Thermodynamic approach for copper and cadmium specific and non-specific adsorption on calcareous soil-biopolymer composite

Mohamed Rashad [a], M.S. Mohy Eldin [b], M. Abd El Latif [c]

a Inst. of Arid Land Cultivation and Develop, Mubarak City
Email: marashad@yahoo.com
b Dept. of Polymers, and c Dept of Fabrication tech., Inst. of Advanced Tech. and New Materials, Mubarak City

The adsorption of Cu^{2+} and Cd^{2+} from aqueous solutions on a composite surface at three temperatures 30°C, 45°C and 55°C was studied using a raw calcareous soil composed with alginate biopolymer. 0.05 M NaCl was used to investigate the specific adsorption of metals on the composite, the adsorption obayed Langmuir adsorption isotherms. Langmuir parameters in the absence of electrolyte were higher than in its presence for Cu^{2+} and Cd^{2+} adsorption. Thermodynamic parameters including change in: enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) were calculated and their values showed that adsorption of heavy metals on composite was an endothermic reaction process, which was favored at high temperatures. The high values of the activation energy (E°_a) indicated that the rate of adsorption is controlled by a slow chemical reaction.

تم دراسة إمتزاز أيونات النحاس والكادميوم على سطح متراكب من التربة وبوليمر حيوى عند ثلاث درجات حرارية مختلفة وتم استخدام ملح كلوريد الصوديوم لدراسة الامتزاز النوعى على سطح المتراكب. كما تم دراسة معدل الامتزاز لكل من أيونات النحاس والكادميوم واتضح انهما يتبعا علاقة لانجمير. كذلك تم حساب التغير فى قيم الدوال الثرموديناميكية واتضح منها أن عملية الامتزاز على سطح المتراكب تزداد بزيادة درجات الحرارة.

Keywords: Heavy metals, Specific adsorption, Thermodynamic parameters, Activation energy, Alginate

1. Introduction

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. In order to solve heavy metals pollution in ecosystem, it is important to bring applicable solutions to the subject. It is possible to clean polluted environment only with long study requiring expensive and complex plants. Therefore, it is important to take effective precautions to prevent water, soils and air pollutions.

There are several methods to treat the metal contaminated effluents such as precipitation, ion exchange and adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment. Adsorption is one of the more popular methods for the removal of heavy metals from the wastewater. In the purification process, low cost purificant-adsorbent systems are pre-ferred. For this reason, industrial wastes and metallurgical by-products are used and also natural substances such as zeolites particularly clays and biopolymers viz alginate as in this study [1-2].

The objective of the present work is to remove some heavy metals such as Cu^{2+}, and Cd^{2+} from aqueous solution and to investigate the specific and non specific adsorption of these metals on soil-biopolymer composite. Also the thermodynamic parameters of these two types of adsorption will be calculated.

2. Experimental

2.1. Materials

Alginate: high viscosity sodium alginate (NaALG) (2% solution= 14000cP) was produced from (Sigma-Aldrich company).
- Calcareous soil
- $CdCl_2$, $CuSO_4.5H_2O$ and NaCl

2.2. Adsorbate

Two stock solutions (1000 ppm) of each metal Cd^{2+} or Cu^{2+} were prepared by dissolving the desired amount of $CdCl_2$ anhydrous(AR grade) or $CuSO_4.5H_2O$ in distilled water and in 0.05 M NaCl, respectively.

2.3. Preparation of Soil-Alginate composite beads (Adsorbent)

Alginate solution of 1.25% concentration was prepared using distilled water. Calcareous soil was collected from the northwestern coast of Egypt fig. 1. The soil was dried at 110°C and allowed to pass through 45 micrometer sieve. The collected fraction (45 μm) in definite weight ratio to alginate, 2.5:1 (w/w) was added to the solution and mixed thoroughly using high speed mechanical stirrer to ensure of homogeneous distribution of soil particles with alginate phase. The soil-alginate mixture was then dropped into 3% $CaCl_2$ crosslinker solution using prestatic pump with gentel stirring at room temperature producing beads with 4 mm outer diameter. The formed composite beads left on $CaCl_2$ solution overnight to harden. The hardened composite beads then separated from $CaCl_2$ solution and washed by distilled water several times, then dried at 50°C to constant weight and kept at closed vessels to prevent moisture absorption.

2.4. Procedure

The experiment was carried out using 100 ml aliquots of Cd^{2+} or Cu^{2+} solutions of known concentrations in (250 ml) Teflon bottles containing accurately weighed amounts (3 g) beads. This investigation was carried out at the initial soil pH (8.2) and three temperatures (30°C, 45°C and 55°C).

To measure the specific and the nonspecific adsorption of Cu^{2+} or Cd^{2+}; two series of 3 g dry beads were placed in 250 ml Teflon bottles with 100 ml of specified nine concentrations of Cu^{2+} or Cd^{2+} as $CuSO_4$ or $CdCl_2$ without and with 0.05 M NaCl. The bottles were shaken under the selected temperatures for a prescribed period of time to attain equilibrium; the equilibrium time was determined according to many attempts to

rich the maximum removal. A significant removal of both metals occurred in 30 min from the stirring time and no appreciable changes in terms of removal were noticed after 2 hours. In all subsequent experiments, the equilibrium time was maintained at 2 hours, which was considered as sufficient period to remove both of Cu^{2+} and Cd^{2+} ions by soil polymer composite. The equilibrium concentrations of heavy metals were determined by Atomic Absorption Spectrophotometry Perkin-Elmer model 5000. The adsorbed amount was calculated from the difference between the initial and the final equilibrating concentrations. An adsorption isotherm was constructed from the data. By measuring the adsorption at various temperatures, it is possible to evaluate both of geometrical $\Delta S°$ (entropy term) and the energetic $\Delta H°$ (enthalpy term) contributions to the driving force $\Delta G°$ (free energy) of the standard adsorption process. The method of Jurinak and Bauer [3] was used to calculate the thermodynamic parameters.

3. Results and discussion

The physicochemical properties of the used soils are represented in table 1. The results indicated that this soil is alkaline (with pH around 8.2), low in organic matter content. The content of $CaCO_3$ is 55.1%. The wide range of Cu^{2+} or Cd^{2+} concentrations, used through the experiments of adsorption produced curvilinear adsorption isotherm normally obtained as in other studies [4-6]. Fig. 2 shows the adsorption isotherms of copper and cadmium by soil-Alginate composite in the absence of the NaCl electrolyte at three temperatures; 30°C, 45°C and 55°C. Fig. 3 illustrates the specific adsorption isotherms of Cu^{2+} and Cd^{2+} by soil-Alginate composite at the same above mentioned conditions. These figures illustrate the adsorption of Cu^{2+} and Cd^{2+} on composite surface and the effect of temperature on this process. The results revealed that Cu^{2+} or Cd^{2+} adsorption increased with increasing temperature indicating that this process is an endothermic reaction. the adsorption of both metals on the calcareous soil-alginate composite is governed by calcium carbonate content ($CaCO_3$ % or lime). Also lime content seems to be an

important parameter that would govern the use of soil polymer composite as an adsorbent, neutralizing agent for acidic wastewater and for the immobilization of heavy metals in a solid matrix, as lime plays an important role in the reaction leading to the formation of a solid matrix [7]. Then calcium carbonate in calcareous soil precipitated Cu^{2+} and Cd^{2+} ions in carbonate form.
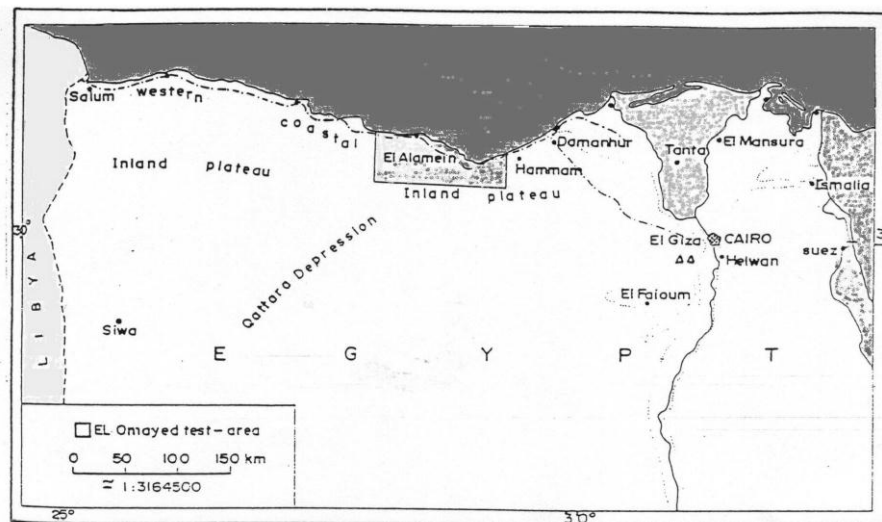

Fig. 1. Study area location at the northwestern coast of Egypt.

Table 1
Some physicochemical properties of the used soil

pH*	EC** (dsm^{-1})	CaCO$_3$ (%)	CEC (cmol kg^{-1})	OM (%)
8.2	4.3	55.1	10.6	0.14

* measured in 1:2.5 soil:water suspension
** measured in 1:1 soil:water extract
EC: Electrical Conductivity
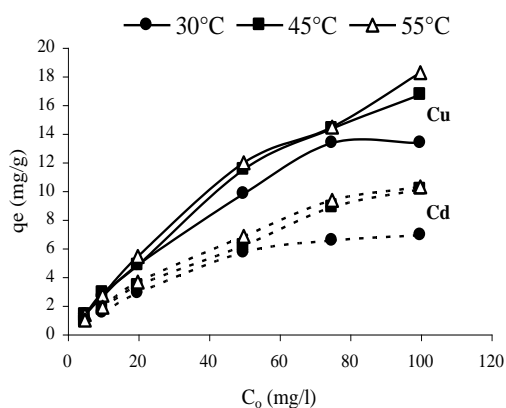CEC: Cation Exchange Capacity
OM: Organic Matter

Fig. 2. Adsorption isotherm of Cu^{2+} and Cd^{2+} on beads without 0.05 M NaCl at different temperatures.
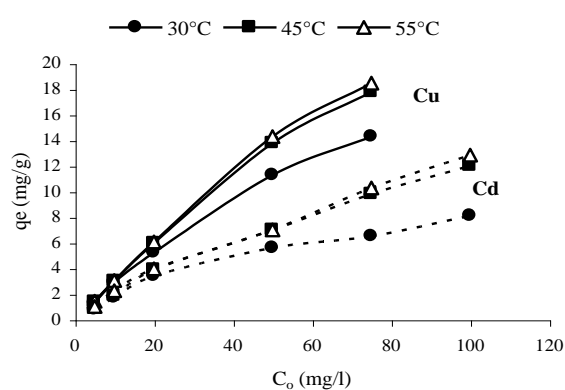

Fig. 3. Adsorption isotherm of Cu^{2+} and Cd^{2+} on beads with 0.05 M NaCl at different temperatures.

The method of Jurinak and Bauer [3] was used to calculate the thermodynamic parameters of adsorbed metals according to eq. (1):

$$\Delta G° = -RT \ln a = -RT \ln (m.\delta). \qquad (1)$$

Where a, m, and δ refer to activity, molality, and activity coefficient respectively, R is the universal gas constant (8.31 J mol^{-1} K^{-1}). δ was calculated by using Debye-Hückel theory [8]. In this method, $\Delta G°$ change accompanying an isothermal process determined by the $\Delta H°$ change, related to the chemical bonding; and the $\Delta S°$ change, related to the ordering or the geometry of the adsorbed ions.

The standard entropy change of adsorption $\Delta S°$ and the standard heat of adsorption $\Delta H°$ were calculated through the following eqs. (2 and 3):

$$- \Delta S° = d (\Delta G°) / \Delta T, \qquad (2)$$

$$\Delta H° = \Delta G° + T \Delta S°. \qquad (3)$$

The thermodynamic values, which calculated from the adsorption data, are given in table 2. The standard free energy change of adsorption ($\Delta G°$) is a measure of the spontaneousiety of the reaction. It was found that, for instance, in the absence of electrolyte the free energy of Cu^{2+} or Cd^{2+} adsorption was much higher than in the presence of electrolyte. This behavior can be attributed to: (i) the competition between copper and the electrolyte ions for the adsorption sites, and (ii) the activity of Cu^{2+} in the presence of electrolyte is lower than in its absence [9].

The general behavior of $\Delta G°$ was that it becomes more negative with increasing temperature. The high negative values of $\Delta G°$ could be attributed to the tendency of Cu^{2+} ions to make complex ions under high pH value (8.2) and/or Cu^{2+} ions become directly bounded to sites on composite surface under alkaline conditions. On the other hand, $\Delta G°$ becomes less negative by introducing the electrolyte (competing effect) [9].

The $\Delta H°$ values indicate that all Cu^{2+} and Cd^{2+} adsorption processes are endothermic reactions, i.e., a positive enthalpy of adsorption is obtained. The decrease of enthalpy by introducing electrolyte reflected the high binding strength of the adsorbed ions.

Energy of activation was calculated according to a relationship between Ea and ΔH [10] for reactions in solution by the following equation:

$$Ea = \Delta H + RT. \qquad (4)$$

Energies of activation below 42kJ mol^{-1} generally indicate diffusion-controlled processes and higher values represent chemical reaction processes [11-14]. In terms of Ea, diffusion or transport controlled reactions are those governed by mass transfer or diffusion of the sorptive from the bulk solution to the sorbent surface and can be described using the parabolic rate law [15]. Conversely, the reaction is surface controlled if the reaction between the sorptive and sorbent is slow compared with the transport or diffusion of the sorptive to the sorbent. For surface-controlled reactions, the concentration of the sorptive next to the sorbent surface is equal to the concentration of the sorptive in the bulk solution and the kinetic relationship between time and sorptive concentration should be linear [16]. In our study, the activation energy values were higher than 42 kJ mol^{-1} as presented in table 2 indicating chemically controlled; the process is divided into precipitation and adsorption and it could be considered as surface-controlled reactions, where the adsorption of copper and cadmium in this study conformed to the Langmuir equation, as presented in figs. 4 and 5 giving a linear relationship. The high values of the activation energy (from 44.11 to 165.95 KJ/mol) indicated that diffusion is not a limiting factor controlling the rate of adsorption. Consequently, adsorption of copper and cadmium by this soil-biopolymer composite appears to occur by chemisorption [16].

The results in table 2 showed that the adsorption of Cu^{2+} and Cd^{2+} ions on the composite surface was accompanied by entropy change with positive values. Since the random motion of the ionic species in solution has become subjected to the restraining adsorption force of the surface, i.e., the entropy change would be expected to have a negative value. But in this study the hydrated nature of

the adsorbed Cu^{2+} or Cd^{2+} must also be considered in order to obtain a complete picture of the entropy change. The adsorbed ions are likely to be partially dehydrated upon entering the adsorbed ionic layer. During the process of dehydration the water molecules, which were originally oriented around the hydrated ions, are liberated and their return to the solution phase tends to increase the disorder of the system i.e., this part of entropy change is positive. Thus, the positive $\Delta S°$ values can be attributed to the contribution of the partial dehydration processes [3,5].

The results in table 2 also indicated that in the presence or absence of electrolyte, the entropy decreased relatively. This is controlled by the dissociation of ions [17]. The general behavior of entropy was it decreased in the presence of electrolyte, for instance from table 2 the entropy for Cd^{2+} decreased from 0.564 EU in the absence of electrolyte to 0.268 EU in the presence of electrolyte and from 0.392 to 0.292 EU for Cu^{2+} at 30°C suggesting that an ordering system would take place. This would be explained through the double layer theory, where its thickness decreases by increasing the electrolyte concentrations.

4. Conclusion

From the results of the present work it can be concluded that $\Delta G°$ of Cu^{2+} or Cd^{2+} adsorption was lower in the presence of 0.05 M NaCl than in its absence and it becomes more negative by increasing temperature. The decr-

easing of enthalpy by introducing electrolyte reflected the high binding strength of the adsorbed ions i.e., positive values of $\Delta H°$ indicated endothermic nature of Cu^{2+} or Cd^{2+} adsorption. Finally, the high values of the activation energy ($E°_a$) indicated that chemical reaction processed under experimental conditions of this work.

List of symbols

a	is the Langmuir constant (L/mg of heavy metal ion) ,
b	is the monolayer coverage (mg of heavy metal ion/g adsorbent),
C_o	is the initial concentration (mg/l),
C_e	is the equilibrium concentration (mg/l),
CEC	is the Cation Exchange Capacity (meq/100g),
EC	is the Electrical Conductivity (dSm^{-1}),
Ea	is the Activation energy (kJ/mol),
EU	is the Entropy Unit,
ΔG	is the Free energy change (kJ/mol),
ΔH	is the Enthalpy change (kJ/mol),
ΔS	is the Entropy change (EU),
OM	is the Organic Matter (%),
qe	is the mass of heavy metal ion adsorbed per gram adsorbent at equilibrium (mg of heavy metal ion/g adsorbent),
R	is the Universal gas constant (8.31 J mol^{-1} K^{-1}),
R^2	is the Correlation coefficient, and
T	is the absolute temperature (K).

Table 2
Thermodynamic parameters for specific and non specific adsorption of copper and cadmium

Parameters	Temp. K	Cu^{2+}	Cd^{2+}	*Cu^{2+}	*Cd^{2+}
$\Delta G°$ KJ/mole		-33.29	-7.45	-32.08	-2.24
$\Delta H°$ KJ/mole	303	85.48	163.44	56.39	78.96
$\Delta S°$ EU		0.392	0.564	0.292	0.268
Ea KJ/mole		87.99	165.95	58.90	81.47
$\Delta G°$ KJ/mole		-34.47	-15.91	-33.25	-6.26
$\Delta H°$ KJ/mole	318	74.83	68.67	72.29	71.96
$\Delta S°$ EU		0.350	0.266	0.332	0.246
Ea KJ/mole		77.47	71.31	74.93	74.60
$\Delta G°$ KJ/mole		-34.81	-19.90	-32.73	-9.95
$\Delta H°$ KJ/mole		122.11	110.97	41.39	111.08
$\Delta S°$ EU	328	0.498	0.399	0.226	0.369
Ea KJ/mole		124.83	113.69	44.11	113.80

* with 0.05 M NaCl

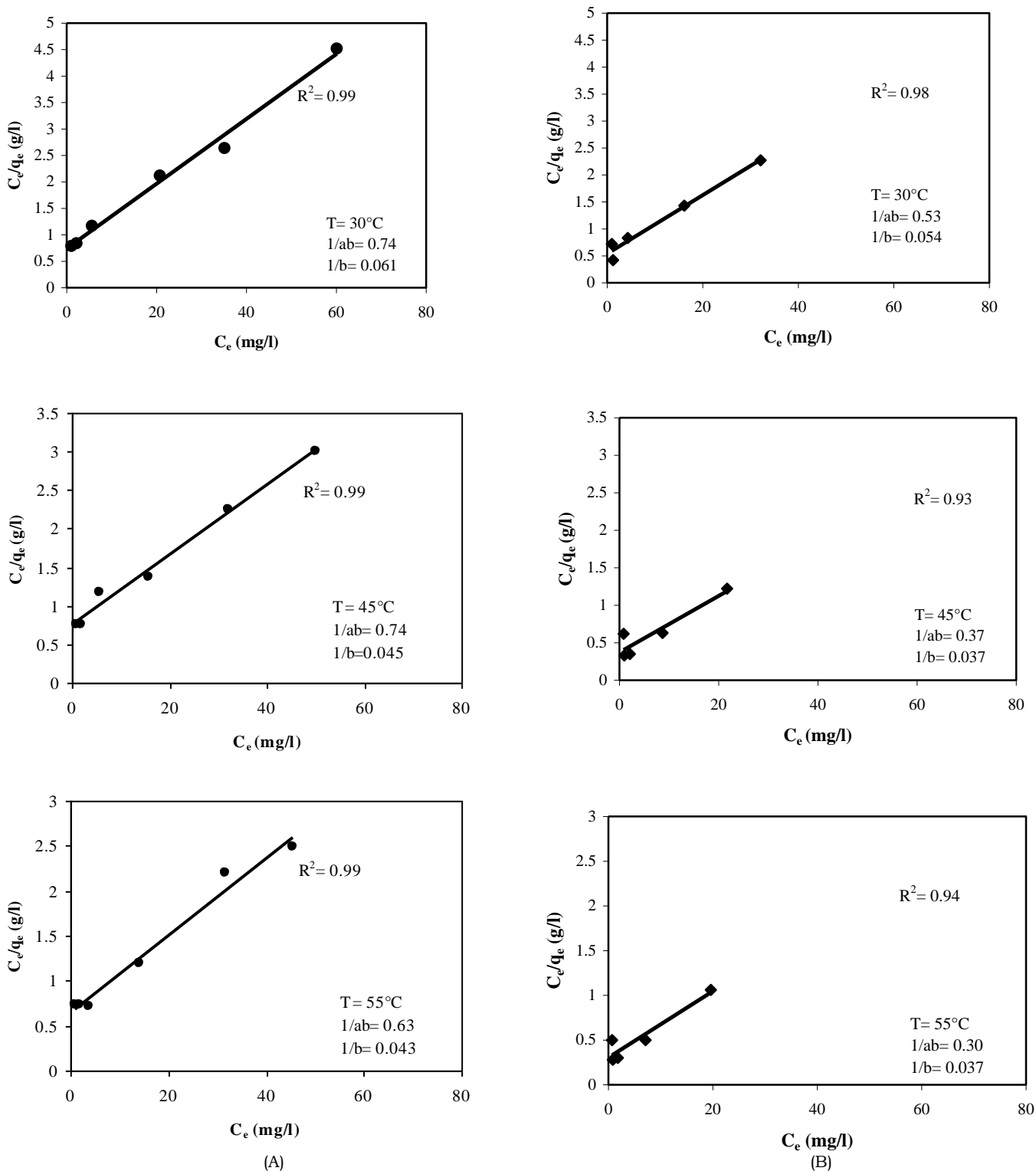Fig. 4. Langmuir adsorption of Cu^{2+} in the absence (A) and in the presence (B) of 0.05 M NaCl at the three temperatures.
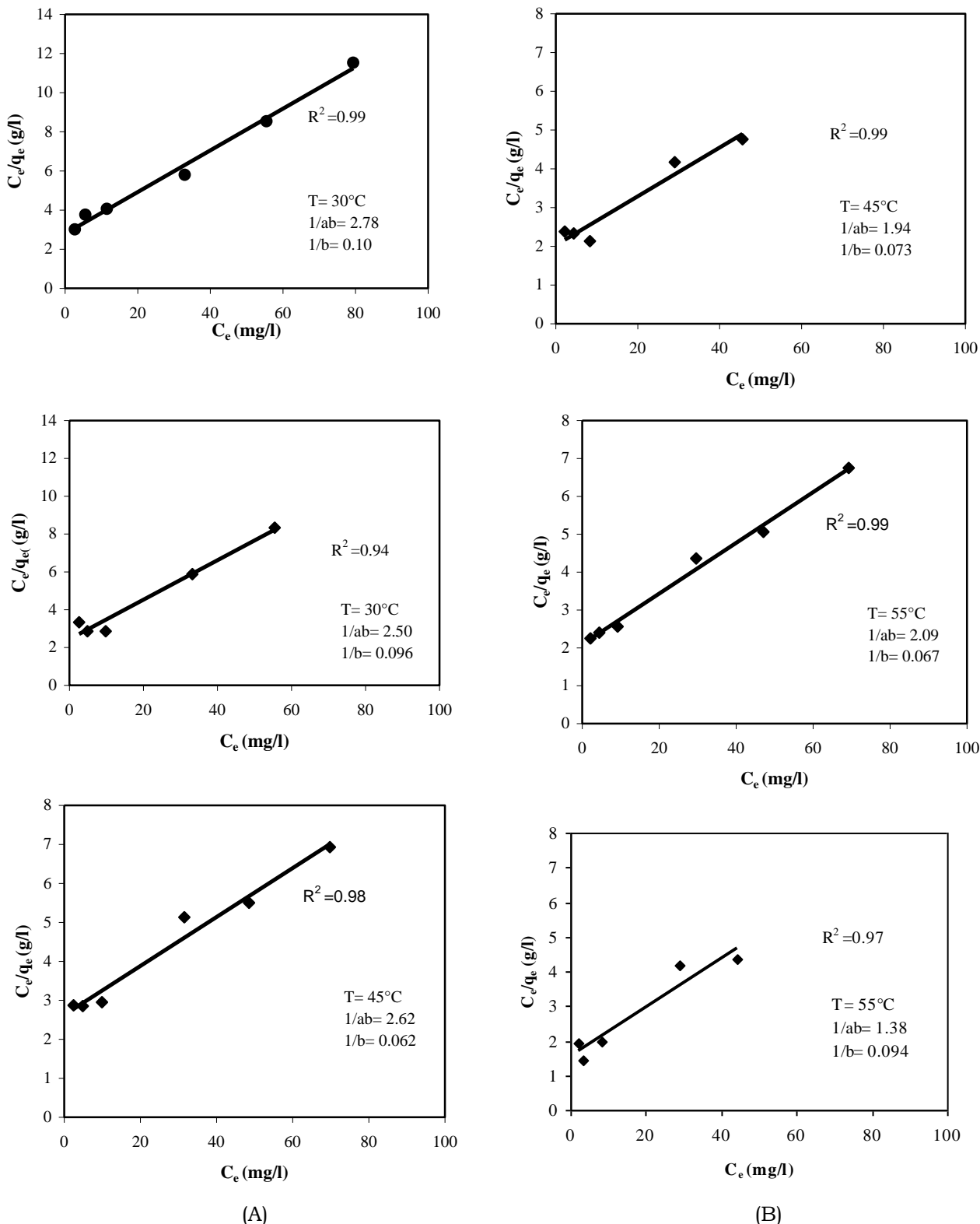
(A)   (B)

Fig. 5. Langmuir adsorption of Cd^{2+} in the absence (A) and in the presence (B) of 0.05 M NaCl at the three temperatures.

References

[1] A.W. Rose, and G.C. Bianchi-Mosquera, "Adsorption of Cu, Pb, Zn, Co, Ni, and Ag on Goethite and Hematite: A Control on Metal Mobilization from Red Beds into Stratiform Copper Deposits," Econ. Geol., Vol. 88, pp. 1226–1236 (1993).

[2] B. Schroth, and G. Sposito, "Effect of Landfill Leachate Organic Acids on Trace Metal Adsorption by Kaolinite," Envron. Sci. Technol., Vol. 32, pp. 1404-1408 (1998).

[3] J.J. Jurinak, and N. Bauer, "Thermodynamic of Zinc Adsorption on Calcite, Dolomite and Magnesite-Type Minerals," Soil Sci. Soc. Am. Proc., Vol. 114, pp. 466-471 (1956).

[4] S.K. Dhillon, P. Sidhu, and M.K. SINHA, Copper Adsorption by Alkaline Soils. J. Soil Sci., Vol. 32, pp. 571-578 (1981).

[5] F.F. Assaad, and D. Nielsen, "A Thermodynamic Approach for Copper Adsorption on Some Danish Arable Soils," Acta Agric. Scand., Vol. 34, pp. 377-384 (1984).

[6] D.A. Laird, and M.L. "Thompson, Sorption and Desorption of Copper on Soil clay Components," J. Environ. Qual., Vol. 28, pp. 334-338 (1999).

[7] T. Viraraghavan, and G. A. K. Rao, , "Adsorption of Cadmium and Chromium from Wastewater by Fly Ash," J. Envir. Sci. Health A, Vol. 26(5), pp. 721–753 (1991).

[8] J. Moore Walter, Physical Chemistry. Longman, UK. (1994).

[9] M.K. Doula, and A. Loannou, "The Effect of Electrolyte Anion on Cu Adsorption-Desorption by Clinoptilolite," Microporous and Mesoporous Materials, Vol. 58, pp. 115-130 (2003).

[10] J.H. Noggle, Physical Chemistry. 3rd ed. Harper Collins Publishers, New York, Vol. 11, p. 1108 (1996).

[11] D.L. Sparks, Kinetics of Ionic Reactions in Clay Minerals and Soils. Adv. Agron. Vol. 38, pp. 231-266 (1985).

[12] D.L. Sparks, Kinetics of Soil Chemical Processes, Academic Press, San Diego, CA, pp. 35-57 (1989).

[13] D.L. Sparks, Environmental Soil Chemistry, Academic Press, San Diego, CA, pp. 267-280 (1995).

[14] D.L. Sparks, "Kinetics of Reactions in Pure and Mixed Systems," pp. 83–178. *In* D.L. Sparks (ed.) Soil Physical Chemistry. 2nd ed. CRC Press, Boca Raton, FL (1999).

[15] W. Stumm, and R. Wollast, "Coordination Chemistry of Weathering. Kinetics of the Surface-Controlled Dissolution of Oxide Minerals," Rev. Geophys. Vol. 28, pp. 53-90 (1990).

[16] K.G. Scheckel, and D.L. Sparks, "Temperature Effects on Nickel Sorption Kinetics at the Mineral–Water Interface," Soil Sci. Soc. Am. J., Vol. 65, pp. 685-694 (2001).

[17] W.L. Lindsay, Chemical Equilibria in Soils, Wiley-Interscince, New York, pp. 449-461 (1979).