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The Investigation of Ni (II) Removal by Biocomposite Synthesized with the Immobilization of *Candida Utilis* on Chitosan

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Abstract: In this study, Ni(II) adsorption was examined with the biocomposite prepared with the immobilization of *Candida utilis* on chitosan polymer. The FTIR and SEM analyses of chitosan-*Candida utilis* biocomposite were carried out before and after adsorption of Ni (II) ions. For the Ni(II) adsorption by *C. utilis* immobilized on chitosan, the Ni(II) concentrations were changed in the concentration range of 10-100 mg/L. For the Ni(II) adsorption by *C. utilis* immobilized on chitosan, the optimum pH value was determined to be 4.0, and temperature was determined to be 25 ^{0}C. Under these experimental conditions, the maximum adsorbed amount of Ni(II) per unit weight of adsorbent was found to be 9.5 mg/g. The adsorption equilibrium data adjusted to the Langmuir isotherm model. The kinetic data were represented by the pseudo-first-order kinetic model. The enthalpy, entropy and Gibbs free energy changes were found to be -4.61 kj/mol, 1.97 j/mol, -10.48 kj/mol, respectively. With respect to the results obtained in this study, new chitosan-*Candida utilis* biocomposites will become an alternative for the removal of heavy metals from wastewaters.

Keywords: Wastewater, chitosan, *Candida utilis*, Ni(II), adsorption.

Candida Utilis'in Kitosana Tutuklanması ile Sentezlenen Biyokompozit ile Ni (II) Gideriminin İncelenmesi

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Özet: Bu çalışmada, kitosan polimeri üzerine *Candida utilis*'in tutuklanması ile hazırlanan biyokompozit ile Ni (II) adsorpsiyonu incelenmiştir. Kitosan-*Candida utilis* biyokompozitinin FTIR ve SEM analizleri Ni (II) iyonlarının adsorpsiyonundan önce ve sonra gerçekleştirildi. Kitosan üzerine tutuklanan *C.utilis*'in Ni (II) adsorpsiyonunda, Ni (II) konsantrasyonları 10-100 mg / L konsantrasyon aralığında değiştirilmiştir. Kitosan üzerine *C.utilis*'in Ni (II) adsorpsiyonu için ile elde edilen optimum pH değerinin 4.0 ve sıcaklık değerlerinin 25 ° C olduğu belirlenmiştir. Bu deney koşulları altında, adsorbanın maksimum adsorbe edilmiş Ni (II) miktarı 9.5 mg / g olarak bulunmuştur. Adsorpsiyon denge verileri Langmuir izoterm modeline uygun olduğu belirlenmiştir. Kinetik veriler, yalancı birinci dereceden kinetik modeline uygun olduğu tespit edilmiştir. Entalpi, entropi ve Gibbs serbest enerji değişimleri sırasıyla -4.61 kj / mol, 1.97 j / mol, -10.48 kj / mol olarak bulunmuştur. Bu çalışmada elde edilen sonuçlarla ilgili olarak, yeni chitosan-*Candida utilis* biyokompozitinin kullanımı, atıksularki ağır metallerin uzaklaştırılmasında bir alternatif haline gelecektir.

AnahtarKelimeler: Atıksu, kitosan, *Candida utilis*, Ni(II), adsorpsiyon.

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1. INTRODUCTION

The presence of heavy metals in wastewater damages human health and it causes health problems in the food chain with its accumulation in living tissues, which has become an important issue in recent years [1]. In addition to classical chemical and physical methods used in the removal of heavy metals, the performances of non-living microorganisms have drawn attention recently due to cost

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effectiveness and their being environment-friendly sorbents [2]. Bacteria such as *Bacillus cereus*, *Escherichia coli*, etc. and fungal adsorbents such as *Aspergillus niger*, *Rhizopusarrhizus*, etc. which are used for the biosorption of heavy metals from aqueous solutions are easily-reproducing biomasses and can also be modified on support [3]. Lijida et al. (2015) examined the immobilization of *candida rugose* lipase on silica SBA-15 and zirconia support [4]. The immobilization which begins with the cell's adsorption to solid surface overcomes the van der Waals forces and electrostatic driving forces [5] after a certain period of time and attaches to the solid surface with the hydrophobic interaction, polar interaction, hydrogen bonds and the interaction of various specific molecules [6]. In their study, Monvisade and Siriphannon (2009), by using this method, added clay (montmorillonite) to chitosan and examined the adsorption of the prepared composite (Chitosan-MMT) in cationic dyes. They are immobilizedbiocomposite materials, which are an alternative method used for the removal of heavy metals from high concentrated solutions or wastewater [7]. In this study, the adsorption of the biocomposite materials prepared with chitosan and *Candida utilis*was examined for Ni (II) ions and it is considered to become an alternative for the treatment of the waters with the high heavy metal pollution.

2. MATERIALS and METHOD

2.1 Reagents

The chemicals used in the experiments are of Sigma-Aldrich brand, and *Candida utilis*is *ATCC® 9950™* ferment strains obtained from Ankara University, Department of Biology.

2.2 Immobilization of *Candida utilis* on chitosan

1 g of chitosan was added to 3 g of wet *Candida utilis* and they were mixed under room conditions. The samples were kept at room temperature for 12 hours and the batch system experiments were performed.

2.3 Batch Reactor Experiments

The optimum reproduction conditions of *Candida utilis* were determined to be 25 ^{0}C and pH 4. *Candida utilis* was left for reproduction at 95 rpm mixing speed for 4 days. *Candida utilis* obtained afterwards was centrifuged and stored in the fridge. The adsorbents used in the experiment are chitosan and the biocomposite material formed with the adsorption of *Candida utilis* on chitosan. Experimental studies were examined in the batch system. Afterwards, a specific amount was taken from the samples and centrifuged and the adsorption values were measured by using the UV spectrometer at 460 nm. The adsorption of Ni(II) solutions prepared in 10-100 mg/L concentration was examined for 10-240 minutes. The maximum adsorption effect of Ni(II) solutions in 100 mg/L concentration between 25-55^{0}C was measured to determine thermodynamic parameters and the adsorption amount was calculated (Equation 1) [8].

$$q_e = \frac{(Co - Ce)V}{m} \tag{1}$$

2.4 Adsorption Isotherms

The dispersion of metal ions between the liquid and solid phase in adsorption processes can be explained by the Langmuir isotherm model (Equation 2) and Freundlich isotherm model (Equation 3) [9].

$$q_e = \frac{Q_{max} a_L C_e}{1 + a_L C_e} \tag{2}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

2.5 Adsorption Kinetics

The equations used to determine adsorption kinetics are as follows.

The pseudo-first-order kinetic model:

$$log\frac{(q_e-q)}{q_e}=-\frac{k_{1,ad}t}{2.303} \qquad (4)$$

The pseudo-second-order kinetic model is expressed as follows and given with the following formula [10]:

$$\frac{t}{qt}=\frac{1}{k_2\ q_e^2}+\frac{t}{q_e} \qquad (5)$$

2.6 Adsorption Thermodynamics

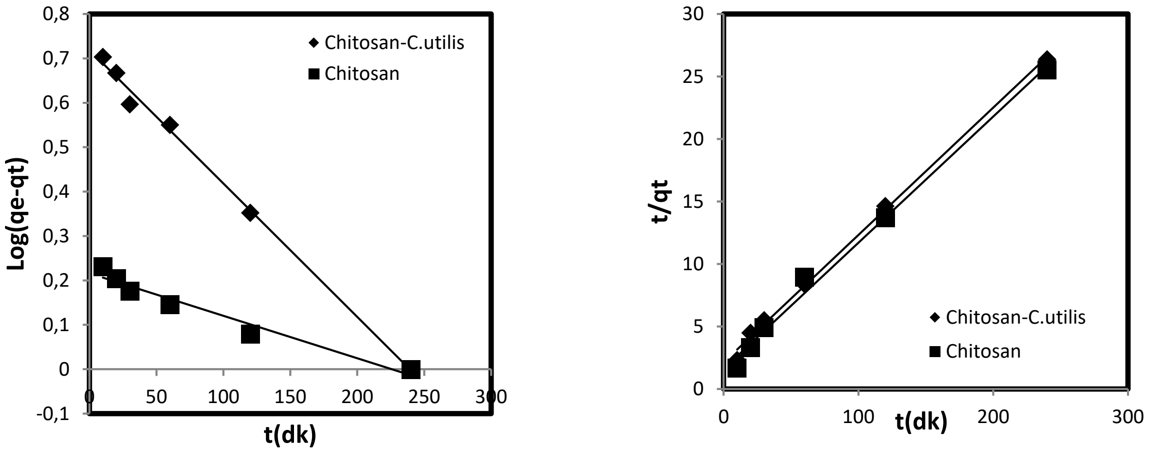
The thermodynamic parameters of enthalpy, entropy and free energy change for the adsorption process are given in Equation 6 [11].

$$\Delta G^0=\Delta H^0-T\Delta S^0 \qquad (6)$$

3. RESULTS and DISCUSSION

3.1 Adsorption Kinetics

The contact time for Ni(II) adsorption was examined in the stationary initial Ni(II) concentration for chitosan and chitosan-*Candida utilis*biocomposite. Although Ni(II) adsorption was rapid at the beginning, it decelerated over time. This decrease showed that the adsorption on the surface was single-layered [12]. When Log (qe-qt) versus t is displayed in a graph, figure 1-a line is obtained; and when t/qt versus t is displayed in a graph, figure 1-b line is obtained. When the experimental qe and correlation values were examined, the biocomposites were observed to be compatible with the pseudo-first-order kinetic model. The constants for the adsorption kinetic model are presented in Table 1 for 100 mg/L Ni (II) concentration.



(a) (b)

Figure 1-(a). Pseudo-first-order kinetic model **(b).**Pseudo-second-order kinetic model for the Ni (II) adsorption of adsorbents.

Table 1. Pseudo-first and second-order kinetic model parameters for Ni (II) adsorption.

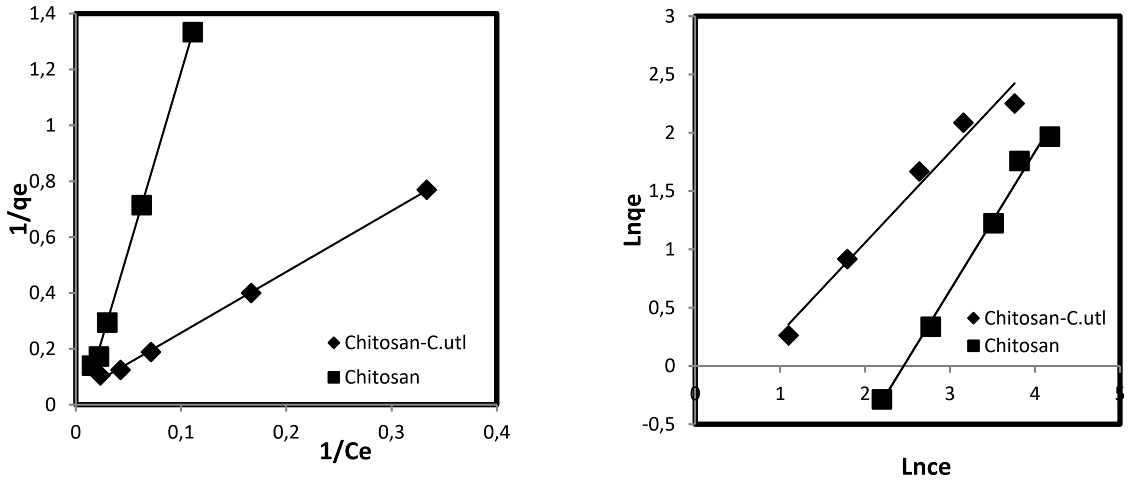
25^0C	Experimental Data		Pseudo first-order kinetic model			Pseudo second-order kinetic model		
	Ce(mgL^{-1})	qe(mgg^{-1})	qe(mg g^{-1})	k$_1$(dk^{-1})	R^2	qe(mg/g)	k$_2$(g mg^{-1} dk^{-1})	R^2
PAN-*C.utl*	38.5	9.51	5.22	0.0069	0.995	9.52	0.0031	0.997
PAN	55.1	7.15	1.65	0.0023	0.957	7.25	0.0045	0.992

3.2 Adsorption Isotherms

R^2 values determine the isotherm type and if R>1, it signifies that it is unfavorable for adsorption, if 0<R<1, it signifies that the condition of favorability for adsorption has been ensured [13]. When the adsorption isotherms were examined, it was observed that chitosan and chitosan-*Candida utilis* biocomposite were compatible with the

Langmuir isotherm model (Figure 2-a) for Ni (II). This situation can be explained by the fact that the biocomposite surface has homogeneous structure and by the presence of bonding regions that will enable single-layered adsorption [14].

Chitosan-*Candida utilis* showed a higher removal for Ni (II) only in comparison with chitosan (Table 2). This situation realizes with Ni (II) ion’s adsorption on the sorption regions on the adsorbent surface with the electrostatic interaction of metal ions in the micro-environment [15].



(a) (b)

Figure 2-(a) Langmuir isotherm (1/Qe- 1/Ce) **(b)**Freundlich isotherm (InQe- InCe) graph.

Table 2. Langmuir and Freundlich isotherm model of Ni(II) chitosan and chitosan-*Candida utilis*biocomposite.

	Langmuir			**Freundlich**		
	Q_e(mg/g)	b	R^2	K_f	n_f	R^2
PAN-*C.utl*	26.31	0.0608	0.999	2.6	1.83	0.980
PAN	22.5	0.0054	0.998	2.1	1.18	0.987

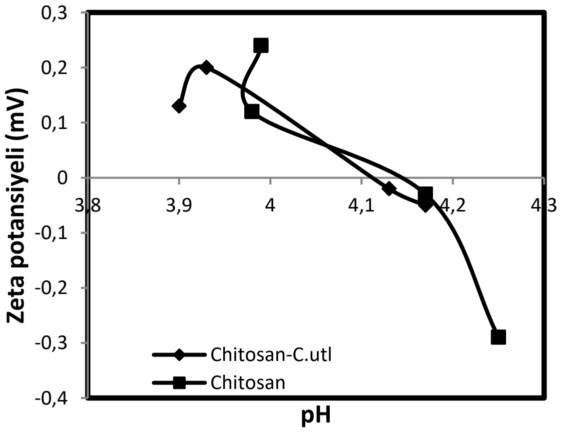


Figure 3. The pH-zeta potential relation of chitosan and chitosan-*Candida utilis*biocomposite for Ni(II).

Candida utilis plays an important role in reproducing in the environments with acidic pH and heavy metal contamination, in adjusting the ambient pH and conducting experimental studies. When the pH range is examined, it is observed that as pH increases, the removal of Ni (II) ions decreases in the range between 3.85 and 4.3 as in figure 3 because with the increase in pH, H^+ ions which decrease in the environment reduce the electrostatic interaction between Ni (II) ions and the composite surface. This is becausethepH of Ni (II) solution is relatedtothecondition of functionalgroups on thebiocompositesurfaceanddifferentresultsareobtainedforbiocomposite. Themobility of H^+ion at lowpH is higherwhencomparedtoNi (II) ion. Thisdecreasestheadsorption of Ni (II). IfthepH of thesolutionincreases, Ni (II) ionwill be adsorbedmoretothesolidsurface since therewill be less H^+ion in theenvironment. pH is one of theimportantfactorsaffectingadsorptionfordifferentbiocompositematerials. ThepH of thesolution has an effect on metal-bindingregions of thebiocompositesurfaceandchangesthephysicochemicalcharacteristics of the metal [16].

3.2 Thermodynamic Parameters

The change of the Gibbs free energy, enthalpy and entropy equilibrium constant with temperature was calculated with the ΔG versus T graph as seen in figure 4. The fact that $\Delta G<0$ originates from the fact that the concentration around the biocomposite is higher when compared to the concentration within the biocomposite. The negative ΔG values indicate that Ni (II) isadsorped spontaneously. The positive ΔS value originates from the increase in randomness and affinity on the solid-liquid interface during adsorption. The negative ΔH value (Table 3) in this spontaneous event due to the equilibrium condition showed that the interaction on the surface was exothermic [17].

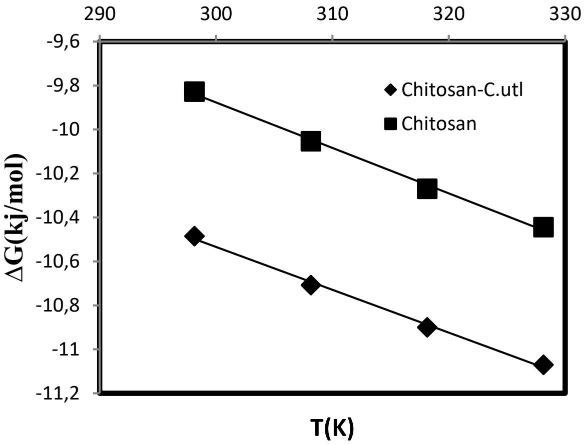


Figure 4. The change of the Gibbs free energy with temperature for Ni(II).

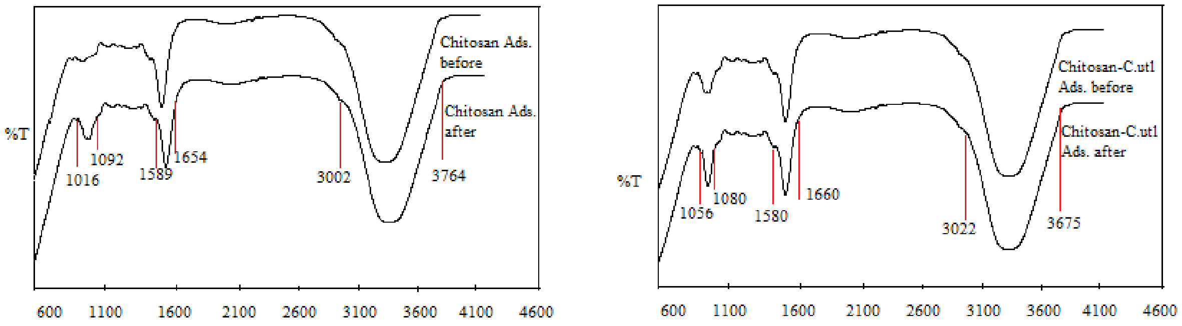
Table 3. Thermodynamic parameters for Ni(II) adsorption.

	ΔG(kj/mol)		TΔS(kj/mol)		ΔH(kj/mol)	
T (K)	chitosan+*C.utilis*	chitosan	chitosan+*C.utilis*	chitosan	chitosan+*C.utilis*	chitosan
298.15	-10.48	-9.82	5.88	6.21	-4.61	-3.71
308.15	-10.71	-10.05	6.08	6.33		
318.15	-10.01	-10.26	6.28	6.54		
328.15	-11.07	-11.07	6.48	6.74		

In this study, the adsorption skills of *Candida utilis* on their own increased the adsorption capacity of a newly-developed biocomposite material.

3.4 FTIR and SEM Analyzes

3.4.1 FTIR



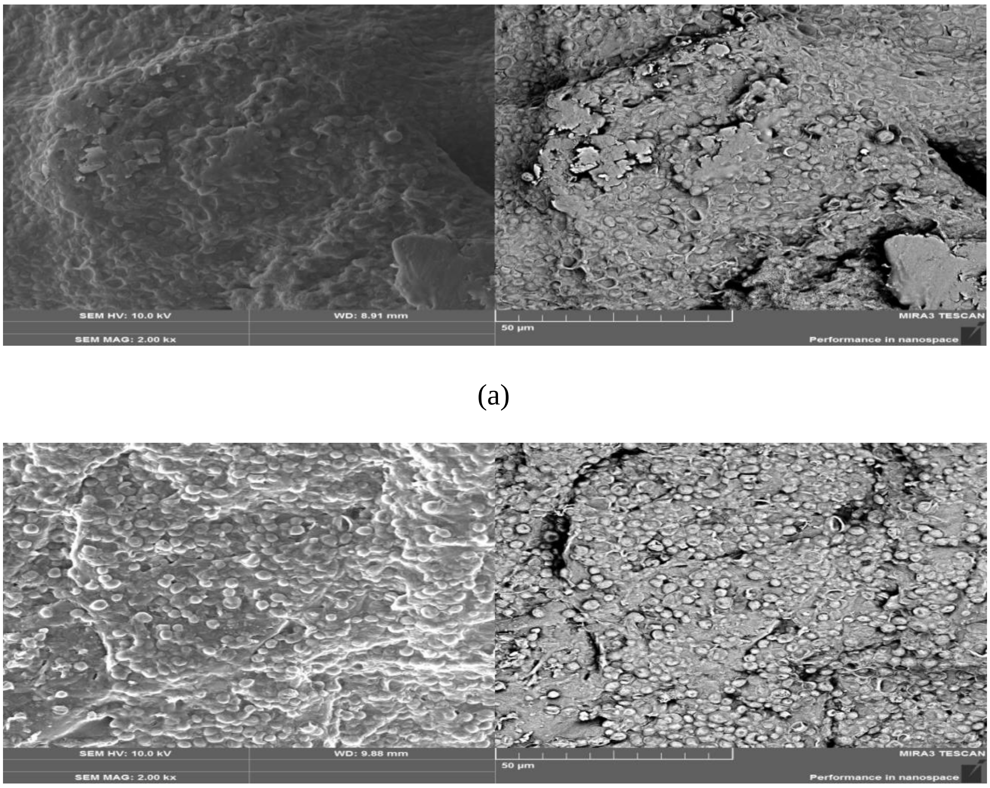
(a) (b)

Figure 5. Pre- and post-adsorption of (a) chitosan (b) chitosan-*Candida utilis*biocomposite.

When the FTIR spectrum was examined, it was observed that the peak severity observed after adsorption for chitosan (figure 5-a) and chitosan-*Candida utilis*biocomposite (figure 5-b) was higher in comparison to the peak severity observed before adsorption. It was considered that the wide peak range at 3022-3675 cm^{-1} wavelength belonged to the hydroxyl bond (-OH) of chitosan, the peak at 1580-1660 cm^{-1} wavelength belonged to amide N-H bending peak, the peak at 1056- 1080 cm^{-1} wavelength belonged to the asymmetrical bending peak of CH_2 for chitosan-*Candida utilis* before adsorption (figure 5-b) [18]. It was observed that after adsorption, chitosan-*Candida utilis*biocomposite had a higher peak severity in comparison to chitosan. This situation originates from the fact that the multi-functional group interacts with Ni (II) ions with the adsorption process and can be explained by the fact that the functional groups in the structure of *Candida utilis* have a higher affinity for Ni (II) ions [19].

3.4.2 SEM

The pre-adsorption and post-adsorption SEM images are presented in figure 6 for chitosan-*Candida utilis*biocomposite. It was observed that chitosan-*Candida utilis*biocomposite had a porous structure before adsorption. It was considered that the surface area of chitosan-*Candida utilis*biocomposite, which increased with the pore size after adsorption, was completely filled with Ni (II) ions [20].



(a)

(b)

Figure 6. Chitosan-*Candida utilis*biocomposite (a) before adsorption (b) after adsorption.

4. CONCLUSION

In this study, Ni (II) adsorption was examined with the biocomposite material prepared with chitosan and *Candida utilis.* The adsorption skills of *Candida utilis* on their own increased the adsorption capacity of a newly-developed biocomposite material. The experimental data were observed to be compatible with the Langmuir isotherm model for chitosan and chitosan-*Candida utilis*biocomposite. Kinetic parameters were calculated using the pseudo-first and second-order kinetic model under optimum conditions. The Gibbs free energy, enthalpy and entropy equilibrium constant were calculated according to the change with temperature for thermodynamic parameters.As a result of the studies, Ni (II) removalfor chitosan-*Candida utilis* composite was higher only in comparison to chitosan. It is considered that chitosan-*Candida utilis*biocomposite will become an alternative for the removal of heavy metals and this study will become an example study for the production of new biocomposite materials due to a limited number of similar studies in the literature.

5. SYMBOLS

C_e: The concentration of the substance left in the solution after adsorption (mg/dm3)
C_a: The amount of the substance kept in the unit mass of the adsorbent (mg/g)
Q_e: The amount of the substance adsorbed on the unit adsorbent (mg/g)
K_F: Adsorption capacity calculated experimentally
K_c: Equilibrium constant
$k_{1.ad}$: First-order rate constant (min^{-1})
k_2: Second-order rate constant (g $mg^{-1}min^{-1}$)
N: Adsorption degree
a_L: Constant dependent on the adsorption energy (dm^3/mg)
ΔG^0: Free energy change (kJ/mol)
ΔH^0: Enthalpychange (kJ/mol)
ΔS^0: Entropy change (kJ/mol K)
T: Absolute temperature (Kelvin)
R: Gas constant (8.314 J/mol K)

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