.
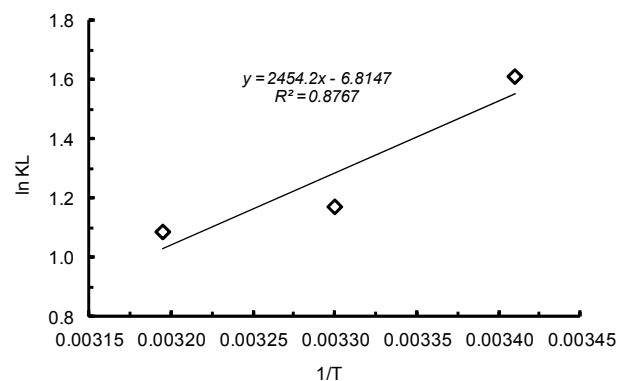

Fig. 13. Influence of temperature on the thermodynamic behavior of adsorption of cadmium onto bacteria-modified red mud adsorbent.

Table 4. Comparison between the estimated adsorption rate constants, q_e, and correlation coefficients associated with the pseudo-first-order and the pseudo-second-order rate equations.

Initial cadmium concn (mg/L)	q_e, exp (mg/g)	Pseudo first-order rate equation			Pseudo second-order rate equation		
		k_1	q_e, cal (mg/g)	R^2	k_2	q_e, cal (mg/g)	R^2
5	0.87	0.0372	1.072	0.9978	0.01890	1.30	0.9960
25	8.65	0.0494	16.51	0.9064	0.00005	24.27	0.9532
50	15.21	0.0495	25.99	0.9509	0.00029	29.15	0.9836
100	28.35	0.0361	27.48	0.9922	0.00066	42.37	0.9691

Table 5. Thermodynamic parameters for the adsorption of cadmium onto bacteria-modified red mud adsorbent.

	ΔH_{ads}^o (kJ·mol⁻¹)	ΔS_{ads}^o (kJ·mol⁻¹)	ΔG_{ads}^o (kJ·mol⁻¹)		
			293 K	298 K	303 K
Bacteria-modified red mud	20.4	-56.65	-16.62	-17.19	-17.75

cept of Van't Hoff plots is presented in Table 4. Gibbs free energy (ΔG) was calculated as:

$$\Delta G^o = \Delta H^o - T\Delta S \qquad (12)$$

The values of thermodynamic parameters for the sorption of cadmium on bacteria-modified red mud adsorbent are given in Table 5. The Gibbs free energy change (ΔG^o) was calculated to be -16.62, -17.19, and -17.75 kJ·mol⁻¹ on bacteria-modified red mud for cadmium adsorption at 293, 298, 303 K, respectively. Negative ΔG^o values indicated the feasibility of the process and spontaneous nature of the adsorption and were obtained for cadmium at each of the temperatures studied. The ΔG^o values decreased with an increase in temperature, indicating an increased trend in the degree of spontaneity and feasibility of cadmium adsorption. The ΔH^o parameter was found to be 20.4 kJ/mol for cadmium adsorption on bacteria-modified red mud. The positive values of ΔH^o further confirmed the endothermic nature of the adsorption process. The heat of adsorption value between 20 and 400 kJ/mol indicates the chemisorptions process [105-107]. Hence, the adsorption of cadmium on bacteria-modified red mud was chemical in nature.

The ΔS^o parameter was found to be -56.65 (kJ/mol K) for cadmium adsorption on bacteria-modified red mud. The negative value of ΔS^o 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 [107-110].

Conclusion

In this study, *Staphylococcus cohnii GC subgroup A*-modified red mud was converted into an adsorbent, and the suitability of the *Staphylococcus cohnii GC subgroup A*-modified red mud 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 s the *Staphylococcus cohnii GC subgroup A*-modified red mud, which is a cheap and abundant material, can be used as an effective adsorbent for removal of cadmium from wastewater. The maximum cadmium removal by adsorbent was at pH 4. The removal of cadmium increases with increasing time in the first 60 min. It is observed that the degree of adsorption increases with increasing temperature and maximum adsorption of cadmium ions are obtained at 30ºC, which is the temperature of the solution. The total amount of metal ions removed from the solutions increases by the amount of adsorbent. The adsorbent concentration increases when the number of adsorbent particles surrounding the metal ions increases. Based on the correlation coefficient values, it has been deduced that the Langmuir model is better fitted to the experimental data. The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of cadmium ions. The kinetic data for the adsorption process obeyed pseudo second-order rate equations. Thermodynamic parameters such as ΔG^o, ΔH^o, and ΔS^o and were calculated. The free energy ΔG^o of the process at all temperatures was negative, indicating that the adsorption is a spontaneous process. The value of ΔH^o was positive indicating the endothermic nature of adsorption. The positive ΔS^o showed a decrease in the degree of freedom of the adsorbed species. The investigation showed that the *Staphylococcus cohnii GC subgroup A*-modified red mud is a valuable material for removal of cadmium ions from aqueous solutions. In addition, the use of bacteria-modified red mud as modified industrial waste material for the removal of cadmium ions from the aqueous solutions can potentially reduce remediation costs.

Acknowledgements

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