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Cooperative binding of Cadmium(II) on PVA-Bentonite complex in water

Khaleel A. Abu-Sbeih[a]*, Mahmoud Salman[a], Idrees Al-Momani[b] and Bassam El-Eswed[c]

[a]Al-Hussein Bin Talal University, Faculty of Sciences, Chemistry Department, Jordan
[b]Yarmouk University, Faculty of Sciences, Chemistry Department, Jordan
[c]Zarqa College, Al-Balqa Applied University, Zarqa, Jordan

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ABSTRACT

The adsorption of Cd(II) on polyvinyl alcohol-bentonite complex was studied using a simplified model derived from Langmuir-Freundlich model. The bentonite used was obtained from Al-Azraq area in Jordan. The adsorptivity of Cd(II) was not affected by the pH change. No temperature dependence of the adsorption of the heavy metal pollutant onto the PVA/bentonite complex was observed implying that ΔH_{ads} is approximately zero and the adsorption process is entropy driven.

Key words: Cadmium, Langmuir-Freundlich, poly vinyl alcohol, bentonite, competitive adsorption
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INTRODUCTION

Among the many adsorbents used for the removal of heavy metals from water, some use a single adsorbent such as tourmaline [1], zeolites [2], clays [3], sepiolite [4], and polyvinyl alcohol [5], and others use a two-component system.

Sari and Tuzen used kaolinite and manganese oxide (MnO_2)-modified kaolinite for the removal of Cd(II) ions from water [6]. New hybrid clay adsorbent based on kaolinite clay and *Carica papaya* seeds were prepared by Unuabonah et al. [7]. With an initial metal concentration of 1 mg/L, the hybrid clay adsorbent reduces the Cd(II) concentration in aqueous solution to ≤4 and ≤20 μg/L, respectively, from the first minute to over 300 min using a fixed bed containing 2 g of adsorbent. The adsorption of heavy metals such as Cd(II) on humic acid- polyaniline was investigated by Terbouche et al. [8].

A bead adsorbents based on poly (vinyl alcohol)/ chitosan were used by Li et al. for the adsorption of heavy metal ions from aqueous solution [9]. PVA/ chitosan beads adsorbed the heavy metal ion Cd(II) following the Freundlich isotherm. The adsorption kinetics of Cd(II) was found to follow the pseudo-second-order kinetic model. The adsorption onto PVA/CS beads was feasible and endothermic in nature [9]. Sulfonated aniline-modified poly (vinyl alcohol)/ K-feldspar composite was prepared by Unuabonah et al. for Cd(II) adsorption. Metal adsorption rate was higher than that on neat feldspar. Freundlich and Langmuir models were found to fit metal-ion adsorption most accurately. Adsorption on neat feldspar was best fitted with a Langmuir model, indicating the formation of adsorbate monolayers. Both pure feldspar and SAPK showed better selectivity for Pb(II) than for Cd(II) [10]. A composite chitosan biosorbent was used for Cd(II) by Madala et al. [11].

Kinetics and isotherms for adsorption of PVA onto bentonite were investigated by Wang et al. They concluded that PVA molecules were adsorbed on the surfaces of bentonite particles with a certain degree of intercalation [12].

The abundance of bentonite in many parts of the world and its low cost make it attracttive for the removal of pollutants [13]. Bentonite has an enormous surface area when hydrated in water. It consists of numerous

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microscopic platelets, each with negative charge on the flat surfaces and positive charge on the edges. When hydrated, the water molecules cause these platelets to separate into a porous structure containing both negative and positive charge. Bentonite consists mainly of silica and alumina oxides. Many studies were conducted on natural bentonite to study its potential as an adsorbent for Cd [14-16].

In the present work, the adsorption of Cd(II) on PVA- bentonite complex was studied. The pH was fixed at 3.0, 3.5, 4.0, and 4.5. The effect of temperature (25-40 ℃) on the adsorption capacity of the heavy metal pollutant onto the HA/bentonite complex was investigated and interpreted as well. Adsorption characteristics are studied using a modified Langmuir-Freundlich model.

MATERIALS AND METHODS

All reagents used were of analytical grade. $CdCl_2$ and Cd standards were from BDH Chemicals Ltd, Poole, England. 70% HNO_3 and poly vinyl alcohol (PVA) were both from Merck, England. Samples of Jordanian bentonite were supplied by the natural Resources Authority from Al-Azraq area. The samples of bentonite rocks were grounded and particles larger than 200 mesh removed by sieving. Only those that passed the 200 mesh were used for the present investigation.

All metal ions were determined in clear supernatants by an Atomic Absorption Spectrophotometer model Varian spectra AA, Australia. The FT-IR spectra were recorded using ThermoNicolet 670 Nexus FTIR spectrophotometer.

Preparation of PVA- bentonite complex
PVA- bentonite complex was prepared following a published procedure [12]. PVA- bentonite complex was prepared by mixing 2 g of PVA with 2 g of Al-Azraq bentonite in water (200 mL) at room temperature. The mixture was stirred at room temperature for 24 hrs then filtered and the complex dried in air. The complex was used without further purification.

### Adsorption of cadmium(II) on PVA- bentonite complex
Stock solutions with Cd(II) concentration of 1000 ppm were prepared by dissolving $CdCl_2$ in deionized water that is 0.1 M in HNO_3 and used for the preparation of more diluted solutions.

An accurate mass of 0.0200 g of PVA- bentonite complex was shaken with 100.0 mL of 10-100 ppm solutions of Cd(II) for 24 hr at a pH of 3.5 and temperatures of 25.0, 30.0, 35.0, and 40.0 °C. Solutions were also prepared at a pH of 3.0, 4.0, and 4.5, and a temperature of 25 ℃. Aliquots of solution were then filtered and analyzed by AAS.
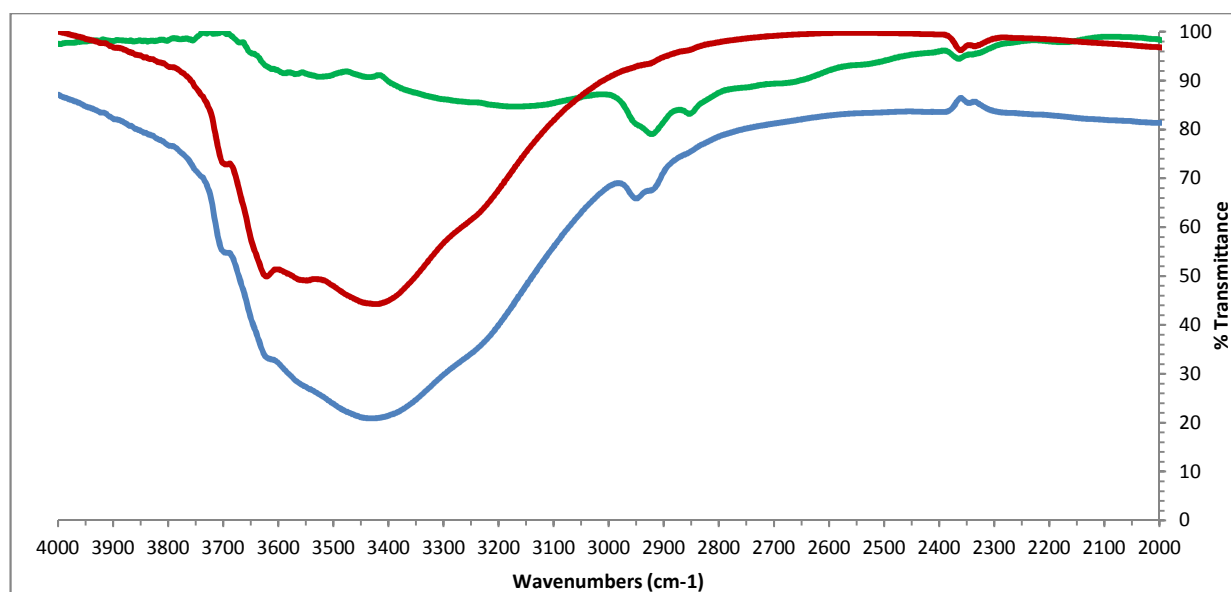
RESULTS AND DISCUSSION

Cadmium(II) adsorption on the PVA-Bentonite complex: IR study
PVA was adsorbed on bentonite obtained from Al-Azraq area in Jordan at room temperature in neutral aqueous solution following a published procedure. The complex was characterized by IR spectroscopy, Figure 1.
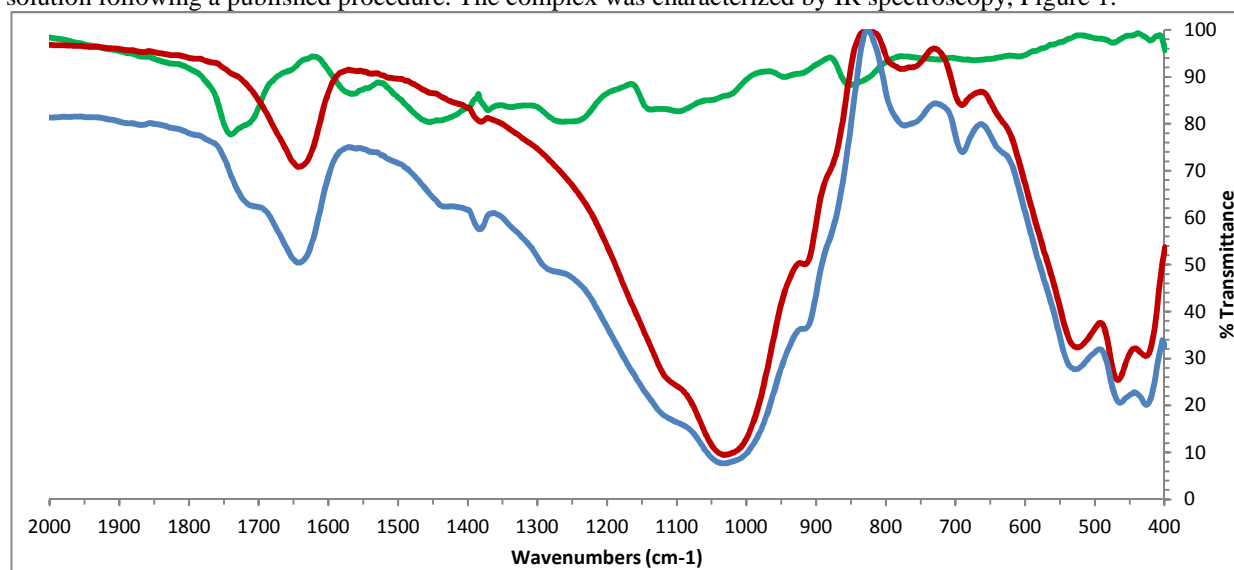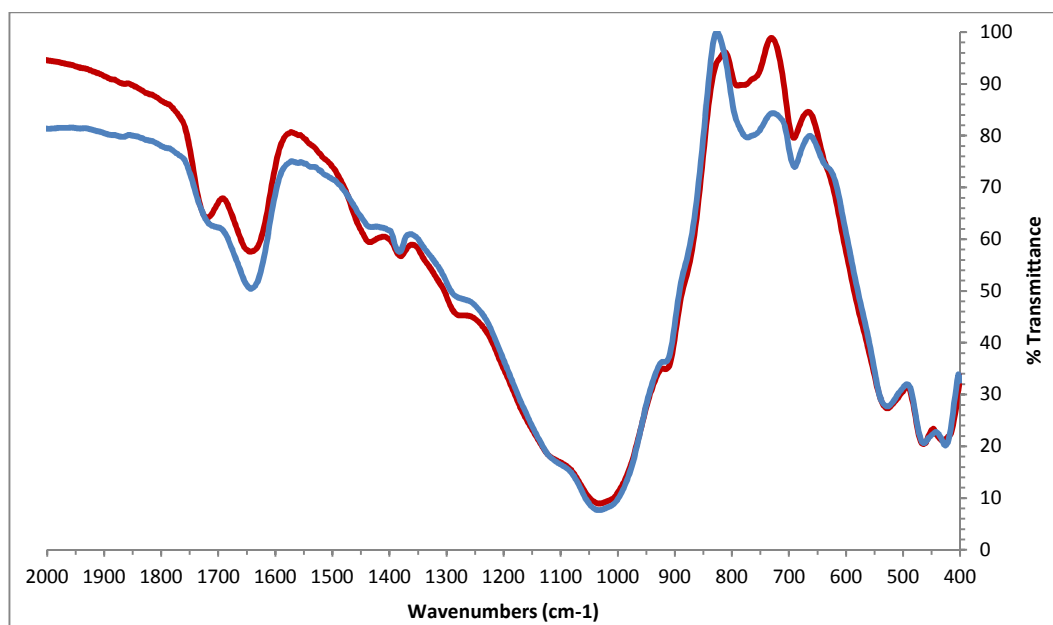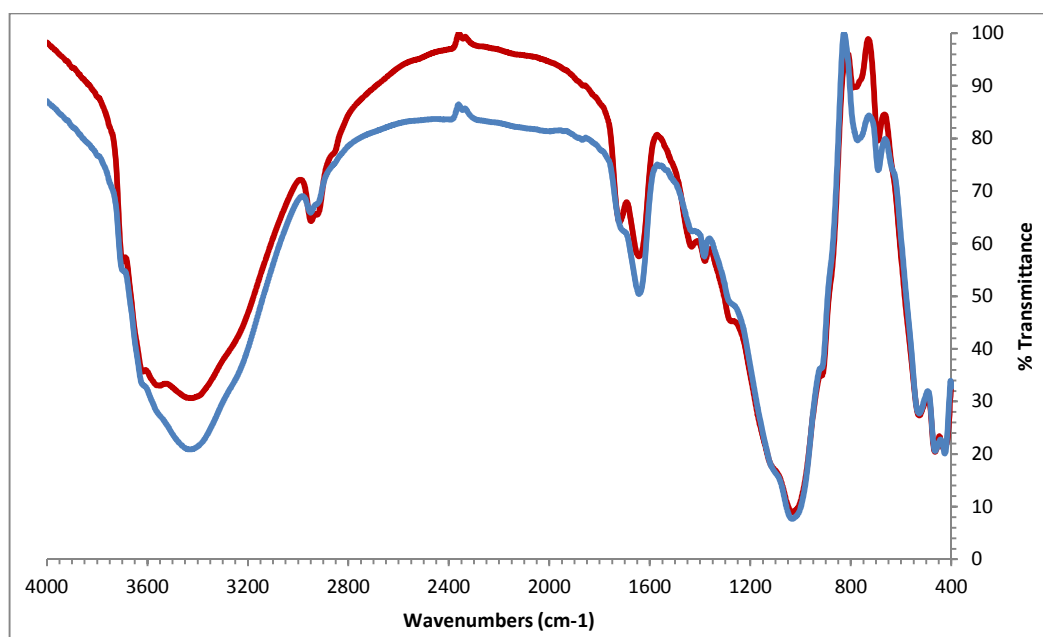

(a)

(b)

Figure 1. IR spectra of PVA (green), Bn (red), and PVA- bentonite complex (blue) in the 400-2000 cm^{-1} range (a), and the 2000-4000 cm^{-1} range (b)

As can be seen from Figure 1 (red lines), the peaks in the range 3700-3560 cm^{-1} in bentonite are assigned to the OH stretching vibration of water molecules within the bentonite interlayer, and the broad peak centered at 3427 cm^{-1} to the OH stretching vibration of bonded (adsorbed) water. The peak at around 1641 cm^{-1} corresponds to the OH deformation of water. The bands observed at around 1109 and 1022 cm^{-1} represent Si–O bond vibrations. Other bentonite peaks appear at 912, 847, 781, 758, 692, 534, 473, and 430 cm^{-1}.

PVA spectrum, Figure 1 (green lines), shows weak broad peaks in the range 3400-3700 attributable to OH vibrations of the hydroxyl groups of PVA. Peaks at 2945, 2924, and 2854 are assigned to CH vibrations. Other peaks appear at 1743, 1572, 1458, 1269, 1242, 1144, 1097, 1034, 948, 922, and 843 cm^{-1}.

(a)

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(b)

Figure 2. IR spectra of PVA-Bn complex (blue) and its Cd-PVA- bentonite complex (red) in the 400-2000 cm^{-1} range (a), and the 2000-4000 cm^{-1} range (b)

The spectrum of the PVA- bentonite complex, Figure 1 (blue lines), shows two additional peaks at 2943 and 2920 cm^{-1} compared to bentonite. These peaks indicate that there are PVA molecules adsorbed on the surface of bentonite. The PVA OH bending vibrations at 1713 and 1441 cm^{-1} also appear in the spectrum of the complex shifted from their positions in free PVA, thus implying their involvement in bentonite surface binding.

Cadmium(II) was adsorbed on the PVA- bentonite complex at a pH of 3.5 and 25ºC. The adsorption was studied with IR spectroscopy, Figure 2. A new peak appears at 3564 cm^{-1} suggesting metal binding to OH of the bentonite part of the complex. The 1714 and 1443 cm^{-1} OH bending vibrations are also more defined and stronger. These peaks, which originate from the PVA part of the complex, can be considered as evidence for the involvement of PVA functionalities in Cd binding.

Kinetics of adsorption of cadmium(II) on PVA- bentonite complex
Kinetics experiments, Figure 3, of the adsorption of Cd(II) on PVA- bentonite complex indicate that the equilibrium was obtained within 4-5 hrs of mixing time at 25 ºC and pH = 3.5. After that, Cd(II) concentration drops slowly.
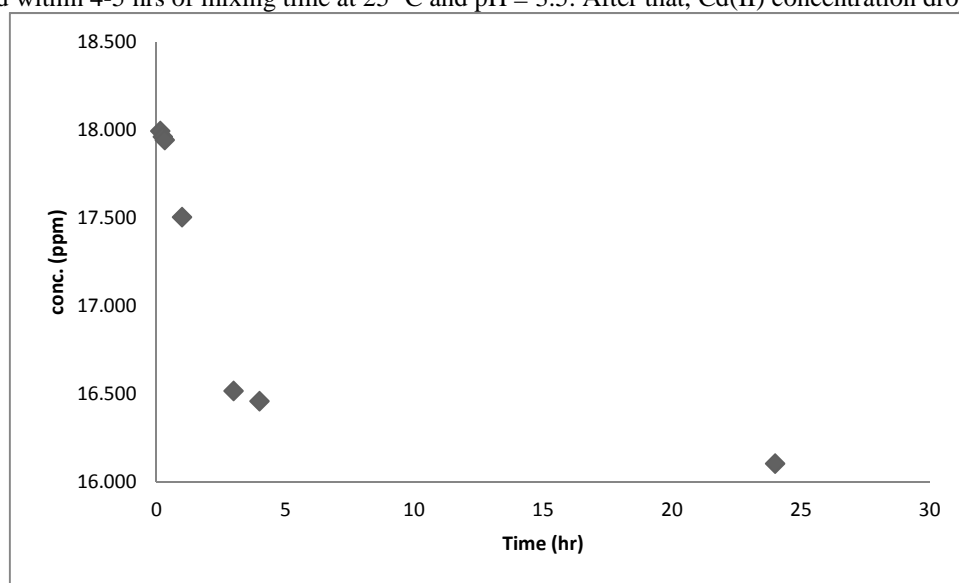

Figure 3. Time-dependence of Cd(II) binding on PVA- bentonite complex at 25 ºC and pH = 3.5

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Adsorption Isotherm

Cd(II) adsorption on previously prepared PVA- bentonite adsorbent was studied at different pH values and different temperatures in aqueous solutions. % adsorption data are provided in Table 1 and Table 2.

Table 1. Adsorption data of Cd(II) on PVA- bentonite adsorbent at different pH

Initial concentration (ppm)	% Adsorption at 25 ºC			
	3.0	3.5	4.0	4.5
40	0	0	0	0
50	6.8	7.3	2.4	4.5
60	0	8.4	0.6	4.3
70	5.9	18	13.6	9
80	14.5	16.2	13.8	15.3
90	16.9	20.8	22.7	19.2
100	23.4	24.1	25.7	24.6

Table 2. Adsorption data of Cd(II) on PVA- bentonite adsorbent at different temperatures

Initial concentration (ppm)	% Adsorption at pH = 3.5			
	25 ºC	30 ºC	35 ºC	40 ºC
40	0	0	0	0
50	7.3	1.07	1.9	3.8
60	8.4	0	11.5	4.0
70	18.0	11.5	16.2	13.1
80	16.2	17.8	19.9	18.0
90	20.8	19.5	23.0	20.2
100	24.1	25.8	29.2	25.6

An interesting S-shape of the adsorption isotherm was observed, Figure 4. The S-shape isotherms were reviewed by Giles et al. [17]. According to Giles et al., in many cases, the S-curve indicates "cooperative adsorption," with solute molecules tending to be adsorbed packed in rows or clusters. In the case of planar aromatic molecules (like p-nitrophenol adsorption on both silica and graphite), this implies association with the aromatic nuclei face-to-face and perpendicular to the surface.

The adsorption data in the present article was fitted using Langmuir-Freundlich (L-F) model. The L-F isotherm, also known as Sip's equation, is a versatile flexible isotherm expression that can simulate both Langmuir and Freundlich behaviors. A general form of Langmuir-Freundlich isotherm equation can be written as [18]:

$$Q = Q\max\frac{(KC)^n}{1+(KC)^n}$$

Where,

Q: is the amount of Cd(II) adsorbed on the PVA- bentonite complex at equilibrium (mg Cd/ g PVA- bentonite complex).

Qmax: is the adsorption capacity of the system (mg of Cd(II)/g PVA-bentonite complex), which can also be expressed as a measure of total number of binding sites available per gram of sorbent.

C: is the aqueous phase concentration at equilibrium (mg Cd(II)/ L).

K: is the affinity constant for adsorption (L/mg).

n: is the index of heterogeneity of surface, which is allowed to vary from 0 and 1. The value of n for a homogeneous material is 1, and it is less than one for heterogeneous materials. Mathematically, when n is set to 1 the L-F isotherm reduces to Langmuir expression.

The L-F model was the basis for derivation of many comprehensive models like Non Ideal Competitive adsorption (NICA) model which was widely used for modeling adsorption of heavy metals on humic acid [19]. However, the NICA model considers "n" as the stoichiometry of the binding reaction; for n = 1, the binding is monodentate, for n = 0.5, the binding is bidentate, for n > 2, the binding corresponds to multiple occupancy. In Cd(II) adorption on PVA- bentonite, "n" was found to be much higher than 2, Tables 3 and 4.
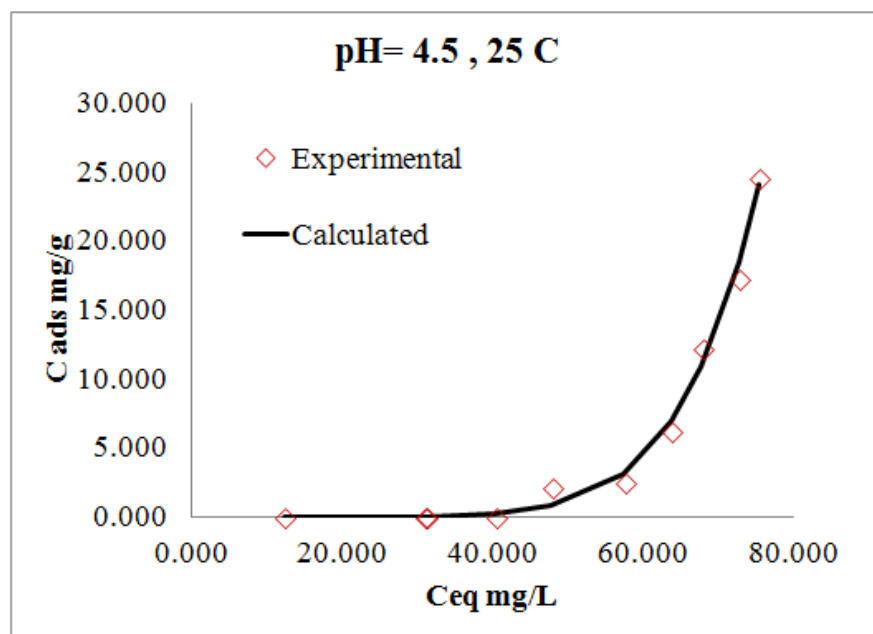
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Figure 4. Fitting of the adsorption data at pH 4.5 and 25 ºC

It is worth to mention that the previously reported adsorption isotherms of Cd(II) on bentonite alone showed normal Langmuir L-shape shape [15,16]. This indicates that the present S-shape behavior is due to modification of the bentonite with PVA.

Effect of pH

As shown in Table 3, the adsorption of Cd(II) is approximately unaffected by pH changes in the range studied here. This indicates that Cd(II) is adsorbed on sites that are pH-independent, in the pH range 3.0–4.5, such as hydroxyl, phenol, and thiol functionalities.

Table 3. Effect of pH at 25 °C

Effect of pH at 25 °C				
pH	3	3.5	4	4.5
Qmax (mg Cd/g)	1739.537	1739.573	1739.606	1739.816
K	0.007622	0.004074	0.007772	0.007521
N	8.122947	3.655292	7.615763	7.51738

Effect of temperature

There was no significant effect of temperature on the adsorption of cadmium(II) on PVA- bentonite, Table 4. Thus ΔH_{ads} is approximately zero and the adsorption process can be considered to be mainly entropy driven.

Table 4. Effect of temperature at pH 3.5

Effect of temperature at pH 3.5				
Temp. °C	25	30	35	40
Qmax (mg Cd/g)	1739.3	1739.194	1739.205	1738.92
K	0.004068	0.006564	0.006257	0.006515
N	3.650778	5.937744	5.116441	5.853651

CONCLUSION

Cadmium(II) adsorption followed a unique sigmoidal adsorption isotherm where multiple Cd(II) binding takes place on the PVA- bentonite complex. The more Cd(II) ions bind to the complex, the easier it appears for more Cd(II) to bind.

The interaction of the complex with metal ions was found to have $\Delta H_{ads} \sim 0$ and to be entropy driven. The adsorptivities of Cd(II) were not affected by pH changes. This indicates that Cd(II) adsorbed on pH-independent sites such as hydroxyl and thiol groups on both PVA and bentonite.

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