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Isotherm and Kinetics of Fe(II) Adsorption onto Chitosan in a Batch Process

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Abstract: In this study removal of Fe(II) by chitosan adsorbent was experimentally investigated in a batch system. The adsorbent dose and pH of the metal solution was fixed at 0.15 g and 4, respectively. Adsorption experiments were carried out at initial concentration range of 10–50 mg lG^1 at 20°C. Equilibrium studies showed that experimental data were well fitted to Langmuir–Freundlich isotherm model. Linear and non-linear forms of pseudo-first-order and pseudo-second-order kinetic models were employed to describe the kinetic adsorption processes. The model parameters were confidently recovered. The kinetics followed the non-linear form of pseudo-first-order model which represents adsorption of Fe(II) on chitosan takes place through a physical process. The examination of kinetic data also revealed that the adsorption rate was dominated by intra-particle diffusion mechanism.

Key words: Chitosan % Intraparticle diffusion % Iron removal % Isotherm models % Pseudo-first-order % Pseudo-second-order

INTRODUCTION

Contamination of water by heavy metal is rapidly increasing in recent years due to extensive industrial and agricultural activities. Besides due to the pollution of environment by these materials, they have harmful effects on human body. Iron can be found in the wastewater streams in large amounts due to its extensive application in many different industries. Although micronutrients are essential for animals and plants, but they become very toxic at high concentrations [1, 2]. Different methods have been used to remove iron from aqueous solutions such as Electrocoagulation[3], ion exchange [4], precipitation [5], extraction [6], membrane technologies [7], adsorption [8], etc. Cost, complexity and efficiency are important factors that affect selection of method for eliminating metal ions from water and waste water [9]. Adsorption technology has been considered as an economical, efficient and promising technology in wastewater treatment for removal of metal ions [10]. Choosing a proper adsorbent plays an important role in the efficiency of adsorption process. Many new

type or traditional adsorbents have been tested in different conditions for this purpose [11, 12]. Chitosan is an effective natural macromolecule adsorbent [13]. It has a great tendency to eliminat metal ions due to large number of carboxylic and amino groups in its structure [14]. Chitosan and its derevetives have been used extensively in adsorption of heavy metals such as Fe (III), Cu (II) and Pb (II) [1], As (III) [15], Hg (II)[16] , Co(II) and Ni(II) [17].

The main objective of the present study was to compare different kinetic models for describing the removal of Fe(II) by chitosan to investigate the adsorption mechanism. Also equilibrium data were analyzed in terms of different isotherm models and model parameters were recovered using a nonlinear fit of experimental data to the model equation.

MATERIALS AND METHODS

Materials: Chitosan with minimum 85% deacetylation was purchased from Sigma-Aldrich (USA). All other chemicals used in this study were purchased from Merk (Germany).

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All reagents were analytic grade and used without further purification. Stock solution of 1000 mg lG[1] of Fe(II) ions was prepared using crystallic heptahydrate ferrous sulfate salt. The stock solution was diluted to give the appropriate concentrations when necessary. Distilled water was used to prepare all the solutions.

Batch Experiments: Batch adsorption experiments were conducted in 250 ml beakers with 100 ml of iron solution. The mixture was equilibrated with chitosan at 180 rpm in incubator shaker (model KS 4000i control, IKA) for 240 min. All experiments were conducted at 20°C. Equilibrium studies were carried out by mixing 0.15 g of sorbent with solutions at pH 4. Initial concentrations of metal solution varied from 10 to 50 mg lG[1]. Samples were taken at fixed time intervals to determine solution concentration. The samples were filtered with 0.45 ìm syringe filter to remove the adsorbent. Iron concentrations in the filtrates were analyzed by using a UV–Vis Spectrophotometer (model 2100 SERIES, UNICO), at 8_{max}=425 nm, according to the 5-sulfosalicylic acid (SSA) method [18].

The amount of metal ion adsorbed by chitosan was calculated according to the following equation [19]:

$$q_e = \frac{C_0 V_0 - C_e V_e}{m} \qquad (1)$$

Where q is the concentration of Fe(II) in solid phase which is known as metal uptake capacity (mg gG[1]), C_0 and C_e are the initial and final metal concentrations (mg lG[1]), V_0 and V_e denotes the initial and final volume (l) respectively and finally m represents the mass of used adsorbent (g).

RESULT AND DISSCUSION

Adsorption Isotherms: The experimental adsorption isotherm is a plot that shows the amount of equilibrium uptake versus the concentration of ion in the solution at the equilibrium state. This was obtained at different temperatures by changing initial Fe (II) concentration from 10 to 50 mg lG[1].

It was observed that the ferrous ion adsorption capacity increased with increasing its concentration. In fact at higher initial concentration, available adsorption sites would be surrounded by more metal ions, therefore metal ions not only adsorbed in a monolayer at the outer interface of chitosan, but also it diffuses within chitosan particles. As a result, the sorption of ions would be carried out more sufficiently. This is a common observed phenomenon refered ferequently in adsorption literature [20, 21].

Equilibrium adsorption data were correlated with Langmuir, Freundlich and Langmuir–Freundlich isotherms. Langmuir model is a widely used model in adsorption. The basic idea behind this model is the coverage of the surface by a monomolecular layer. This model is determined as:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \qquad (2)$$

Equation (3) represents Freundlich isotherm which is used for the adsorption on a heterogeneous surface with uniform energy:

$$q_e = k_F C_e^{1/n} \qquad (3)$$

Langmuir–Freundlich model is a three parameter model expressed by equation (4). This model can be used in the case of failure of the two-parameter isotherm models in describing the adsorption data [22].

$$q_e = \frac{q_m (k_{L.F} C_e)^b}{1 + (k_{L.F} C_e)^b} \qquad (4)$$

Where q_e is the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg gG[1]), C_e is the equilibrium metal concentration in solution (mg lG[1]), q_m is the maximum uptake of adsorbate (mg gG[1]), k_L and k_F and $k_{L.F}$ are the Langmuir, Freundlich and Langmuir–Freundlich equilibrium constants, respectively. 1/n is heterogeneity coefficient and b is a coefficient in Langmuir–Freundlich model.

As it can be seen in Fig. 1., all three models can fit experimental data well.

The model parameters are listed in Table 1. According to regression coefficient, data exhibit the best fit to the Langmuir–Freundlich model. Values of 1/n parameter in Freundlich model lie between 0 and 1 indicating favorable adsorption.

The equilibrium constant of the Langmuir isotherm model can be expressed in terms of a dimensionless separation factor (R_L). This factor is used to predict the favorability of adsorption process. R_L is determined as follows:

$$R_L = \frac{1}{(1 + k_L C_i)} \qquad (5)$$

These values indicate the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L obtained for adsorption of Fe (II) onto chitosan is shown in Table 1. All the values of R_L lie at range 0-1, indicating favorable adsorption of Fe (II) ions onto chitosan.

Table 1: Adsorption isotherm constants for Fe(II) ions adsorbed by chitosan

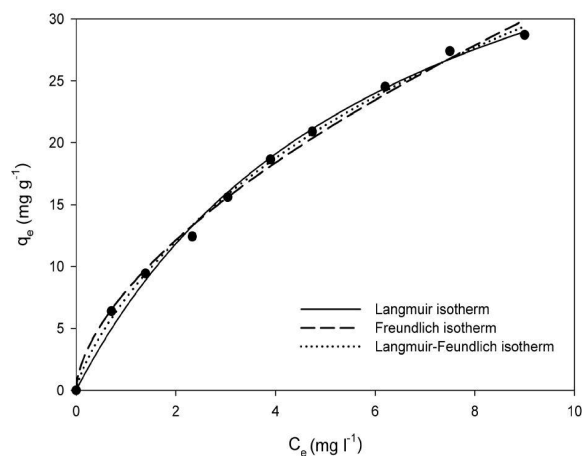| Langmuir				Freundlich			Langmuir-Freundlich			
k_L	q_m	R^2	R_L	k_F	n	R^2	k_{LF}	q_m	b	R^2
0.1574	49.40	0.9953	0.11-0.38	8.0027	1.66	0.9955	0.0554	80.27	0.78	0.9972

Fig. 1: Sorption isotherms of Fe(II) onto chitosan fitted to the Langmuir ,Freundlich and Langmuir – Freundlich models at 20°C.

Adsorption Kinetics: Kinetics study is an important part of researches in adsorption area because the mechanism of the process can be realized by kinetic constants. Knowledge about kinetic parameters provides valuable insight into the reaction pathway. As well the rate of adsorption which controls the resistance time is determined by kinetics [23]. In the present study,three different kinetic models have been used to fit the experimental rate data.

Pseudo-first-order Kinteic Model: The pseudo-first-order rate expression of Lagergren is a widely used kinetic model for adsorption data analysis. This kinetic model is used for reversible reaction with an equilibrium being

established between liquid and solid phases [24]. it is represented by [25],

$$\frac{dq}{dt} = k_1(q_e - q) \tag{6}$$

Integrating Eq. (6) for the boundary conditions *t = 0* to *t = t* and *q = 0* to *q = q_t* , results to the following Eq. ,

$$\ln\frac{(q_e - q_t)}{q_e} = -k_1 t \tag{7}$$

Which may be rearranged to form,

$$q_t = q_e(1 - e^{-k_1 t}) \tag{8}$$

Where q_t is the metal uptake capacity (mg g⁻¹) at any time t, q_e denotes the metal uptake capacity (mg g⁻¹) at equilibrium and k_1 (min⁻¹) is the the observed rate constant of pseudo-first-order kinetic model. Azizian [26] reported that k_1 is not the intrinsic adsorption rate constant which was mistakenly reported in the literature. He explained that it is a combination of adsorption (k_a) and desorption (k_d) rate constants.

Eq (8) may also be rearranged to obtain a linear form,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{9}$$

k_1 and q_e values will be obtained by plotting log (q_e–q_t) versus t. It is obvious that in the absence of experimentally determined q_e values, Eq. (9) may not be applicable [27].

Table 2: Pseudo-first-order kinetic parameters for Fe(II) ions adsorption by chitosan

| C_0 (mg l⁻¹)	$q_{e,exp}$ (mg g⁻¹)	Linear form			Non-linear form		
		q_e (mg g⁻¹)	k_1 (min⁻¹)	R^2	q_e (mg g⁻¹)	k_1 (min⁻¹)	R^2
10	6.39	4.720630	0.029478	0.9592	6.2901	0.0442	0.9883
15	9.43	9.774623	0.038000	0.9947	9.6936	0.0334	0.9976
20	12.41	14.38467	0.041454	0.9792	12.8161	0.0316	0.9959
25	15.59	13.39368	0.029018	0.9796	15.6309	0.0347	0.9934
30	18.64	18.38654	0.026485	0.9798	19.0641	0.0251	0.9939
35	20.9	20.59207	0.019576	0.9774	21.8722	0.0177	0.9676
40	24.51	23.99938	0.027636	0.9927	24.559	0.0285	0.9878
45	27.4	27.37789	0.023951	0.9957	27.9328	0.0231	0.9969
50	28.71	28.26181	0.016812	0.9937	29.7977	0.0162	0.9955
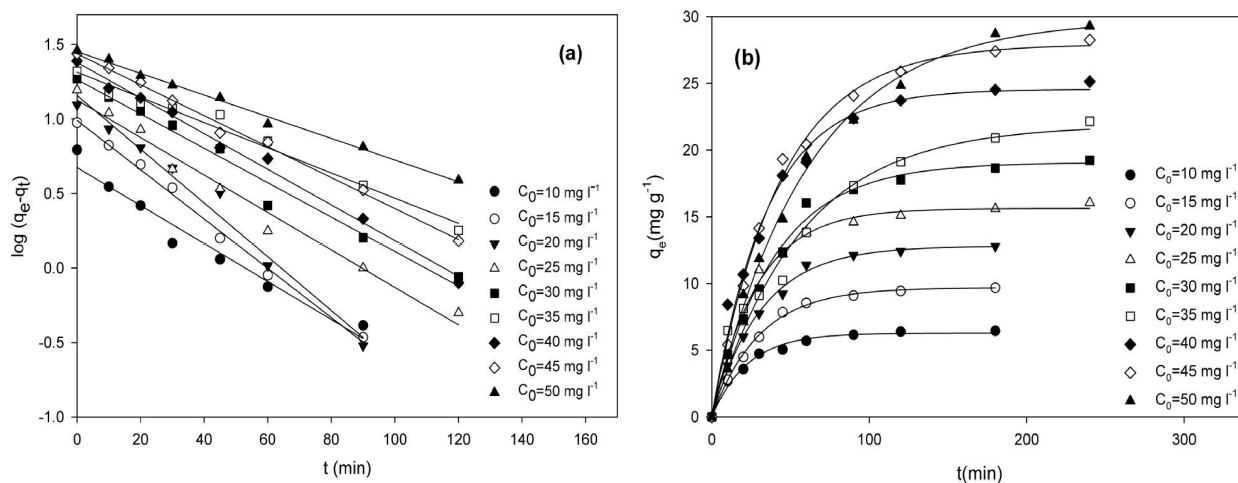
Fig. 2: Pseudo-first-order kinetic model of Fe(II) adsorption on chitosan, (a) linear and (b) non-linear form.

Fig. 2. shows kinetic data fitted to Eqs. (8) and (9).

Model parameters are presented in Table 2. Non-linear form of pseudo-first-order kinetic model gives a better fit to the experimental data due to higher correlation coefficient. Also equilibrium sorption capacity predicted by non-linear form is more reasonable almost in all different concentrations and it is in agreement with the experimental q_e values.

Pseudo-Second-Order Kinteic Model: Most of the sorption systems followed a pseudo-second-order kinetic model which is based on the assumption that the rate-limiting factor may be chemisorptions [24]. In chemisorptions (chemical adsorption), the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [28]. In other words chemisorption involves valence forces through sharing or exchange of electrons between the metal ions and the adsorbent. The rate law for this system is expressed as [25],

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{10}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, gives,

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{11}$$

Eq. (11) may be rearranged to form following Eq.,

$$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t} t \tag{12}$$

As mentioned before, q_t and q_e are the metal uptake capacity (mg g⁻¹) at any time t and at equilibrium. Azizian [26] also reported that k_2 (g mg⁻¹ min⁻¹) is the observed rate constant of the pseudo-second-order model which is a complex function of the initial concentration of solute. Linearized form of Eq. (12) is determined as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{13}$$

The plot of t/q_t as a function of t yields a straight line from which k_2 and q_e are calculated. Fig. 3. shows two forms of pseudo-second-order kinetic model.

From Table 3, it can be observed that the calculated kinetic parameters and their corresponding R^2 values do not vary for the two forms of the pseudo-second-order kinetic model. But it should be noted that different linear forms of the same model would significantly effect on obtained values of parameters, for example Yuh-Shan Ho [29] examined four linear forms of pseudo-second-order equations to fit the kinetic sorption data. As a result using linear regression method is not appropriate for comparing the best-fitting and Non-linear method is a better way to find the kinetic parameters.

From Table 2 and Table 3, high correlation coefficients (R^2) of non-linearized form of two models show that both of them can well describe experimental data. However, the difference between the experimental adsorption capacity of Fe(II) and the value predicted from the pseudo-first-order model was considerably lower than

Table 3: Pseudo-second-order kinetic parameters for Fe(II) ions adsorption by chitosan

| C_0 (mg l^{-1})	$q_{e,exp}$ (mg g^{-1})	Linear form			Non-linear form		
		q_e (mg g^{-1})	k_2 (gmg^{-1} min^{-1})	R^2	q_e (mg g^{-1})	k_2 (gmg^{-1} min^{-1})	R^2
10	6.39	7.022472	0.008339	0.9992	7.265233	0.00768	0.9952
15	9.43	11.31222	0.003478	0.9933	11.69863	0.00312	0.9873
20	12.41	15.01502	0.002500	0.9946	15.49422	0.002233	0.9903
25	15.59	17.69912	0.002512	0.9967	18.13636	0.002305	0.9849
30	18.64	22.42152	0.001273	0.9943	23.02214	0.001177	0.9856
35	20.9	26.73797	0.000732	0.9807	27.26519	0.000664	0.9766
40	24.51	28.32861	0.001268	0.9974	28.85714	0.001164	0.9917
45	27.4	33.89831	0.000693	0.9936	34.14108	0.000706	0.9916
50	28.71	39.68254	0.000338	0.9783	38.40397	0.000393	0.9943
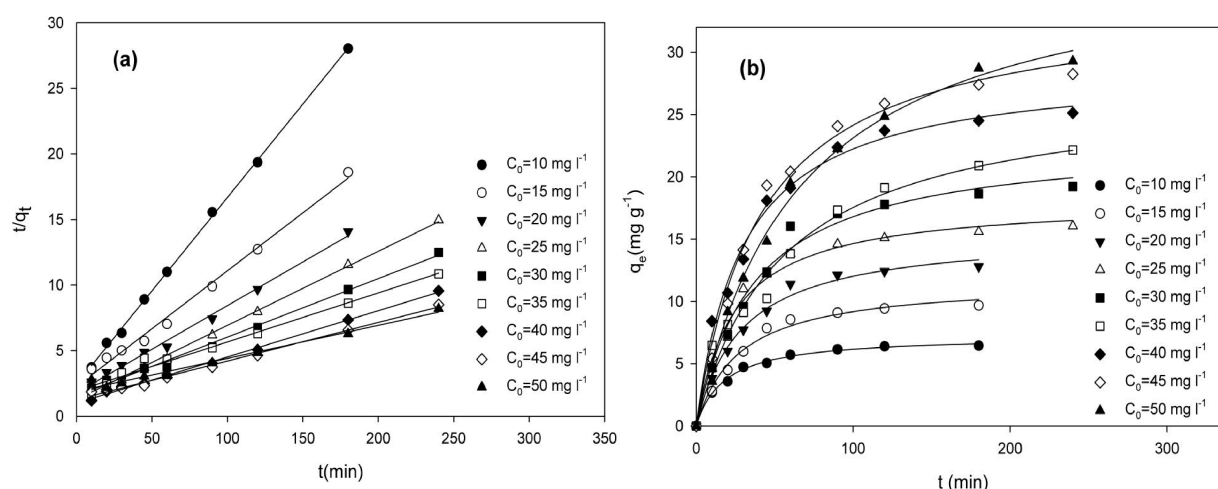
Fig. 3: Pseudo-second-order kinetic model of Fe(II) adsorption on chitosan, (a) linear and (b) non-linear form.

those predicted by the pseudo-second-order. Hence, in this study the non-linearized form of pseudo-first-order model can be considered as a more suitable kinetic model to describe Fe(II) adsorption. So the adsorption of Fe(II) onto chitosan may take place through a physical process.

Intraparticle Diffusion Model: Since pseudo-first-order and pseudo-second-order equations can not identify the diffusion mechanisms, the intraparticle diffusion model was also tested. Such plots may present a multilinearity, indicating that two or more steps are taking place. The rate determining step of adsorption reaction may be external film diffusion, intraparticle diffusion or interaction step. The first, sharper portion is the external surface sorption or instantaneous sorption stage. The external film diffusion is usually eliminated by stirring. So the adsorption rate may be controlled by other steps. In the second portion which is the gradual sorption stage, intraparticle diffusion controls the rate. The third portion is the final equilibrium stage where intraparticle diffusion
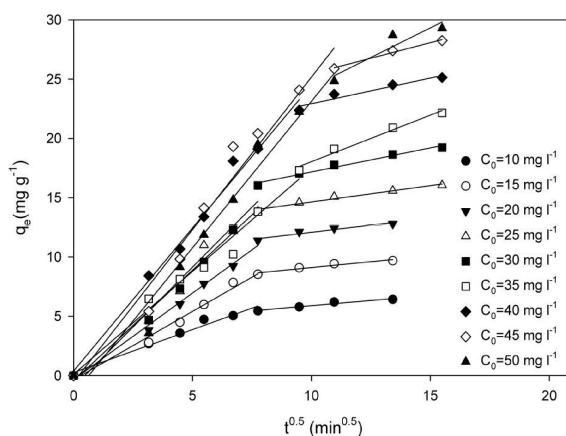

Fig. 4: Intraparticle diffusion kinetic model for the adsorption of Fe(II) on chitosan.

starts to slow down because of extremely low adsorbate concentrations in the solution. In fact the metal ions are slowly transported via intraparticle diffusion into the particles and are finally retained in micropores [30, 31]. This model is presented as,

Table 4: Intraparticle diffusion kinetic model parameters for Fe(II) ions adsorption by chitosan

C_0 (mg l^{-1})	k_{id1} (mg g^{-1}min$^{-1/2}$)	R^2	k_{id2} (mg g^{-1}min$^{-1/2}$)	R^2
10	0.7239	0.9745	0.1749	0.9523
15	1.1540	0.9865	0.1985	0.9290
20	1.4593	0.9931	0.2410	0.9313
25	1.8656	0.9777	0.2763	0.9688
30	2.0203	0.9741	0.4069	0.9774
35	1.7365	0.9779	0.7854	0.9788
40	2.4132	0.9893	0.4319	0.9303
45	2.5726	0.9703	0.5239	0.9872
50	2.4703	0.9742	0.9991	0.8789

$$q_t = k_{id}\, t^{0.5} \qquad (14)$$

Where k_{id} is the intra-particle diffusion rate constant (mg g^{-1}min$^{-1/2}$).

As Fig. 4. shows, the external surface sorption (stage 1) is absent because of fast completion. All plots have same general features, initial linear portion (stage 2) followed by second linear portion (stage 3).

The recovered intraparticle rate constants as well as regression correlation coefficients are presented in Table 4. It is obvious that the intraparticle diffusion model fits the experimental data well for an initial period (stage 2) of the adsorption process with respect to higher correlation coefficient.

CONCLUSION

Removal of Fe(II) from aqueous solution by adsorption onto chitosan adsorbent was carried out at a constant temperature. Equilibrium studies revealed that Langmuir–Freundlich hybrid isotherm can describe equilibrium data better than Langmuir and Freundlich models. Linear and non-linear forms of pseudo-first and pseudo-second-order kinetic models were applied to fit the kinetic data. It cab be concluded that non-linear forms of kinetic models are more acceptable with respect to higher correlation coefficients. Finally results showed that metal uptake capacity values predicted by non-linearezed form of pseudo-first-order kinetic model was closer to experimental ones. As well intra-particle diffusion model was applied to identify the mechanism of transport. The results demonstrated that pore diffusion and surface diffusion occur in parallel within chitosan particles during adsorption.

Nomenclature:

b Langmuir-Freundlich isotherm constant
C_0 Initial metal concentrations (mg l^{-1})
C_e Equilibrium metal concentrations (mg l^{-1})

k_1 Observed rate constant of pseudo-first-order kinetic model (min^{-1})
k_2 Observed rate constant of pseudo-second-order kinetic model (g mg^{-1}min^{-1})
k_a Adsorption rate constant
k_d Desorption rate constant
k_F Freundlich equilibrium constant (mg g^{-1} (l mg^{-1})$^{1/n}$)
k_{id} intra-particle diffusion rate constant (mg g^{-1}min$^{-1/2}$)
k_L Langmuir equilibrium constant (l mg^{-1})
k_{LF} Langmuir–Freundlich equilibrium constant (l mg^{-1})
m Mass of used adsorbent (g)
n Freundlich isotherm constant
q_e metal uptake capacity at equilibrium (mg g^{-1})
$q_{e\,exp}$ experimental value of adsorption capacity at equilibrium (mg g^{-1})
q_m Maximum uptake capacity obtained by models (mg g^{-1})
q_t Metal uptake capacity at any time t (mg g^{-1})
R_L Separation factor
R^2 Correlation coefficient
V_0 Initial volume of the solution (l)
V_e Final volume of the solution (l)
t Time (min)
T Solution temperature (°C)

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