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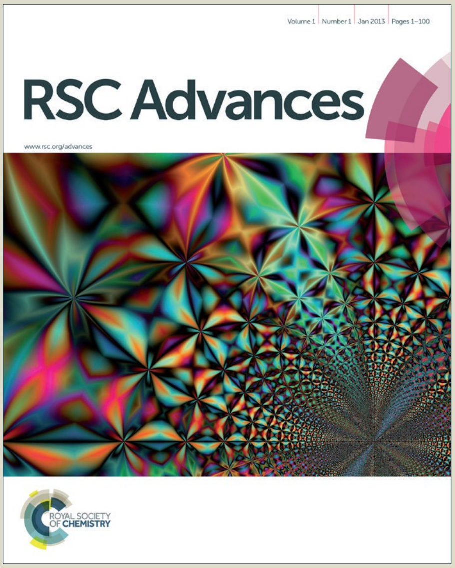

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Adsorption of EDTA onto calcium oxalate monohydrate

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Abstract: Adsorption of EDTA onto calcium oxalate monohydrate crystals was investigated and the adsorption characteristics were analyzed. Experiments were carried out to study the effects of such factors as contact time, initial concentration of EDTA, temperature and solution pH on the EDTA adsorption. The experimental results showed that the EDTA adsorption on calcium oxalate monohydrate crystals increased with its initial concentration in the aqueous solutions. High temperature was beneficial to the adsorption process. However, the adsorption capacity of EDTA on calcium oxalate monohydrate crystals decreased as the pH increased from 5 to 8. The kinetic data fitting analysis suggested the pseudo-second-order kinetic model described the adsorption process better. The adsorption equilibrium data analysis indicated that the Langmuir isotherm model fit better than the Freundlich isotherm model, based on the R^2, RMSE and χ^2 values. Thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 for EDTA adsorption had also been estimated. The results demonstrated that the adsorption nature was feasible, spontaneous and endothermic. This study would provide a foundation for the modification of the oxalate-degrading enzyme using EDTA or its derivatives, in order to endow the enzyme with the adsorption ability of calcium oxalate stones.

Keywords: Adsorption; EDTA; Calcium oxalate monohydrate; Adsorption kinetics; Isotherms; Thermodynamics

1. Introduction

Due to the high prevalence of urinary calculi and high recurrence rates, urolithiasis is a major health problem and associated with a high cost to society [1]. About 13% of men and 7% of women experience urolithiasis in their lifetime [2], and as high as 70% of the calculus recurs after treatment [3]. Calcium oxalate (CaOx) is the most common constituent of urinary calculi. Studies show that about 70% ~ 80% of calcium stones are calcium oxalate stones [3-5]. Calcium oxalate crystals exist in monohydrate, dihydrate and trihydrate form, and the CaOx monohydrate (COM) is the stable form of thermodynamics [6]. Researches have announced that the risk factors of CaOx stone formation are associated with low urine volume, hypercalciuria, hyperoxaluria, hypocitraturia, hyperuricosuria and high urine sodium [3]. Moreover, it has also been found that obesity, diabetes, hypertension, hyperlipidemia may be correlated with stone formation [7-9]. With this rising prevalence and high recurrence rates, it is very urgent to take effective approaches for stone prevention and treatment.

At present, the treatment of prevalence and recurrence of CaOx stones is majorly carried out by dietary modifications, drug therapies and other physical therapies, but the curative effect is unsatisfactory [4]. An important reason leads to CaOx calculi is the lack of oxalate-degrading metabolic pathways in human body, thus the studies of using of oxalate-degrading enzyme for CaOx stones prevention become a research hotspot. Oxalate-degrading enzymes with the bio-catalytic activities for degradation of oxalate and oxalic acid have been classified into three categories: oxalate decarboxylase (OXDC, EC 4.1.1.2), oxalate oxidase (OXO, EC 1.2.3.4) and oxalyl-CoA decarboxylase (EC 4.1.1.8) [10]. Study of Thalji *et al.* [11] indicated that the solubility increased about 15-fold by adding 200 μg OXDC to CaOx monohydrate crystals because the enzyme degraded oxalate in the solution. Grujic *et al.* [12] investigated oral therapy with a crystalline of OXDC (cross-linked formulation) on the lab mice, they found that oral therapy with 200 mg OXDC can reduce both urinary (44%) and fecal oxalate (72%), which suggested that oral therapy with OXDC could reduce hyperoxaluria and prevent urolithiasis. However, one problem, in practical application, is that the concentration of the enzyme agent will be rapidly diluted in urinary system under the flow state. Therefore, it is anticipated to modify the oxalate-degrading enzyme with some kinds of CaOx crystals affinity groups and make it a bifunctional enzyme, which has the capacity of strong adsorption on CaOx crystals and the ability catalyzed the degradation of oxalate.

Ethylenediaminetetraacetic acid (EDTA), an aminopolycarboxylic acid with a hexadentate (six-toothed) ligand, is used as anthropogenic chelating agent for its high ability to sequester metal ions such as Ca^{2+} and Mn^{2+}. It is widely applied to rubber, textile, and electroplating, photographic, medicine, paper-making and cosmetic industries as well as in household cleaning chemicals. In the previous study of our group, it showed the EDTA can adsorb on the CaOx monohydrate crystals more strongly than the other molecules being screened, and should be an candidate molecule for purpose of OXDC modification. However, the adsorption of EDTA on CaOx crystals in aqueous solutions has not been reported until now. The aim of this work is to explore the adsorption characteristics and mechanism of EDTA onto CaOx monohydrate crystals. The effect of such experimental factors as contact time, initial concentration of EDTA, temperature and solution pH was investigated. The kinetics of EDTA adsorption was analyzed by fitting kinetic models (including pseudo-first-order, pseudo-second-order and intraparticle diffusion models). Adsorption thermodynamic parameters including the Gibbs free energy and enthalpy and entropy were studied. Langmuir isotherm model and Freundlich isotherm model were used to fit the adsorption equilibrium data and error analysis was also carried out to test adequacy and accuracy of the model equations.

2. Materials and methods

2.1. Materials

High Performance Liquid Chromatography (HPLC) analysis was conducted in the Agilent 1260 Infinity Quaternary LC which purchased from Agilent Technologies Inc. CaOx monohydrate was purchased from Tianjin Damao Chemical reagent Factory. The specific surface area of CaOx monohydrate (employing BET method) was determined using a JW-004 Specific Surface Area Analyzer (Beijing JWGB Sci. &Tech. Co., Ltd, China) using N_2 as the adsorbate and was found to be 2.65 m^2/g. The point of zero charge (pH_{pzc}) of CaOx monohydrate was determined by mass titration [13] and found to be about 2.9 ± 0.25. Ethylenediaminetetraacetic acid disodium salt dehydrate ($Na_2H_2EDTA{\cdot}2H_2O$) was obtained from Beijing seaskybio technology Co., Ltd. Water was purified with a Synergy® Water Purification Systems (Merck Millipore, Germany). In this work, Measured amount of $Na_2H_2EDTA{\cdot}2H_2O$ was dissolved into ultrapure water to make up EDTA stock solution. All other reagents were of analytical reagent grade. The glassware soaked by 12 h in 0.1 mol/L NaOH and then washed by ultrapure water was used in all experiments.

2.2. Methods

2.2.1. Adsorption experiments

A saturated aqueous solution of CaOx at pH 5 was prepared by adding 10 g of CaOx monohydrate to Erlenmeyer flask containing 250 mL water. The flasks were agitated at 37 ℃ for 1 day in a rotary shaker, adjusting the pH to 5 using Mettler-Toledo DELTA 320 pH meter with 0.1 mol/L HCl or 0.1 mol/L NaOH solutions, then leaving the solutions to stand for a further 2 days to equilibrate. The residual CaOx crystals were separated by vacuum filtration through a 0.45 μm membrane filter (mixed cellulose ester) and discarded.

Adsorption experiments were carried out by varying pH, contact time, initial concentration of EDTA and temperature under the aspects of kinetic study, adsorption isotherms and adsorption thermodynamics. In 100 mL-stoppered Erlenmeyer flasks, 1 g of CaOx monohydrate adsorbent was added to 20 mL saturated aqueous solutions of CaOx, and then the EDTA was added to a series of final concentration (100 - 1000 mg/L). The initial solution pH was adjusted to the range from 5 to 8 with either 0.1 mol/L HCl or 0.1 mol/L NaOH. The flasks were placed in a rotary shaker and incubated at 25, 32, 37, 45 °C with gentle stirring for the required time period (during 12 h). The solutions were centrifuged by a centrifuge (Thermo Scientific Sorvall ST 16R, Germany) at 12000 rpm for 10 min and the supernatants were filtered and analyzed for EDTA concentration using HPLC method [14, 15]. All adsorption experiments were performed in triplicate and average values were used for further calculations. Standard deviations were found to be within ±5%. The equilibrium adsorption capacity (q_e, mg/g) was calculated as follows:

$$q_e = V(C_0 - C_e)/m \qquad (1)$$

where C_0 (mg/L) is the initial concentration of EDTA, and Ce (mg/L) is the concentration of

EDTA at equilibrium. *V* is the volume of the solution (L). *m* is the mass of CaOx monohydrate adsorbent (g).

2.2.2. Analytical measurements

Agilent 1260 Infinity Quaternary LC was employed to determine the concentration of EDTA in the supernatant according the reported methods [14, 15]. The calibration curve was obtained using $Na_2H_2EDTA \cdot 2H_2O$ solutions ranged from 0.00 to 400 mg/mL, and the standard curve ($y = 9.995x - 29.462$) showed a linear variation with a correlation coefficient (R^2) of 0.9993. In this study, the analytical column was AichromBond-AQ C18 (4.6 mm×250 mm, 5μm) column (Abel Industries® Canada Ltd., Canada). The mobile phase was composed of 75% mixture (pH 4) containing 0.03 mol/L sodium acetate together with 0.02 mol/L tetrabutylammonium bromide and 25% methanol. Before use the mobile phase was filtered using a 0.45 μm membrane filter (mixed cellulose ester). The chromatographic conditions were: flow rate 1.0 mL/min, column temperature 25 °C, injection volume 20 μL, the detection wavelength UV 254 nm.

2.2.3. Modeling

In this study, the adsorption data were fitted by selected models, and all the model fitted parameters were evaluated by regression analysis using OriginPro 9.0 software (OriginLab Corp., USA).

3. Results and discussion

3.1. Effect of contact time on EDTA adsorption

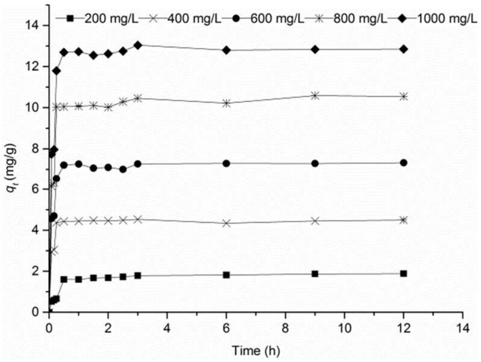

Fig. 1 Effect of contact time on the adsorption of EDTA onto CaOx monohydrate at various initial concentrations (adsorbent dosage= 50 g/L, temperature= 37℃, pH= 5.0)

In order to determine the necessary equilibrium time, the adsorption of EDTA (various initial concentrations) onto CaOx monohydrate was investigated with different contact time. q_t (mg/g) is the adsorption capacity at different times. Fig. 1 showed that the adsorption process of EDTA was similar in spite of its initial concentrations different. Took the adsorption process of the 1000 mg/L initial EDTA concentration for example, the adsorption rate increased fast in the first 0.5 h (12.70 mg/g) contact time and, thereafter, it decreased gradually and reached to equilibrium in about 3 h (13.04 mg/g). When the contact time was increase to 12 h, the adsorption rate of EDTA increased only about 0.31% comparing with those at 3 h contact time. It could be due to the competition of EDTA for the adsorption site of CaOx monohydrate surfaces and the remaining vacant surface sites on CaOx monohydrate crystals are difficult to be occupied because of the formed repulsion among EDTA molecules. After 3 h contact time, the adsorption capacity increases from 1.79 to 13.04 mg/g with an increase in initial EDTA concentration from 200 to 1000 mg/L. Since the difference in the adsorption capacity at 3 h and at 12 h was very small, in order to ensure adsorption equilibrium was reached, 3 h contact time was conducted for subsequent experiments.

3.2. Adsorption kinetics

Adsorption kinetics models are used to describe the uptake rate of adsorbate on adsorbent and to explore the adsorption process [16]. In this study, the adsorption rate constants for the adsorption of EDTA onto CaOx monohydrate crystals were studied with initial EDTA concentrations at 200, 400, 600, 800 and 1000 mg/L. The experimental data were analyzed with the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic equations.

Table 1 Kinetic parameters for the adsorption of EDTA onto CaOx monohydrate crystals at various initial concentrations (adsorbent dosage=50 g/L, temperature=37 ℃, pH= 5.0).

C_0 (mg/L)	$q_{e,\,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
		$q_{e,\,cal}$ (mg/g)	k_1 (1/h)	R^2	$q_{e,\,cal}$ (mg/g)	k_2 (g/mg/h)	R^2	k_{id} (mg/g/h$^{0.5}$)	c_i	R^2
200	1.7890	1.1143	1.3021	0.8111	1.9608	1.7326	0.9886	1.0185	0.2843	0.8078
400	4.5321	0.8847	1.4748	0.5547	4.5792	5.5006	0.9995	1.7883	2.1375	0.4820
600	7.2687	1.0208	1.1202	0.1236	7.2786	3.3058	0.9988	2.9212	3.2851	0.5078
800	10.4621	2.5113	1.1743	0.4862	10.5519	1.6540	0.9988	4.2880	4.5550	0.5183
1000	13.0417	3.2488	1.1985	0.4979	13.1510	1.3573	0.9990	5.4023	5.6064	0.5399

The Lagergren pseudo-first-order kinetic model has been widely used to predict adsorption kinetics. The equation is given in Eq. (2) [17].

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

and the linear form of the pseudo-first-order kinetic model can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time (h) respectively, k_1 (1/h) is the adsorption rate constant of pseudo-first-order reaction. The values of ln(q_e-q_t) were calculated from the kinetic data and the values of k_1 (Table 1) were calculated from the plots of ln(q_e-q_t) versus t (Fig. 2).

Ho's pseudo-second-order kinetics model is based on the assumption that the sorption follows second-order chemisorption [18]. It is expressed by Eq. (4):

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

which can be rewritten as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t (mg/g) are definited as above. k_2 (g/mg/h) is the adsorption rate constant, its value was determined from the plots of t/q_t against t (Fig. 3).

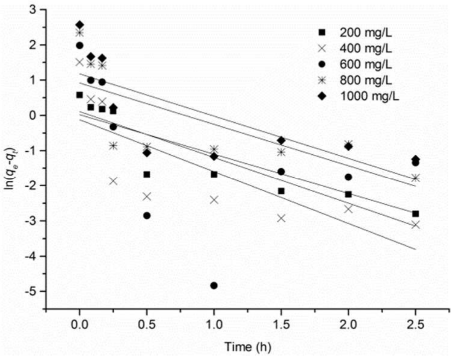

Fig. 2 Pseudo-first-order kinetic fit for adsorption of EDTA onto CaOx monohydrate crystals at various initial concentrations (adsorbent dosage=50 g/L, temperature=37 ℃, pH= 5.0).

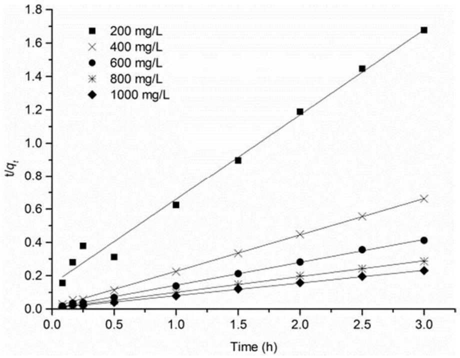

Fig. 3 Pseudo-second-order kinetic fit for adsorption of EDTA onto CaOx monohydrate crystals at

various initial concentrations (adsorbent dosage=50 g/L, temperature=37 ℃, pH= 5.0).

In order to investigate the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic data were also analyzed by the intraparticle diffusion model [19], which is expressed as:

$$q_t = k_{id} t^{0.5} + c_i \tag{6}$$

where k_{id} (mg/g/h$^{0.5}$) is the intraparticle diffusion rate constant, c_i is associated to the boundary layer thickness. If intraparticle diffusion occurs, then q_t versus $t^{0.5}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion would be involved [16].

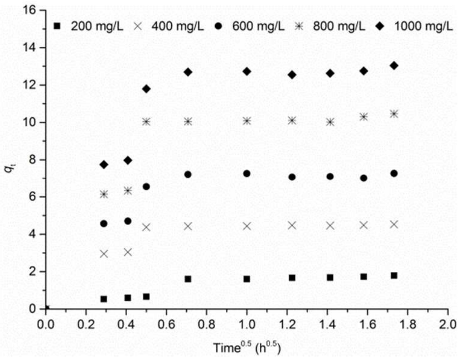

Fig. 4 Intraparticle diffusion model for adsorption of EDTA onto CaOx monohydrate crystals at various initial concentrations (adsorbent dosage=50 g/L, temperature=37 ℃, pH= 5.0).

All kinetic parameters ($q_{e,\ cal}$, k, c_i) were determined from the slope and the intercept by plotting ln(q_e-q_t) versus t (Fig. 2), t/q_t against t (Fig. 3) and q_t versus $t^{0.5}$ (Fig. 4) for pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models, respectively. The values of fitting kinetic parameters were tabulated in Table 1. As shown in Table 1, Low correlation coefficients (R^2) and notable variances between the experimental ($q_{e,\ exp}$) and theoretical adsorption capacity ($q_{e,\ cal}$) manifested clearly the poor fitting of pseudo-first-order model. Thus, the adsorption of EDTA onto CaOx monohydrate crystals was not a first-order reaction. However, at all studied initial EDTA concentrations, the R^2 values obtained from pseudo-second-order kinetic model are greater than 0.98, which were much higher than the values coming from pseudo-first-order kinetic model. In addition, the $q_{e,\ cal}$ and $q_{e,\ exp}$ values were also in good agreement in the case of pseudo-second-order kinetics. These indicated the applicability of the pseudo-second-order kinetic model to describe the adsorption process of EDTA onto CaOx monohydrate crystals. For the intraparticle diffusion model, the poor R^2 values (Table 1) and the linear plots of q_t versus $t^{0.5}$ (Fig. 4) at each concentration did not pass through zero suggested that the intraparticle diffusion was not the rate determining step of the adsorption mechanism.

3.3. Effect of initial EDTA concentration its adsorption

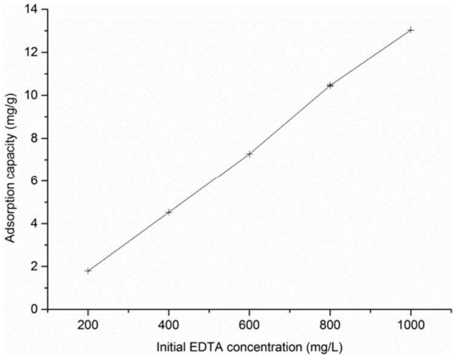

Fig.5 Effect of initial EDTA concentration for the adsorption of EDTA onto CaOx monohydrate crystals (adsorbent dosage= 50 g/L, temperature= 37℃, pH= 5.0, contact time=3 h).

The effect of initial EDTA concentration on its adsorption on CaOx monohydrate crystals was investigated and is shown in Fig. 5. The EDTA adsorption on CaOx monohydrate crystals increases with its concentration in the aqueous solutions. The adsorption capacity of EDTA adsorbed on CaOx monohydrate crystals is 1.79 mg/g, 4.53 mg/g, 7.27 mg/g, 10.46 mg/g and 13.04 mg/g for the initial EDTA concentration of 200 mg/L, 400 mg/L, 600 mg/L, 800 mg/L and

1000 mg/L, respectively. Similar trends have been reported for adsorption of EDTA on activated carbon and [Fe(III)–EDTA]$^-$ on granular activated carbon [20, 21]. There would be three reasons for this phenomenon. Firstly, the mass-transfer impetus between the liquid bulk and the surface of CaOx monohydrate increased with the initial EDTA concentration in the aqueous solution. Secondly, the diffusivity of EDTA also increased with its concentration. Thirdly, the EDTA on the CaOx monohydrate surface in equilibrium with the EDTA in the solution increased with its concentration in the solution

3.4. Effect of temperature on EDTA adsorption

To study the effect of temperature on EDTA adsorption, experiments were carried out at 25, 32, 37 and 45 ℃ with different initial EDTA concentrations. The results shown in Fig. 6 demonstrated that EDTA adsorption increased with temperature rising from 25 to 45 ℃. This may be attributed to the fact that the reaction rate between EDTA and the surface functional groups on the CaOx monohydrate crystals increases with temperature. Moreover, the diffusivity of sorbate through the external laminar layer into the micropores of the adsorbent also increases with temperature as diffusion is an endothermic process. Similar effects have also been reported for adsorption of EDTA on activated carbon and [Fe(III)–EDTA]$^-$ on granular activated carbon [20, 21].

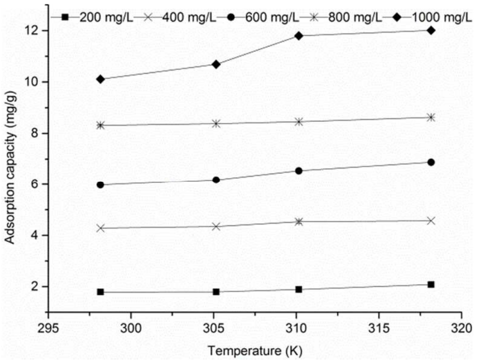

Fig. 6 Effect of temperature for the adsorption of EDTA onto CaOx monohydrate

crystals (adsorbent dosage=50 g/L, pH= 5.0, contact time=3 h).

3.5. Adsorption thermodynamics

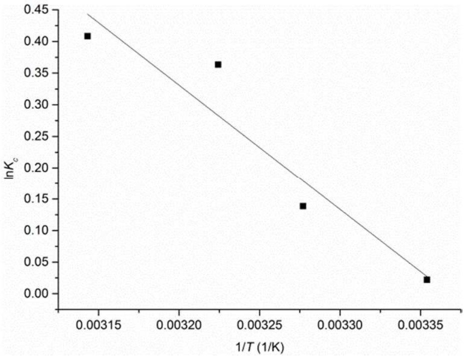

Fig. 7 Van't Hoff plot for the adsorption of EDTA onto CaOx monohydrate crystals

(initial EDTA concentration= 1000 mg/L, adsorbent dosage=50 g/L, pH= 5.0, contact time=3 h).

Equilibrium constant for the adsorption of EDTA onto CaOx monohydrate crystals, K_c, is defined as follows:

$$K_c = C_{AE}/C_e = (C_0 - C_e)/C_e \quad (7)$$

where C_{AE} is the adsorbed amount of adsorbate at equilibrium, C_0 is the initial concentration of adsorbate (mg/L), and C_e is the equilibrium concentration of adsorbate (mg/L).

Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change of adsorption can be determined as follows:

$$\Delta G^0 = -RT\ln K_c \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

$$\ln K_c = \Delta S^0/R - \Delta H^0/RT \quad (10)$$

where ΔG^0, ΔH^0 and ΔS^0 are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the gas constant (8.314 J/mol/K), T is the temperature in Kelvin (K). The ΔH^0 and ΔS^0 values are obtained from the slope and intercept of the van't Hoff plot of $\ln K_c$

versus 1/T (Fig. 7, Table 2). The ΔG^0 values were calculated using Eq. (8) (Table 2).

Table 2 Thermodynamic parameters for the adsorption of EDTA onto CaOx monohydrate crystals (adsorbent dosage=50 g/L, pH= 5.0, contact time=3 h).

C_0	ΔG^0 (kJ/mol)				ΔH^0	ΔS^0
(mg/L)	25 ℃	32 ℃	37 ℃	45 ℃	(kJ/mol)	(J/mol/K)
200	-0.1397	-0.2227	-0.2300	-0.2367	1.2305	4.6697
400	-0.3495	-0.4405	-0.6901	-0.7569	6.2541	22.1285
600	-0.1295	-0.1531	-0.4709	-0.7845	10.2395	34.5048
800	-0.1969	-0.2419	-0.2947	-0.4159	3.0721	10.9110
1000	-0.0544	-0.3516	-0.9372	-1.0799	16.3954	55.2167

Thermodynamic parameters for the adsorption of EDTA onto CaOx monohydrate crystals at different temperatures for the initial EDTA concentrations of 200 – 1000 mg/L are listed in Table 2. It was shown that ΔG^0 values at all temperatures were negative, which indicated the adsorption process was feasible and spontaneous. The positive value of ΔH^0 suggested the endothermic nature of all the adsorption process, which supported by the increasing adsorption of EDTA with the increase of temperature. The adsorption process in the solid–liquid system would be a combination of two processes: (a) the desorption of the molecules of solvent (water) previously adsorbed, and (b) the adsorption of adsorbate species. The EDTA ions should displace more than one water molecule for their adsorption and these results in the endothermicity of the adsorption process [22, 23]. Also, positive ΔS^0 value demonstrated the increased randomness at the solid/solution interface during the adsorption process. The change of positive standard entropy may be attributed to the release of water molecule produced by ion exchange reaction between the adsorbate and the functional groups on the surfaces of CaOx monohydrate crystals [24].

3.6. Effect of pH on EDTA adsorption

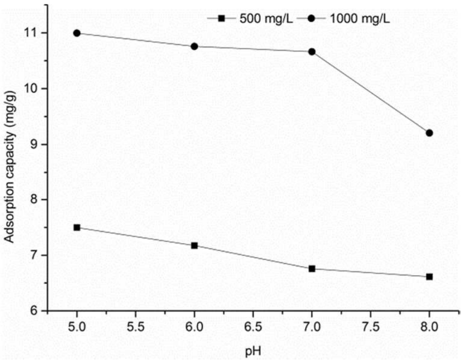

Fig. 8 Effect of pH on the adsorption of EDTA onto CaOx monohydrate crystals (adsorbent dosage=50 g/L, initial EDTA concentration=500 and 1000 mg/L, temperature=37 ℃, contact time=3 h).

Experiments were performed at different pH (5 – 8) with the different initial EDTA concentrations of 500 and 1000 mg/L to investigate the effect of pH on EDTA adsorption. The results shown in Fig. 8 suggested that the adsorption capacity of EDTA on CaOx monohydrate crystals decreased as the pH increased from 5 to 8. As the pH increased from 5 to 8, the amount of EDTA decreased from 7.50 mg/g to 6.61 mg/g and 10.99 mg/g to 9.21 mg/g for the initial concentrations of 500 and 1000 mg/L, respectively. This phenomenon could be attributed to the existing forms of EDTA in the aqueous solution and the ions dispersion on CaOx monohydrate surface under different pH. The forms of EDTA existed in aqueous solution including H_6Y^{2+}, H_5Y^+, H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}. When solution pH changing from 5 to 8, the main form of EDTA is H_2Y^{2-} or HY^{3-}, which is negatively charged [25]. On the other hand, the pH_{pzc} of CaOx monohydrate was found to be about 2.9 ± 0.25, which meant the adsorbent surface carried a negative charged under the testing condition, and become more negative as the pH values increased from 5 to 8. In this case, the negatively charged EDTA species (H_2Y^{2-} or HY^{3-}) would be repelled by the negatively charged CaOx monohydrate surface molecules, resulted in the decrease of EDTA adsorption. Moreover, Ca^{2+} and $C_2O_4^{2-}$ were potential-determining ions for a calcium oxalate system and H^+ and OH^- exerted an indirect potential-determining role [26]. As Fernández *et al.* [26] have pointed out, Ca^{2+} was the preferable ion adsorbing to the CaOx monohydrate surface at acidic pH, but $C_2O_4^{2-}$ at basic pH. Therefore, it was unfavourable for EDTA to be adsorbed on the CaOx monohydrate surface when the solution changed from acidic to basic.

3.7. Adsorption isotherms

Equilibrium data, commonly known as adsorption isotherm, is the plot of adsorption capacity (q_e) and the equilibrium adsorbate concentration (C_e), gives information for predicting and exploring the adsorption behavior [27]. In this study, adsorption equilibrium of EDTA onto CaOx monohydrate crystal under different pH was investigated to evaluate the best-fit isotherm model, the initial EDTA concentrations was ranging from 100 to 1000 mg/L. Langmuir isotherm model [28] and Freundlich isotherm model [29] were applied to fit the adsorption equilibrium data. The isotherms are expressed as follows:

Langmuir isotherm model $$q_e = \frac{q_m b C_e}{1 + bC_e} \quad (11)$$

Freundlich isotherm model $$q_e = K_F C_e^{1/n} \quad (12)$$

In the Langmuir model, q_e and C_e are the adsorption capacity at equilibrium (mg/g) and the equilibrium concentration of adsorbate (mg/L). q_m is the maximum adsorption capacity (mg/g). b (L/mg) is the Langmuir constant related to the affinity of binding sites or binding energy. In the Freundlich isotherm equation, K_F (mg/g (L/mg) $^{1/n}$) is the Freundlich constant and n the Freundlich exponent. The $1/n$ value is a dimensionless factor that measures the adsorption intensity or surface heterogeneity. In general, $1/n$ value ranges between 0 and 1. It indicates the adsorption nature to be either favourable (0.1<*1/n* <0.5) or unfavourable (*1/n* >2).

In this study, both isotherm model parameters were evaluated by non-linear regression using OriginPro 9.0 software. Correlation coefficient R^2 is a common parameter to evaluate the goodness-of-fit of the equation to the experimental data [30]. Apart from the R^2, the chi-square test (χ^2) and the residual root mean square error (RMSE) were also applied to measure the goodness-of-fit and to test the adequacy and the accuracy. The χ^2 and RMSE can be defined as:

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_e - q_c)^2}{q_c} \qquad (13)$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{n-2}\sum_{\mathrm{i}=1}^{\mathrm{n}} (q_e - q_c)^2} \qquad (14)$$

where q_e is the calculated value from the batch experiment, q_c is the estimated value from the isotherm for corresponding. n is the number of observations in the experimental isotherm. The smaller χ^2 value indicates the data from isotherm model are similar to the experimental data [31, 32]. Also, the smaller the RMSE value is, the better the curve fits [33].

The Langmuir isotherm and Freundlich isotherm parameters as well as the error analysis results were tabulated in Table 3. Since the value of R^2 nearer to 1 indicates that the equation fits the experimental data better, and the smaller of χ^2 and RMSE value suggests that the data calculated from isotherm models are similar to the experimental data. From the Table 3, it can be found that the Langmuir isotherm model (R^2>0.92) exhibited better fit to the adsorption equilibrium data of EDTA adsorbed on CaOx monohydrate crystals than the Freundlich isotherm model. The maximum adsorption capacity (q_m) of EDTA adsorption would be 115.34 mg/g at pH 5.0. The constant *b* indicates affinity between the adsorbent and adsorbate. The higher the value of *b*, the higher the affinity will be. Table 3 showed that there was no specific trend between the constant *b* and the solution pH. But the value of *b* at pH 5.0 is the highest under the experiment condition. Moreover, the values of 1/*n* were all lower than 1, which indicated the favorable nature for the adsorption of EDTA onto CaOx monohydrate crystals.

Table 3 Langmuir and Freundlich isotherm parameters for the adsorption of EDTA onto CaOx monohydrate crystals (adsorbent dosage=50 g/L, temperature=37 ℃, contact time=3 h).

Isotherm model	Parameter	pH			
		5	6	7	8
Langmuir	q_m (mg/g)	115.3349	77.8504	50.5629	42.8531
	b (L/mg)	1.0051×10^{-3}	0.4913×10^{-3}	0.7748×10^{-3}	0.3348×10^{-3}
	R^2	0.9397	0.9373	0.9343	0.9279
	χ^2	0.4018	0.4254	0.5055	0.7001
	RMSE	0.7626	0.7576	1.0265	1.1069
Freundlich	K_F	0.0783	0.0476	0.0631	0.0416
	n	1.0294	1.0657	1.1365	1.1776
	R^2	0.9314	0.9262	0.8602	0.8392
	χ^2	0.8576	0.8757	1.5854	1.9057
	RMSE	0.7827	0.7909	1.0641	1.1667

In our previous study [34], we investigated the adsorption of glutamic acid and aspartic amino onto CaOx monohydrate crystals; the maximum monolayer adsorption capacity of glutamic acid and aspartic amino was found to be 8.64 and 8.77 μg/g, respectively. Moreover, Fleming *et al.* [35] had studied the adsorption of 20 amino acids on to CaOx monohydrate crystals, and they found that the most strongly adsorbed one was γ-carboxyglutamic acid (about 0.20 $\mu mol/m^2$). In this study, the maximum monolayer adsorption capacity of EDTA adsorption reached to 115.34 mg/g, which indicated EDTA owned an very strong adsorption ability on the CaOx monohydrate crystals. That means the EDTA or its derivatives should be candidate for the modification of the oxalate-degrading enzyme, so that endow the enzyme with the adsorption ability to calcium oxalate stones.

4. Conclusion

In this study, the adsorption of EDTA onto CaOx monohydrate crystals under employed conditions was investigated. According to the experimental results, the following specific conclusions can be drawn.

(1) The effect of such experimental factors as contact time, initial concentration of EDTA, temperature and solution pH on EDTA adsorption was studied. The adsorption of EDTA on CaOx monohydrate crystals increased with the initial concentration in the aqueous solutions. High temperature was beneficial to the adsorption. As the pH value increased, the adsorption capacity decreased.

(2) The adsorption kinetic data were analyzed by pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic equations. The pseudo-second-order kinetic model described the adsorption process best.

(3) Thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 for EDTA adsorption were estimated. A negative ΔG^0 values indicated that the adsorption process was feasible and spontaneous nature and positive value of ΔH^0 suggested the endothermic nature of the adsorption reaction. Positive ΔS^0 value demonstrated the increasing randomness of the solid/solution interface during the adsorption of EDTA on the CaOx monohydrate crystals.

(4) Langmuir isotherm and Freundlich isotherm models were used to fit the adsorption equilibrium data. The Langmuir isotherm model (R^2>0.92) was exhibited better fit to the adsorption equilibrium data than the Freundlich isotherm model. The maximum adsorption capacity (q_m) obtained from of the Langmuir isotherm model would be 115.34 mg/g.

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