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Kinetics, equilibrium and thermodynamics studies on Cd(II) removal from aqueous solution by magnesite tailing

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Magnesite tailing for the removal of Cd(II) from aqueous solutions has been investigated using batch process. The effects of various parameters such as initial *p*H, adsorbent dosage, contact time and temperature on the removal of Cd(II) have been investigated. Kinetic models are applied to describe the adsorption kinetics of Cd(II) onto magnesite tailing. The adsorption kinetics follows well the pseudo second order kinetic model. The Langmuir, Freundlich and D-R isotherm models have been used for the analysis of adsorption equilibrium. The Langmuir isotherm model fits the equilibrium data. The monolayer adsorption capacity of magnesite tailing is found to be 38.46 mg/g at 45°C. The thermodynamic parameters show that the adsorption process is feasible, spontaneous and endothermic. The Cd(II) - magnesite tailing interactions are confirmed by the Scanning electron microscope (SEM) and the Fourier transform infrared spectroscopy (FTIR). A single stage batch adsorber was designed for different adsorbent dosage using Langmuir isotherm. It is determined that approximately 99% of Cd(II) from aqueous solution could be removed at a *p*H value of 6, an adsorbent dosage of 0.3 g / 50 mL solution, a contact time of 24 h, an initial solution concentration of 10 mg/L and a temperature of 25°C. The results indicate that magnesite tailing could effectively be used for the removal of Cd (II) from aqueous solutions.

Keywords: Cd (II) adsorption, Isotherm, Kinetics, Magnesite tailing, FTIR

One of the main causes of industrial pollution is the discharge of effluents including heavy metal ions into aquatic system. Cadmium is one of the most important heavy metal used in the production of copper, lead, silver and aluminium alloys. It is also used in metal finishing, ceramic manufacture, photography, dyeing, textile printing, paper and cadmium-nickel battery manufacture. Salts of cadmium are used as a catalyst for organic reactions, as insecticides and as antiparasitic agents. Cadmium is especially dangerous since it may combine synergistically with other toxic substances. Cadmium poisoning causes lung, liver and kidney damage, bone lesions, cancer and hypertension[1,2]. World Health Organization (WHO) recommends a drinking water standard of 0.01 mg/L for cadmium[3]. Hence, it is essential to remove cadmium contents from wastewater and water before transport and cycling into the natural environment.

Several methods have been developed for removal of heavy metal ions from wastewater discharges. These methods are chemical precipitation, coagulation/ flocculation, ion exchange, solvent extraction, adsorption, and membrane processes. Among the methods, adsorption is the most effective and economic one for heavy metal ions containing wastewater treatment. Locally and naturally available inexpensive materials and industrial / municipal wastes are used as adsorbents and these materials can be efficiently used for the removal of heavy metal ions from aqueous solutions. When the solid wastes and tailings could be used as low cost adsorbents, their volumes could be decreased and these low cost adsorbents could remove the contamination of wastewaters at a lower cost. Thus, the use of natural minerals and tailings as a low cost alternative adsorbent has attracted notably attention. Magnesite[4-6], calcite[7-9], hydroxyapatite[8], dolomite[10], sepiolite[11], kaolinite[12,13], montmorillonite[12], bentonite[14], palygorskite[15], zeolite[16,17], vermiculate[18,19], tourmaline[20], chabazite[21], clay[22], pyrite[23], serpentine[24], red mud waste[25], low-rank coals[26], marble waste[27], colemanite ore waste[28], pyrophyllite mine waste[29], blast furnace slug[30], sewage sludge ash[31] and activated carbon prepared from waste material[32] have been tested for use as potential adsorbents for the removal of heavy metal ions from water and wastewater systems. However, there is no study on the removal of Cd(II) using magnesite tailing in literature.

The adsorbent used in this study is magnesite tailing obtained from the magnesite plant in Turkey. It was used as an adsorbent for the adsorption of Cd(II) due to its abundance and low cost. The objective of present study was to investigate the removal of Cd(II) from aqueous solutions by magnesite tailing. The effects of initial *p*H, adsorbent dosage, contact time and temperature on the removal of Cd(II) were investigated. Adsorption kinetics and adsorption isotherms were tested to evaluate the experimental data. Thermodynamic studies were also directed to estimate the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) values.

Experimental Section

Materials

The magnesite tailing was supplied from the KÜMAŞ Plant in Turkey. It was crushed, ground and sieved to pass 75 µm using ASTM standard sieves, and dried at 100°C for 5 h. The X-ray diffractogram of magnesite tailing showed the existence of magnesite ($MgCO_3$), quartz (SiO_2) and dolomite ($CaMg(CO_3)_2$) (Philips X'pert Pro diffractometer). Its chemical composition was determined using X-ray fluorescence analyzer (XRF ARL 8610). The specific surface area and an average pore diameter of the magnesite tailing were evaluated with a surface area analyzer (Quantachrome, Autosorb-1 C). The chemical composition and physical properties of magnesite tailing are given in Table 1. Scanning electron microscope (SEM) measurements of adsorbent before and after adsorption were carried out using a SEM-JEOL JSM 5600. Fourier transform infrared spectroscopy (FTIR) studies were carried out to identify the functional groups on the surface of adsorbent before and after adsorption over the range of 400-4000 cm^{-1} using KBr pellets (Perkin-Elmer spectrum 100 Model infrared spectrophotometer).

The chemicals used in this study were analytical and reagent grade Merck products. The cadmium sulfate octahydrate ($3CdSO_4.8H_2O$) (99% Merck) was used as the source of cadmium metal. Stock solution of 500 mg/L Cd(II) was prepared by dissolving 0.3457 g of $3CdSO_4.8H_2O$ in 1000 mL of deionized water. Other solutions for adsorption experiments were prepared by variable dilutions from this stock solution. The 0.1 M HCl or 0.1 M NaOH solutions were used to adjust the *p*H values of the solutions. The *p*H values of the solutions were measured by a *p*H meter (Hanna HI 8314).

Table 1 — Chemical composition and physical properties of magnesite

Component (%,w/w)			
MgO	37.80	BET surface area	23.12 m^2/g
SiO_2	11.17	Average pore diameter	9.26 nm
CaO	6.25		
Fe_2O_3	0.77		
Al_2O_3	0.13		
MnO	0.05		
K_2O	0.01		
P_2O_5	0.01		
Na_2O	▯ 0.01		
TiO_2	▯ 0.01		
L.O.I	43.70		

Methods

Adsorption studies were performed in batch-mode experiments. Magnesite tailing samples were added into 100 mL capped volumetric flasks containing 50 mL of the cadmium sulfate solution. The experiments were carried out on a temperature-controlled water bath with shaker at 150 rpm. The *p*H of Cd (II) solution was varied between 2 and 8 by addition of 0.1 M HCl or 0.1 M NaOH solutions. The *p*H values of Cd (II) solutions were below the precipitation levels. The effect of adsorbent dosage was evaluated by varying the adsorbent dosages from 0.01 to 0.5 g / 50 mL. The adsorption kinetics was determined at different time intervals and temperatures of 25, 35 and 45°C. Adsorption isotherms were studied by varying the initial solution concentration from 10 to 50 mg/L at temperatures of 25, 35 and 45°C.

After adsorption, the adsorbent was removed by centrifugation. The supernatant was analyzed for Cd(II) ion concentration using an atomic absorption spectrometer. The amount of Cd(II) adsorbed per gram of adsorbent (q_e (mg/g)) and the removal of Cd(II) were calculated using the following equations, respectively:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad \text{... (1)}$$

$$\text{Cd (II) removal (\%)} = \frac{(C_0 - C_e)}{C_0} \text{ x } 100 \qquad \text{... (2)}$$

where C_0 is the initial concentration of Cd(II) (mg/L), C_e is the concentration of Cd(II) at equilibrium (mg/L), V is the volume of solution (L) and M is the mass of magnesite tailing (g).

Results and Discussion

Initial *p*H effect

The *p*H of solution is one of the most important parameters in adsorption process. It influences the solution chemistry and the functional groups in the adsorbent. The adsorption capacity of magnesite tailing increased from 0.50 30.26 mg/g when *p*H increased from 2 to 8. The effect of *p*H can be clarified in terms of surface charge of the adsorbent and species of cadmium existing in the solution. At *p*H values lower than 8, cadmium is present in the divalent ionic form[18,19]. At lower *p*H values, the increased number of protons on the sites of magnesite tailing surface inhibited the approach of Cd(II) due to the repulsive forces. At higher *p*H values, the positive surface charge of the adsorbent decreased and the number of negatively charged sites increased. Thus, the adsorbent surface attracted more positively charged adsorbate particle, Cd(II). Similar results were observed using natural mineral and mineral waste for the adsorption of Cd(II)[10,12,13,15-18,20,21,27,29]. So, the removal of Cd (II) was carried out at an initial *p*H value of 6 which is close the natural *p*H value of initial solution.

Adsorbent dosage effect

Adsorbent dosage is a significant factor which determines the maximum removal yield for given initial solution concentration. Therefore, the removal of Cd(II) was studied by varying adsorbent dosage from 0.01 g to 0.5 g at a 50 mL solution of 10 mg/L Cd(II) (Fig. 1). There was a substantial increase in the removal of Cd(II) when the adsorbent dosage increased from 0.01 to 0.3 g. On the other hand, the increase was slow up to 0.5 g. This may be due to the decrease in the Cd(II) concentration of solution. Thus, the optimum adsorbent dosage can be taken as 0.3 g. In this adsorbent dosage, yield of 99% Cd(II) removal was achieved by magnesite tailing.

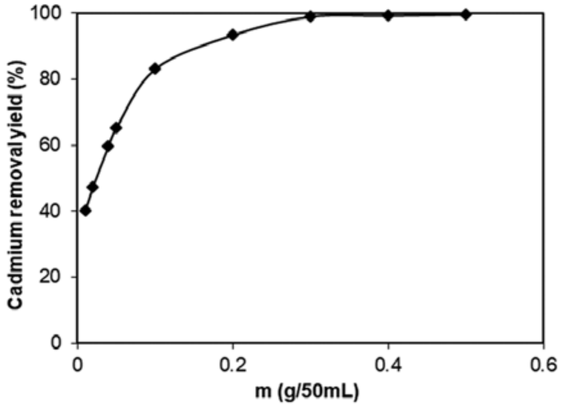

Fig. 1 — Effect of adsorbent dosage on the removal of Cd(II) on magnesite tailing (*p*H = 6.0, contact time = 24 h, temperature = 25°C, initial concentration = 10 mg/L).

Adsorption kinetics

Contact time is an important parameter for efficient use of adsorbents in technology. The effect of contact time on the adsorption of Cd(II) was investigated at three different temperatures for an initial concentration of 10 mg/L. The results are presented in Fig. 2. The adsorption rate was initially fast, and 70% adsorption was completed within 5 min for all temperatures. The adsorption increased with time and reached equilibrium in about 12, 8 and 6 h for 25, 35 and 45°C, respectively.

Three kinetic models, pseudo first order, pseudo second order kinetic equations and intraparticle diffusion model were used to describe the adsorption kinetics of Cd(II) onto magnesite tailing. The linear forms of kinetic models can be given as follows[33-35].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{... (3)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{q_e} \quad \text{... (4)}$$

$$q_t = k_p\, t^{1/2} + C \quad \text{... (5)}$$

where q_e and q_t are the respective amounts of Cd(II) adsorbed (mg/g) at equilibrium and at time t (min), k_1 (1/min) is the rate constant of the pseudo first order adsorption, k_2 (g/mg min) is the rate constant of pseudo second order adsorption, k_p (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant, and C is constant related to the boundary layer thickness.

By plotting *log* (q_e-q_t) versus t, t/q_t versus t and q_t versus $t^{1/2}$, the first order rate constant k_1, the second order rate constant k_2 and the intraparticle diffusion rate constant k_p, the equilibrium capacity q_e and the

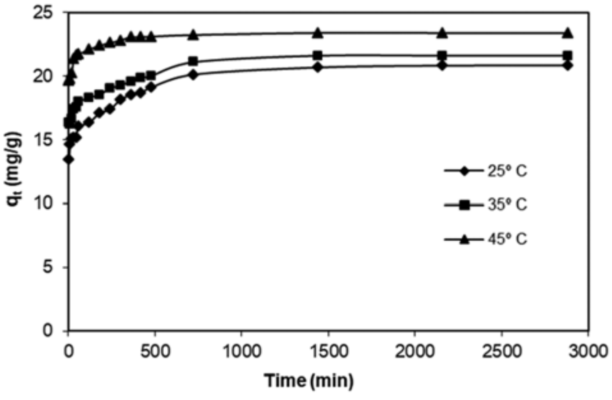

Fig. 2 — Effect of contact time on the adsorption of Cd(II) on magnesite tailing at different temperatures (*p*H = 6.0, adsorbent dosage = 0.01 g/50 mL, initial concentration = 10 mg/L).

boundary layer thickness *C* were obtained from the slope and intercept, respectively (Fig. 3 for t/q_t vs. t). The kinetic parameters and linear correlation coefficients were presented in Table 2. For the pseudo first order kinetic model, the correlation coefficients were lower, and the calculated q_e values were also different from the experimental values. Thus, the adsorption of Cd(II) ions onto magnesite tailing does not follow the pseudo first order kinetic model. For intraparticle diffusion model, the plots of q_t versus $t^{1/2}$ did not pass through the origin. This shows some degree of boundary layer control and that the intraparticle diffusion was not only the rate-limiting step. The correlation coefficients of pseudo second order kinetic model were higher and the calculated q_e values fitted very well with the experimental data.

Adsorption isotherms

The equilibrium adsorption study is an important step for the design of adsorption process. Adsorption isotherm can be indicated graphically by plotting the amount of adsorbed Cd(II) per the unit amount of magnesite tailing against equilibrium concentration of Cd(II) (Fig. 4). The adsorption capacity of magnesite tailing increased with initial concentration. When the initial solution concentration increased from 10 to 50 mg/L, the adsorption capacities increased from 16.15 to 31.88 mg / g at 45°C.

The Langmuir, Freundlich and D-R isotherm models were used to describe the equilibrium adsorption isotherms at different temperatures (25-45°C). The Langmuir isotherm is the most common isotherm model. The saturated monolayer curve can be represented by the following expression[36]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \text{... (6)}$$

The linear form of this equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \text{... (7)}$$

where q_e is the adsorbed Cd(II) ion amount per amount of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of Cd(II) ion in the solution (mg/L) and the Langmuir constants, q_m (mg / g) and K_L (L/mg), are the monolayer adsorption capacity and the adsorption equilibrium constant, respectively. Fig. 5(a) indicates the non-linear Langmuir isotherms obtained for the adsorption of Cd(II) onto magnesite tailing at different temperatures. The linear correlation

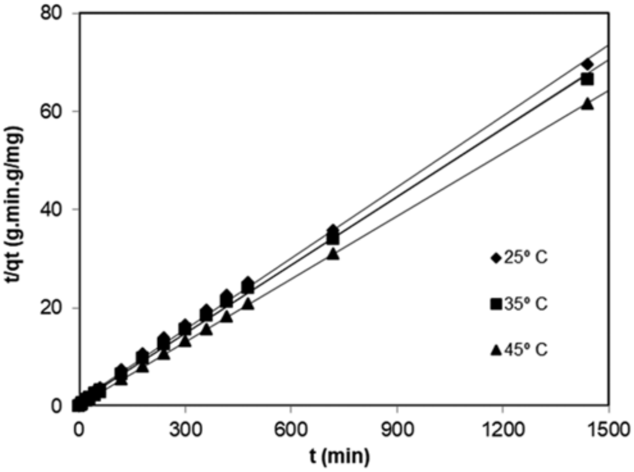

Fig. 3 — Pseudo second order kinetics for the adsorption of Cd(II) on magnesite tailing.

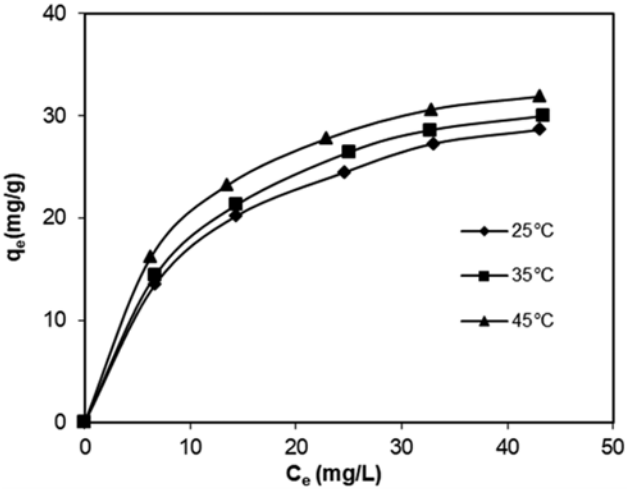

Fig. 4 — Isotherms for the adsorption of Cd(II) onto magnesite tailing.

Table 2 — Kinetic parameters for the adsorption of Cd (II) on magnesite tailing at different temperatures

		Pseudo first order			Pseudo second order			Intraparticle diffusion		
T (°C)	q_{exp} (mg/g)	q_e (mg /g)	k_1 (1 / min)	R^2	q_e (mg / g)	k_2 (g / mg min)	R^2	k_p (mg /g min$^{1/2}$)	C (mg / g)	R^2
25	20.69	6.44	3.22×10^{-3}	0.98	20.66	2.18×10^{-3}	0.99	0.208	14.09	0.94
35	21.61	5.06	2.76×10^{-3}	0.96	21.55	2.71×10^{-3}	0.99	0.160	16.36	0.95
45	23.41	2.57	4.38×10^{-3}	0.93	23.42	9.28×10^{-3}	0.99	0.109	20.48	0.73

coefficients and isotherm constants are given in Table 3. The Langmuir isotherm model effectively described the adsorption data with R^2 values higher than 0.99. Thus, Cd(II) was adsorbed in a monolayer by magnesite tailing.

The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant separation factor (R_L)[37]. The R_L value is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad \text{... (8)}$$

where C_0 is the initial Cd(II) concentration (mg / L). The values of R_L calculated from Eq. (8) are in Table 3. When the initial concentration was in the range of 10-50 mg/L, the R_L values ranged from 0.15 to 0.54. The R_L values between 0 and 1 show that the isotherm is favorable[37,38]. So, these results indicate that magnesite tailing is a suitable adsorbent for adsorption of Cd(II) from aqueous solutions. The maximum adsorption capacities were found as 36.23 mg/g at 25°C, 37.74 mg/g at 35°C and 38.46 mg/g at 45°C, respectively.

The Freundlich isotherm can be applied for adsorption on heterogeneous surfaces and multilayer adsorption. Freundlich isotherm may be written as [39]:

$$q_e = K_f Ce^{1/n} \qquad \text{... (9)}$$

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \qquad \text{... (10)}$$

where K_f (L/g) and n are Freundlich adsorption isotherm constants, indicating the adsorption capacity and the adsorption intensity, respectively. Fig. 5(b) shows the non-linear Freundlich isotherms obtained for the adsorption of Cd(II) onto magnesite tailing at different temperatures. The 1/n values between 0 and 1 indicated that the adsorption of Cd(II) was favorable at the studied conditions. The R^2 values were found to be lower than 0.99 (Table 3).

Langmuir and Freundlich isotherms are insufficient to determine the physical and chemical characteristics of adsorption. D-R isotherm is more general than Langmuir isotherm. The D-R isotherm is expressed as[40]:

$$\ln q_e = \ln q_d - \beta \varepsilon^2 \qquad \text{... (11)}$$

where q_d is the D-R adsorption capacity (mg / g), β is the constant related with adsorption energy (mol^2 / kJ^2), and ε (= $RT \ln(1+(1/C_e))$) is the Polanyi potential.

By plotting In qe versus ε^2, it is possible to determine the value of q_d from the intercept and the value of β from the slope. The mean energy of adsorption (E) is also calculated by using the following equation:

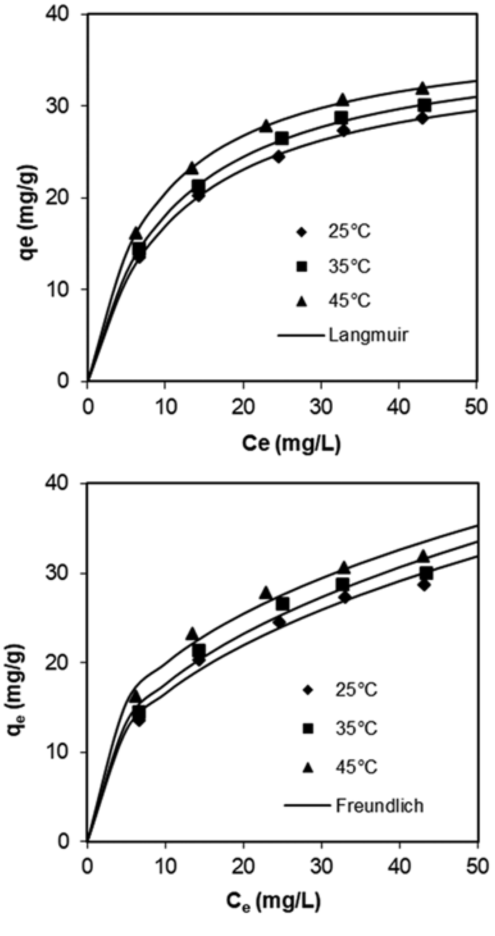

Fig. 5 — Langmuir (a) and Freundlich (b) isotherm plots for the adsorption Cd(II) on magnesite tailing.

Table 3 — Isotherm constants for the adsorption of Cd (II) on magnesite tailing at different temperatures

	Langmuir				Freundlich			D-R			
Temperature (°C)	q_m (mg / g)	K_L (L/mg)	R^2	R_L	K_f (L/g)	n	R^2	q_d (mg / g)	β (mol^2 / kJ^2	E (kJ / mol)	R^2
25	36.23	0.09	0.999	0.19-0.54	6.47	2.45	0.981	26.89	6.10^{-6}	0.29	0.933
35	37.74	0.09	0.999	0.18-0.53	6.98	2.49	0.977	28.40	6.10^{-6}	0.29	0.936
45	38.46	0.12	0.999	0.15-0.47	8.74	2.80	0.975	30.14	4.10^{-6}	0.35	0.933

$$E = (2\beta)^{-0,5} \quad \ldots(12)$$

The values of E were calculated as 0.29 kJ/mol, 0.29 kJ/mol and 0.35 kJ/mol at 25, 35 and 45°C, respectively (Table 3). These low values of *E* showed that the adsorption has a physical nature.

The comparison of maximum adsorption capacity for adsorption of Cd(II) onto various adsorbents is given in Table 4. As it can be seen, the magnesite tailing has quite high adsorption capacity for Cd(II). This indicates that the magnesite tailing could be used as a good adsorbent. Moreover, it can be obtained cheaply in large amounts since it is a cheap and locally available adsorbent.

Temperature effect and thermodynamic parameters

As seen in Fig. 2, the increasing in the temperature decreased the time required to reach the adsorption equilibrium. This may be due to the higher rate of diffusion of Cd(II) onto the magnesite particle surface at higher temperatures. The adsorption capacity of magnesite tailing increased slightly with increasing temperature from 25 to 45°C. This result indicated that the adsorption process was endothermic

Table 4 — Comparison of the Langmuir adsorption capacity (q_m) for the adsorption of Cd (II) onto different adsorbents

Type of adsorbent %, w/w %, w/w	q_m (mg/g)	Temperature (°C)	*p*H	Refs
Calcite	16.3	22	6.0	[7]
Dolomite	1.62	20	5.5	[10]
Kaolinitete	6.80	30	5.5	[12]
Montmorillonite	30.7	30	5.5	[12]
Bentonite	7.64	30	3.0	[14]
Palygorskite	4.54	22	6.0	[15]
zeolite	5.16	25	< 3	[16]
Jordanian natural zeolite	19.01	25	6.4	[17]
Vermiculite	63.29	25	6.2	[18]
Turmaline	33.11	25	4.0	[20]
	40.16	35	4.0	
Chabazite	50	25	5.5	[21]
Indigo clay	0.50	30	6.5	[22]
Pyrite	3.43	45	6.0	[23]
Serpentine	8.91	25	6.0	[24]
Red mud	13.04	30	4.0	[25]
Low rank coal	19.90	22		[26]
Marble waste	30.92	25	7.0	[27]
Colemanite ore waste	29.70	20	5.0	[28]
Pyrophyllite mine waste	4.58			[29]
Blast furnace slug	13.30	25	7.0	[30]
Sewage sludge ash	7.10	20	6.0	[31]
Magnesite tailing	36.23	25	6.0	Present study
	37.74	35	6.0	Present study
	38.46	45	6.0	Present study

Thermodynamic parameters are important to determine the feasibility, spontaneity and heat change of the adsorption process. The changes in free energy (*ΔG°*), enthalpy (*ΔH°*) and entropy (*ΔS°*) can be calculated from the variations of the Langmuir equilibrium constants (K_L) with temperature using the following equations:

$$\Delta G^o = - R\,T \ln K_L \quad \ldots (13)$$

$$\text{In}\, K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \ldots (14)$$

where R is the gas constant (8.314 J / mol K) and T is the solution temperature (K). The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the plot of In K_L versus 1/T. The thermodynamic parameters are presented in Table 5. The negative values of *ΔG°* (-33.19, -34.21, -35.32 kJ/mol) imply the process to be feasible and spontaneous. Also, the increase in free energy change with temperature increasing from 25 to 45°C shows an increase in feasibility of adsorption at higher temperatures. The positive value of *ΔH°* (10.40 kJ / mol) suggests that the adsorption of Cd(II) is endothermic in nature. The enthalpy change is less than 40 kJ/mol. This indicates that physical adsorption dominates the adsorption of Cd (II) onto magnesite tailing[41]. The positive value of *ΔS°* (0.11 kJ /mol K) indicates the affinity of magnesite tailing toward Cd(II) and suggests an increase in the degree of freedom at the solid / solution interface. Similar results were presented for some other natural and waste adsorbents[6,14,16,20,21,23,27-31].

Morphological studies

The surface morphology of magnesite tailing before and after Cd(II) adsorption was analyzed by SEM. SEM images of magnesite tailing are shown in Fig. 6. The surface of magnesite tailing appeared irregular and porous (Fig. 6 (a)). Its specific surface

Table 5 — Thermodynamic parameters for the adsorption of Cd (II) on magnesite tailing

Temperature (°C)	*ΔG°* (kJ/mol)	*ΔH°* (kJ/mol)	*ΔS°* (kJ/mol K)
25	-33.19	10.40	0.11
35	-34.21		
45	-35.32		

area is 23.12 m^2 / g and its average pore diameter is 9.26 nm (Table 1). Magnesite tailing has a high surface area compared to similar minerals[7-10]. The surface of magnesite tailing changed after Cd(II) adsorption, and the porous surface was filled with Cd (II) (Fig. 6 (b)). This situation showed that Cd(II) was adsorbed to the functional groups on the adsorbent surface.

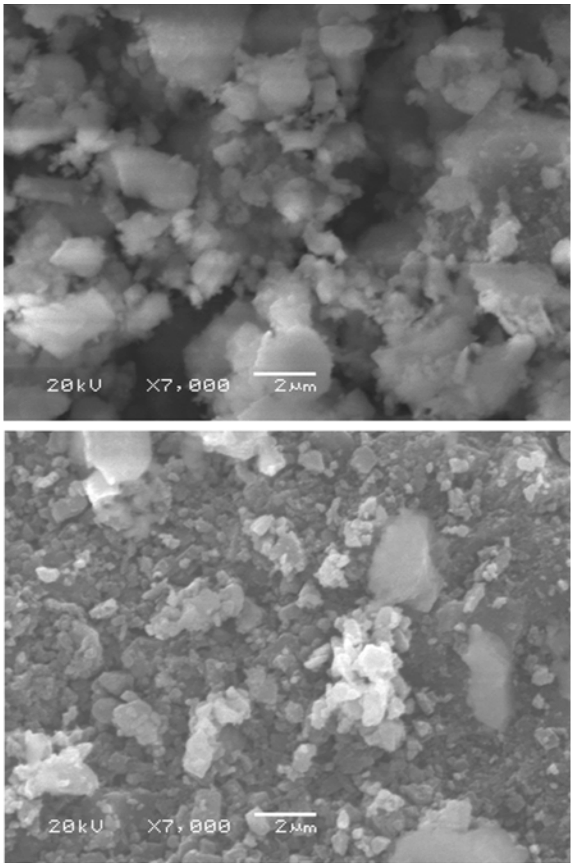

Fig. 6 — SEM micrographs of magnesite tailing before (a) and after (b) adsorption of Cd(II).

Table 6 — Functional groups in magnesite tailing before and after adsorption of Cd (II)

Functional group	Wavenumber (cm^{-1})	
	Before adsorption	After adsorption
-OH stretching	3358	3351
-OH stretching	2925	2925
CO_3^{2-} symmetric stretching + in plane bending	2539	2537
CO_3^{2-} symmetric stretching + asymmetric stretching	1822	1824
CO_3^{2-} asymmetric stretching	1471	1471
CO_3^{2-} symmetric stretching	1092	1094
CO_3^{2-} out of plane bending	889-856	889-856
CO_3^{2-} in plane bending	749	749
Si-O or Fe-O bending vibration	442	443

he FTIR spectra of the adsorbent before and after the adsorption of Cd(II) are given in Fig. 7 and the band positions of the possible functional groups were presented in Table 6. The absorption bands of –OH groups were observed at 3358-2925 cm^{-1} and at 3351-2925 cm^{-1} before and after Cd (II) adsorption, respectively. After adsorption, the intensities of these peaks slightly increased. The absorption bands at 2539-1822-1092 cm^{-1} showed the characteristic stretching of $–CO_3$ group before adsorption (Fig 7 (a)). After adsorption, these bands slightly shifted to 2537-1824-1094 cm^{-1} and an intensity increase was observed. Furthermore, a slight splitting was also observed at 1094 cm^{-1}. This split shows a decrease in the symmetry of the carbonate group due the adsorption of Cd (II) by magnesite tailing. There is no shifting in the strong broad absorption band at 1471 which is indicative of the existence of $–CO_3$ strength (Fig 7 (b)). Before adsorption, the sharp absorption bands at 889-856-749 showed the characteristic bending of $–CO_3$ group. A shifting was not observed but the intensities of these peaks slightly increased after adsorption. The absorption bands appearing at 442 cm^{-1} and at 443 cm^{-1} before and after adsorption, respectively, indicated the existence of –Si-O or -Fe-O bending vibrations[42]. The differences observed in the FTIR spectrum after

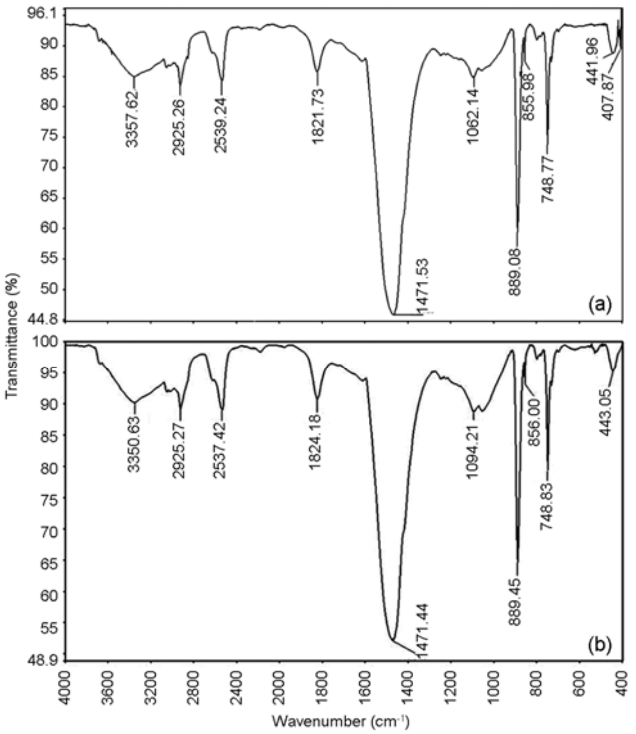

Fig. 7 – FTIR spectra of magnesite tailing before (a) and after (b) adsorption of Cd(II).

adsorption may be attributed to interaction between the functional groups and Cd(II) due to adsorption. These results suggest that the presence of these important groups in the magnesite tailing plays an essential role in binding the Cd(II) ions.

Batch adsorption design

Adsorption isotherms can be used to estimate the design of batch stage adsorption systems. The schematic diagram is shown in Fig. 8. The Cd(II) removed from the aqueous solution equals that adsorbed by magnesite tailing. This mass balance can be given as[43]:

$$V\,(C_0 - C_1) = M\,(q_1 - q_0) = M\,q_1 \qquad \text{... (15)}$$

where C_0 is the initial concentration of Cd(II) (mg / L), C_1 is the concentration of Cd(II) after adsorption process (mg/L), V is the volume of solvent (L) and M is the mass of magnesite tailing (g), q_0 ($q_0 = 0$) is the initial concentration of Cd(II) ion on the adsorbent (mg/g) and q_1 is the concentration of Cd(II) ion on the adsorbent after adsorption process (mg/g).

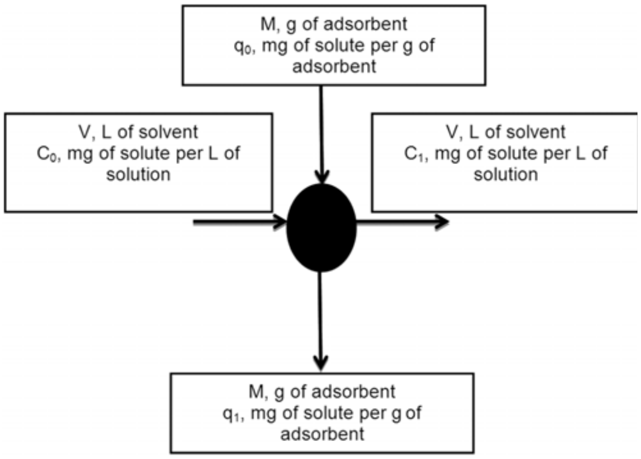

Fig. 8 — A single-stage batch adsorber.

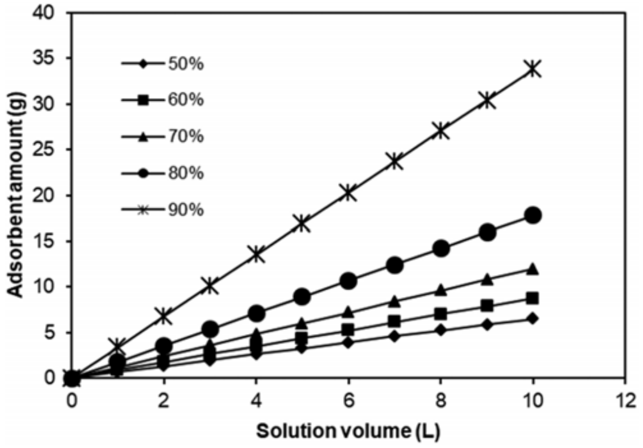

Fig. 9 — Adsorbent amount versus solution volume for different removal yields.

The Langmuir isotherm model fit well the equilibrium data. Thus, the above equation can be arranged for equilibrium conditions, and Langmuir equation can be substituted for q_e:

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{\dfrac{q_m K_L C_e}{1 + K_L C_e}} \qquad \text{... (16)}$$

The amounts of magnesite tailing required to remove Cd(II) ion from the initial solution concentration of 25 mg / L for 50, 60, 70, 80 and 90% removal yield at various solution volumes were calculated from Eq.16. The plots of adsorbent amount versus solution volume are showed in Fig. 9. The amounts of magnesite tailing required for the 90% removal yield from an initial solution concentration of 25 mg / L are 6.76 g, 13.52 g, 20.29 g, 27.05 g and 33.81 g for the solution volume of 2 L, 4 L, 6 L, 8 L and 10 L, respectively.

Conclusion

The results of batch adsorption studies show that the removal of Cd (II) from aqueous solution is influenced by initial *p*H, adsorbent dosage, contact time and temperature. The kinetics data were illustrated very well by a pseudo second order kinetic model. The Langmuir isotherm model show a better fit than the Freundlich and D-R isotherm models. The maximum Langmuir adsorption capacities are found as 36.23 mg/g at 25°C, 37.74 mg/g at 35°C and 38.46 mg/g at 45°C. The thermodynamic studies show the feasible, spontaneous and endothermic nature of the process. The SEM and FTIR analyses verified the Cd (II) – magnesite tailing interactions. A single stage batch adsorber is designed for different adsorbent dosage using Langmuir isotherm. About 99% of Cd (II) from aqueous solution is removed at a *p*H value of 6, an adsorbent dosage of 0.3 g / 50 mL solution, a contact time of 24 h, an initial solution concentration of 10 mg/L and a temperature of 25°C. These results indicate that the magnesite tailing could be used as a very effective and low-cost adsorbent for the removal of Cd (II) from wastewater.

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