Adsorption kinetics of phosphate from aqueous solutions by waste iron sludge Weiwei Zhang^{1*}, Yan Shi²

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The kinetics of phosphate adsorbed on waste iron sludge was investigated in this study. Static batch adsorption experiments were performed at different initial phosphate concentrations, initial pH and temperature of solution. The initial adsorption rate increased with increasing the phosphate concentration. A shorter time, however, was required to reach adsorption equilibrium at low phosphate concentration due to external surface adsorption. Although the efficacy of phosphate adsorbed on waste iron sludge depended significantly on pH of solution, the adsorption kinetics was relatively independent on pH. Increasing solution temperature contributed to accelerating reaction rate of adsorption and raising the uptake of phosphate adsorbed on waste iron sludge. The kinetic process of phosphate adsorbed on waste iron sludge could be well described by both pseudo second-order and Elovich kinetic models, indicating chemisorption occurred. The simulation of intra-particle and Boyd model demonstrated that the intra-particle diffusion occurred, but the liquid film diffusion was the rate-limiting step. The of apparent activation energy of adsorption value (33.40 kJ·mol⁻¹) also indicated that chemical reaction was not the only rate-limiting step and diffusion was involved within the whole adsorption process. Results of these findings suggested that the intra-particle diffusion occurred in the entire adsorption process, but the mass transfer in the liquid film was the dominant rate-limiting step.

Key words: phosphate; waste iron sludge; adsorption; kinetics

INTRODUCTION

Phosphorus is the most important element causing eutrophication of water bodies, such as lakes and reservoirs [1]. Hence the removal of phosphate from wastewater has drawn much attention.

Chemical precipitation using various precipitants is an effective way to remove phosphate from wastewater, but large amounts of chemical sludge are produced in these processes [2]. Phosphate can be also removed by metabolism of microorganisms, but removal efficiency of phosphate is sensitive to environmental factors, such as temperature, pH and dissolved oxygen [3]. The removal of phosphate by adsorption has aroused wide attention because of simple operation, sustainable efficiency and producing less sludge [4]. The key for adsorption is to seek out an appropriate adsorbent.

Many types of adsorbents for phosphate removal have been investigated in recent years, such as aluminum oxides/aluminum hydroxide [5], calcium silicate [6], zeolite [7], calcined Mg-Mn-layered double hydroxides [8], iron oxide tailings [4], Fe–Mn binary oxide [9], polymeric ligand exchanger [10]. In order further to reduce costs, using industrial wastes, such as activated red mud [11], blast furnace slag [12] or fly ash [13], as adsorbents to remove phosphate from aqueous solutions has become a hot topic.

Dewatered aluminum or iron sludges are produced during the process of drinking water treatment when aluminum or iron salts are used as coagulants to remove turbidity. Previous studies [14, 15] mainly focused on using dewatered aluminum sludge to adsorb phosphate from aqueous solutions because of aluminum salt being more used as coagulant. However, iron salt, as an alternative coagulation, are considered more and more due to the physiological disorders caused by the residual aluminum [16]. Large amounts of iron based coagulants used in drinking water treatment plant will produce dewatered iron sludge. Thus the utilization of dewatered iron sludge is urgent. Ding studied the efficacy, equilibrium and thermodynamics of phosphate adsorbed on dewatered iron sludge [2]. However, there is a significant gap in knowledge on the kinetic characteristics of phosphate adsorbed on dewatered iron sludge, which is crucial to better understanding the removal mechanism of phosphate and designing the reactor of adsorption.

Accordingly, this study is aimed to (1) investigate the effects of environmental factors, such as initial phosphate concentration, initial pH of solution and temperature of solution, on kinetics of phosphate adsorbing on waste iron sludge; (2) find an appropriate kinetic model to quantitative describe the kinetics of phosphate adsorbed on waste iron sludge; (3) analyze the diffusion mechanism of phosphate from bulk solution to surface of waste iron sludge.

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MATERIALS AND METHODS

Adsorbent

Dewatered iron sludge was supplied by a local drinking water treatment. The sludge was dried at 105° C for 8 h, then it was ground and sieved. The particles whose diameters were below 100 μ m were used as adsorbents in this study.

Chemicals and adsorbate

All chemicals used in this study were AR grade, and purchased from Sinopharm Chemical Reagent Co., Ltd., China. Potassium dihydrogen phosphate (KH₂PO₄) was used as adsorbate in this study. And a stock solution of phosphate (P, 50 mg L^{-1}) was prepared by dissolving accurately weighed sample of potassium dihydrogen phosphate in ultra-pure water. Test samples with various concentrations of phosphate used in adsorption experiments were prepared by diluting the stock solution with distilled water where needed.

Adsorption procedure

The effects of different phosphate concentrations, initial pH of solution and temperatures of solution on the kinetics of phosphate adsorbed on waste iron sludge were investigated by batch adsorption mode. Taking 5 mg L^{-1} phosphate adsorbed on waste iron sludge as an example illustrated experimental process. First, waste iron sludge (0.2 g) was added into a series of conical flasks containing 50 mL phosphate solution with the concentration of 5 mg P/L, respectively. These conical flasks were sealed with lids. Then they were put into water bath and were mixed at a constant speed of 150 rpm at 303 K. These samples were taken out at preset time intervals and filtered using a 0.45 membrane, respectively. The phosphates in filtrates were measured using a UVvisible spectrophotometer (UV-2450PC, Shimadzu, Japan) at 700 nm according to standard method [17]. The similar kinetic experiments were conducted at other conditions. All experiments were carried out in triplicate and average values were reported herein.

The amount of phosphate adsorbed on iron sludge at any time, q_t (mg P/g), is calculated by equation (1).

$$q_t = (C_0 - C_t)V/m \tag{1}$$

Where C_0 and C_t (mg L⁻¹) are the concentration of phosphate in aqueous solution at initial and time t, respectively; V (L) is the volume of solution, m (g) is the mass of iron sludge.

RESULTS AND DISCUSSION

Effect of initial phosphate concentration on kinetics

The experiments were conducted by varying initial phosphate concentration from 5 to 15 mg/L in order to study the influence of initial phosphate concentration on the kinetics of phosphate adsorbed on waste iron sludge. The results are depicted in Fig. 1. They demonstrate the similar trend for all initial phosphate concentrations: initially the amount of phosphate adsorbed on waste iron sludge increases rapidly, then increases slowly with increasing adsorption time, and finally keeps approximately constant.



Fig. 1. Adsorption kinetics of phosphate on waste iron sludge at different initial phosphate concentrations (Conditions: 0.2 g adsorbent, 50mL solution, 150rpm stirring speed, 303K temperature, pH 7.0).

This indicated that the adsorption of phosphate on waste iron sludge was fast at initial stage of adsorption. This was because the abundantly unused active adsorption sites adsorbed swiftly phosphate from aqueous solutions at initial stage of adsorption. The adsorption rate, however, decreased gradually with increasing adsorption time. This was attributed to the sharp reduction of available adsorption sites. In addition, it was also observed from Fig. 1 that the initial adsorption rate increased with increasing initial phosphate concentration. This could be explained by the fact that high phosphate concentration accelerated the diffusion process of phosphate from bulk solution to the adsorbent surface [18]. Compared to high phosphate concentration (10 mg L⁻¹, 15 mg L⁻¹), the time required to reach adsorption equilibrium was shorter at low phosphate concentration (5 mg L^{-1}). This might be because the external surface of adsorbent played a major role at low phosphate concentration, resulting in shorter equilibrium time. On the other hand it took longer time for phosphate to diffuse high phosphate into the pores at concentration, leading to the longer time required to reach equilibrium. The uptake of phosphate increased rapidly with increasing phosphate concentration from 5 to 10 mg L⁻¹, also indicating that phosphate diffused into pore and the internal sites were made full use of. However, the uptake of phosphate increased slightly when concentration of phosphate varied from 10 mg L^{-1} to 15 mg L^{-1} , showing that the active sites had been exhausted.

Effect of initial pH of solution on kinetics

The value of solution pH is a key factor for adsorption due to affecting the chemical performances of adsorbent and adsorbate. In order to investigate the effect of initial pH of solution on the kinetics of phosphate adsorbed on waste iron sludge, experiments were performed at varying initial pH from 3.0 to 11.0 with 0.1 M HCl or 0.1 M NaOH solutions. The results were shown in Fig. 2.

Fig. 2 shows that the uptake of phosphate adsorbed on waste iron sludge varied indistinctly when pH of solution ranged from 5.0 to 7.0, showing phosphate could be well removed by waste iron sludge.



Fig. 2. Adsorption kinetics of phosphate on waste iron sludge at different initial pH of solution (Conditions: 10 mg/L phosphate concentration, 50mL solution, 0.2g adsorbent, 150rpm stirring speed, 318K temperature).

However, the uptake of phosphate decreased slightly with increasing pH of solution to 9.0. This could be explained by the concept of isoelectric point. The isoelectric point of iron or aluminum oxides/hydroxides was usually considered as around pH 8.0 [19, 20]. The surfaces of waste iron sludge were charged negatively at pH 9.0. The electrostatic repulsion between surface of adsorbent and phosphate ions in solution made it difficult that phosphate ions were adsorbed on waste iron sludge, resulting the decrease in uptake of phosphate. It was also observed from Fig. 2 that the uptake of phosphate decreased rapidly when pH of solution increased from 9 to 11. This might be because the hydroxyl ions competed for adsorption sites with phosphate ions besides electrostatic repulsion at pH 11.0. However, the uptake of phosphate increased swiftly with decreasing the value of pH from 4.0 to

3.0. Hydrogen ions interacting with the basic functional groups of iron sludge made it easier to remove phosphate by the chemistry chelating of ferric or ferrous ions at pH 3.0, causing the increase in uptake of phosphate. Although the efficacy of phosphate adsorbed on waste iron sludge depended on pH of solution (shown in Fig. 2), the time achieving the adsorption equilibrium at different pH of solution kept approximately identical. This implied that the kinetics of phosphate adsorbed on waste iron sludge was independent on the initial pH of solution.

Effect of temperature of solution

The effects of solution temperature on the kinetics of phosphate adsorbed on waste iron sludge were investigated by varying solution temperature from 293 K to 318 K. The results were given in Fig. 3.



Fig. 3. Adsorption kinetics of phosphate on waste iron sludge at different temperature of solution (Conditions: 10 mg/L phosphate concentration, 50mL solution, 0.2g adsorbent, 150rpm stirring speed, pH 7.0).

The rate of phosphate adsorbed on waste iron sludge increased rapidly with raising solution temperature from 293 K to 318 K at initial stage of adsorption. From a view of kinetics, the higher the solution temperature is, the faster the motion of phosphate ions in solution. This accelerated the diffusion rate of phosphate ions from bulk solution to surface of waste iron sludge, resulting in an increase in the rate of phosphate adsorbed on iron sludge. In addition, elevating solution temperature contributed to phosphate ions in solution gaining energy and becoming activated ions, accelerating reaction rate of adsorption. Meanwhile, the decrease in dynamic viscosity of water and resistance with increasing solution temperature made phosphate easy to diffuse from bulk solution onto surface of adsorbent [21]. This was also a reason causing the rapid increase in adsorption rate. Fig. 3 also demonstrated that for an identical time,

the uptake of phosphate adsorbed on waste iron sludge increased with elevating solution temperature. This might be because high temperature enhances phosphate penetration into the internal pores thus making internal adsorption sites fully used.

Kinetic model of phosphate adsorbed on waste iron sludge

Quantitatively data on kinetics of phosphate adsorption on waste iron sludge contribute to analyze and predict adsorption mechanism as well as to provide useful parameters for designing adsorption unit. Some frequently used kinetic model equations include pseudo first-order, pseudo second-order and Elovich ones.

Based on the assumption that the rate of change of adsorbed solute with time is proportional to the difference in equilibrium adsorption capacity and the adsorbed amount, the pseudo-first-order kinetic model [22] can be expressed by equation (2).

$$q_t = q_e \left[1 - \exp(-k_1 t) \right] \tag{2}$$

Where $q_e (mg g^{-1})$ is the amount of phosphate adsorbed on waste iron sludge at equilibrium; *t* (min) is adsorption time; $k_1 (min^{-1})$ is the rate constant of pseudo first-order model.

The pseudo second-order kinetic model [23] is based on the assumption that the rate-limiting step involves chemisorption which involved covalent forces through sharing or exchange of electrons between adsorbent and adsorbate, and is described by equation (3).

$$q_t = k_2 q_e^2 t / (1 + k_2 q_e t)$$
(3)

Where k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo second-order model.

The Elovich kinetic model [24] is a semiempirical model used to describe the chemical adsorptive behavior of adsorbate adsorbed on heterogeneous surface, and is given by equation (4).

$$q_t = \frac{1}{\beta} \ln\left(1 + \alpha\beta t\right) \tag{4}$$

Where α (mg g⁻¹ min⁻¹) is the initial adsorption rate constant; β (g mg⁻¹) is related to the extent of surface coverage and activation energy for chemisorption.

These three kinetic models were used to fit these experimental data of phosphate adsorbed on waste iron sludge under various environmental conditions in this study. All the model parameters and correlation coefficient (R^2) were evaluated by non-linear regression using OriginPro 8.5 software. The standard deviation was calculated by equation (5).

$$S.D. = \sqrt{\frac{\sum \left[(q_{t,\exp} - q_{t,cal}) / q_{t,\exp} \right]^2}{n-1}}$$
(5)

Here *n* is the number of data points, and $q_{t,exp}$ is the experimental value of uptake at time *t*, and $q_{t,cal}$ is the value of uptake calculated by kinetic model at time *t*. The fitted results are given in Table 1, and the validity of different kinetic models is evaluated by correlation coefficient and standard deviation.

It is shown in Table 1 that compared to the pseudo second-order and Elovich kinetic models, the values of correlation coefficient fitted by the pseudo first-order kinetic model are much smaller. However, the values of standard deviation are much larger. In addition, for the pseudo first-order model, equilibrium adsorption capacity obtained from experiments do not agree with the values calculated by model. These results show that the pseudo firstorder kinetic model do not describe well the kinetic process of phosphate adsorbed on waste iron sludge.

For the pseudo second-order and Elovich kinetic models, the correlation coefficients with high values $(R^2 > 0.98)$ are close and the standard deviations with small values are close too. The equilibrium adsorption capacity obtained from experiments perfectly agrees with the values by second-order pseudo model. These results demonstrate that the pseudo second-order and Elovich kinetic models can well describe the kinetic process of phosphate adsorbed on waste iron sludge, implying that chemical sorption occurres in the adsorption process

Diffusion mechanism of phosphate onto waste iron sludge

The removal process of pollutant adsorbed on adsorbent generally included three consecutive ratelimiting steps [25]: (1) pollutants from bulk solution crossed the boundary film formed around adsorbent to external surface of adsorbent, which was called as liquid film diffusion; (2) pollutants diffused from external surface into internal adsorption sites of pores, which was called as intra-particle diffusion; (3) pollutants were adsorbed onto adsorption sites. The influence of the third step on whole adsorption rate was usually negligible because of the fact that adsorption reaction was very fast. Thus the whole adsorption rate of pollutants adsorbed on adsorbent was generally controlled by the liquid film or/and intra-particle diffusion.

The intra-particle diffusion model [23] was expressed by equation (6).

$$q_t = k_{id} t^{1/2} + C_i (6)$$

e iron sludge.	ch model (1+abt)/b)	R ² S.D. (%)		4 0.9990 1.42	8 0.9985 4.07	6 0.9957 2.52		2 0.9962 2.20	3 0.9990 1.07	8 0.9986 1.61	0 0.9977 1.91	4 0.9945 4.60		2 0.9903 3.85	5 0.9962 2.34	1 0.9948 2.34
on wast	Elovi (qt=ln	β		7.716	5.427	5.339		6.364	5.094	4.697	4.594	4.366		7.414	6.813	5.529
ido first-order model, pseudo second-order model, and Elovich model of phosphate adsorbed		α		0.4506	1.3855	1.5124		202.1656	2.7719	1.2558	0.7553	0.1743		3.2111	5.9797	8.0229
	Pseudo second-order model (qi=(k2tqe²)/(1+k2qet))	S.D. (%)		4.97	7.91	3.84		2.28	4.44	6.36	4.34	9.99		5.15	5.50	3.89
		\mathbb{R}_2		0.9866	0.9899	0.9925		0.9967	0.9886	0.9803	0.9910	0.9720		0.9838	0.9832	0.9921
		k2 (g/(mg min))		0.0733	0.0564	0.9925		0.0874	0.0568	0.0479	0.0431	0.0300		0.1693	0.2289	0.4899
		qe,cal (mg/g)		0.917	1.437	1.476		2.015	1.647	1.610	1.542	1.317		1.190	1.365	1.704
	Pseudo first-order model $(q_i=q_e(1-exp(-k_it)))$	S.D. (%)		10.10	11.95	8.78		5.61	8.89	11.25	9.75	16.93		8.34	9.46	7.94
		\mathbb{R}^2		0.9405	0.9497	0.9562		0.9777	0.9489	0.9292	0.9496	0.9174		0.9462	0.9450	0.9622
		kı (1/min		0.9405	0.0542	0.0534		0.0903	0.0610	0.0525	0.0458	0.0275		0.0667	0.0748	0.0716
		qe,cal (mg/g)		0.836	1.324	1.363		1.921	1.526	1.477	1.409	1.184		1.102	1.269	1.588
ole 1. Pseu		qe (mg/g)		0.914	1.450	1.485		2.014	1.650	1.613	1.525	1.362		1.175	1.380	1.696
Tab	Factors		$C_0(mg/L)$	S	10	15	Ha	ю	5	7	6	11	T(K)	293	303	318

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Where k_{id} (mg g⁻¹ min^{-1/2}) was the intra-particle diffusion rate constant, and C_i represented the boundary layer effect which meant that the larger the intercept was, the greater the contribution of the surface sorption in the rate controlling step.

Based upon the intra-particle diffusion theory, the intra-particle diffusion was the only rate limiting step of adsorption process if the plot of q_t against $t^{1/2}$ was a straight line and passed the origin, otherwise, other steps along with intra-particle diffusion might be also involved.

In order to interpret the diffusion removal process of phosphate from bulk solution onto waste iron sludge, the intra-particle diffusion model was used to fit the experimental data of kinetics at different initial phosphate concentrations (5 mg L⁻¹ and 10 mg L⁻¹) in this study. The results are presented in Fig. 4 and Table 2. The fitted results demonstrate that the plots of q_t versus $t^{1/2}$ are not linear within the whole adsorption time, but each plot is divided into two segments and each segment gives a good linear form. However, all these lines do not pass through the origin. These results above imply that the intra-particle diffusion is not the only rate-limiting step and other diffusion process, such as liquid film diffusion, affects the adsorptive rate of phosphate adsorbed on waste iron sludge.



Fig. 4. Plots of intra-particle diffusion model for the adsorption of phosphate on waste iron sludge at different initial phosphate concentrations.

In order to ascertain the factual rate-limiting step during the process of phosphate adsorbed on waste iron sludge, Boyd model was used to further fit the kinetic data at different initial phosphate concentrations. The Boyd model [26] was given by equation (7).

$$Bt = -0.4977 - \ln(1 - \frac{q_t}{q_e}) \tag{7}$$

Where *B* is a constant.

The value of Bt at different adsorption time t was calculated by equation (7), and the values of Btwere plotted against t. Based on the Boyd model it must be expected that the adsorption process on is controlled by the intra-particle step if the plots of Btversus t were linear and passed through the origin. Otherwise, the adsorption rate must be controlled by the liquid film diffusion.

The results fitted by the Boyd model are given in Fig. 5 and Table 3. Fig. 5 demonstrates that although Boyd plots give well straight lines at different initial phosphate concentration, they both do not pass through the origin, implying that the adsorption rate of phosphate on waste iron sludge was dominantly controlled by the liquid film diffusion. The value of B was obtained from the slope of the plot of Bt versus t, and they were also listed in Table 3. It was observed from Table 3 that the values of B at different initial phosphate concentrations were much smaller than 1, further verifying that the removal rate of phosphate adsorbed on waste iron sludge was mainly affected by the liquid film diffusion [27].



Fig. 5. Boyd plots of phosphate adsorbed on waste iron sludge at different initial phosphate concentrations.

 Table 2. Constants and correlation coefficients of intra-particle diffusion model for phosphate adsorption on waste iron sludge

C	Intra-particle diffusion model									
(mg/L)	K _{id1} (mg/(mL min ^{1/2}))	C ₁	R ²	$\frac{K_{id2}}{(mg/(mL min^{1/2}))}$	C ₂	\mathbb{R}^2				
5	0.0436	0.3514	0.9480	0.0201	0.5577	0.9829				
10	0.0655	0.6173	0.9764	0.0228	1.0212	0.9583				

Apparent activation energy of adsorption

The conventional thermodynamic parameters, such as standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0), cannot describe the reaction rate of adsorption. An empirical equation of Arrhenius type [28], shown in Equation (8) is given to describe the relation of temperature and the constant of reaction rate.

$$\ln(k_2) = \ln A - \frac{E_a}{RT} \tag{8}$$

Where k_2 (g·mg⁻¹·min⁻¹) was the rate constant obtained from the pseudo second-order kinetic model, E_a (kJ·mol⁻¹) was the apparent activation energy of adsorption, T (K) was the absolute temperature of solution, R (8.314 J·mol⁻¹·K⁻¹) was the molar gas constant and C was a constant.

According to equation (8), a straight line of $\ln(k_2)$ against 1/T can be obtained, and the value of E_a can be calculated by the slope of the straight line above. The magnitude of apparent activation energy of adsorption can give an idea what control the reaction rate of adsorption. The experimental data of kinetics at different temperature of solution (shown in Table 1) were used to calculate the apparent activation energy of phosphate adsorbed on waste iron sludge (shown in Fig. 6). Fig. 6 showed that the plot of ln(k₂) against 1/T gave a good straight line (R²=0.9770). The apparent activation energy of phosphate adsorbed on waste iron sludge calculated by the slope $(k_{slope}=-4017.1)$ was 33.40 kJ·mol⁻¹, indicating that chemical reaction was not the only rate-limiting step and diffusion (liquid film and pore diffusion) was involved within the whole adsorption process [29]. These were consistent with the results of kinetics and diffusion mechanism studies.



Fig. 6. Arrhenius plot of phosphate adsorbed on waste iron sludge.

CONCLUSION

The present study showed that the kinetics of phosphate adsorbed on waste iron sludge was affected to varying degrees by various environmental factors. The initial adsorption rate increased with increasing the phosphate concentration. The shorter time, however, was required to reach adsorption equilibrium at low phosphate concentration due to external surface adsorption. Although the efficacy of phosphate adsorbed on waste iron sludge depended on pH of solution significantly, the adsorption kinetics was relatively independent on pH of solution. Elevating solution temperature contributed to accelerating reaction rate of adsorption and raising the uptake of phosphate adsorbed on waste iron phosphate adsorbed on waste iron sludge depended on pH of solution significantly, the adsorption kinetics was relatively independent on the solution pH.

Elevating solution temperature contributed to accelerating reaction rate of adsorption and raising the uptake of phosphate adsorbed on waste iron sludge. Both pseudo-second-order and Elovich kinetic models could well describe the kinetic process of phosphate adsorbed on waste iron sludge. The intra-particle diffusion and chemisorptions occurred in whole adsorption process, but the liquid film was the dominant rate-limiting step.

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КИНЕТИКА НА АДСОРБЦИЯТА НА ФОСФАТИ ОТ ВОДНИ РАЗТВОРИ ВЪРХУ ОТПАДЪЧНА ЖЕЛЯЗНА ТИНЯ

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(Резюме)

Изследвана е кинетиката адсорбцията на фосфати върху отпадъчна желязна тиня. Проведени са статични експерименти в периодичен режим при различни начални концентрации, стойности на pH и температури. Началните скорости на адсорбция нараства с нарастване концентрацията на фосфати. По-кратки времена са нужни за достигане на равновесие при по-ниски концентрации на фосфати поради адсорбцията на външна повърхност. Въпреки че ефективността на адсорбция зависи значително от pH на разтвора, кинетиката остава относително независима от pH. Повишението на температурата води до повишаване скоростта на адсорбция и повишаване на усвояването на фосфатите, адсорбирани от желязната тиня. Кинетиката на адсорбция може да се опише добре както с уравнение от псевдо-втори порядък, така и с кинетичния модел на Елович, показвайки възможността за хемисорбция. Симулационните експерименти по модела на Бойд и с вътрешна дифузия и адсорбция показват, е налице вътрешна дифузия, но масопренасянето в течния граничен слой е скоросто-определящия стадий. Определената привидна активираща енергия на адсорбция (33.40 kJ·mol⁻¹) също показва, че химичната реакция не е единствения скоросто-определящ стадий и че дифузията има влияние върху цялостния процес на адсорбция.