Optimization and kinetic modeling of cadmium desorption from citrus peels: A process for biosorbent regeneration

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ABSTRACT

Citrus peel biosorbents are efficient in removing heavy metals from wastewater. Heavy metal recovery and sorbent regeneration are important for the financial competitiveness of biosorption with other processes. The desorbing agents HNO_3, $NaNO_3$, $Ca(NO_3)_2$, EDTA, S, S-EDDS, and Na-Citrate were studied at different concentrations to optimize cadmium elution from orange or grapefruit peels. In most cases, desorption was fast, being over 90% complete within 50 min. However sodium nitrate and 0.001 M nitric acid were less efficient. Several new models for desorption kinetics were developed. While zero-, first- and second-order kinetics are commonly applied for modeling *adsorption* kinetics, the present study adapts these models to describe *desorption* kinetics. The proposed models relate to the number of metal-filled binding sites as the rate-determining reactant concentration. A model based on first order kinetics with respect to the remaining metal bound performed best. Cd bound in subsequent adsorption after desorption was similar to the original amount bound for desorption by nitric acid, but considerably lower for calcium nitrate as the desorbent. While complexing agents were effective desorbents, their cost is higher than that of common mineral acids. Thus 0.01–0.1 M acids are the most promising desorbing agents for efficient sorbent regeneration.

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1. Introduction

Heavy metal ions such as cobalt, copper, nickel, chromium, cadmium, and zinc are present in the waste streams from mining operations, tanneries, textile mills, electronics, electroplating and petrochemical industries [1]. Heavy metals have a harmful effect on human physiology and other biological systems when they exceed the tolerance levels. They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders.

Conventional methods used to remove heavy metals from waste water (precipitation, ion exchange, redox processes, reverse osmosis, etc.) often involve high capital and operating cost, especially when the metals are dissolved in large volumes of solution at relatively low concentrations (around 1–100 mg/L), and when high effluent quality is desired [2]. Studies are thus turning towards cost-effective methods. Biosorption, using biosorbents from industrial or natural sources, provides an efficient and competitive solution to treat wastewater, particularly for high volumes of dilute solutions [3].

Biosorption can be defined as the sequestering of metals by materials of biological origin. Biosorption is metabolism-independent such that non-living biomass can act as a biosorbent [4]. Metal ion binding may involve complexation, coordination, chelation, ion exchange, adsorption and inorganic microprecipitation depending on the type of biosorbent [5]. Recent studies have determined biosorption using citrus peels as being efficient in the removal of heavy metals from wastewater with sorption capacities of 0.35–1.15 mmol/g (39–128 mg/g) of Cd per biosorbent dry weight [6,7]. The economic feasibility and subsequent advantage of this process over others will depend on the amount of metal bound by the biosorbent and the ability to meet legal wastewater discharge standards and biosorbent regeneration for use in multiple adsorption–desorption cycles [8,9].

The desorption mechanism is similar to that of biosorption and may involve ion exchange or complexation, where metals are eluted from the biosorbent by an appropriate solution to produce a small, concentrated volume of metal-containing solution [10], from which metals could potentially be recovered. Studies have shown that the protons of mineral acids such as HCl, H_2SO_4 and HNO_3 can displace metals from the sorbents binding sites [8,11] and that the strong chelating agent EDTA is also an efficient desorbing agent [12,13], causing metal desorption by reducing the concentration of free metal ions in solution. Taking the above points into consideration, and considering the fact that citrus peels are efficient in

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the removal of cadmium from waste water, one objective of this study was to examine the efficiencies of selected desorbing agents (HNO_3, $NaNO_3$, $Ca(NO_3)_2$, NaCitrate, Na_2EDTA, and S,S-EDDS) at varying concentrations in order to determine the most economic highly effective desorption agent. Since there are currently no published studies on modeling desorption kinetics, with the notable exception of Singh et al. who described Cu^{2+} and Pb^{2+} desorption by 0.1 M HCl using 1st and 2nd order Lagergren models [14], a second objective was to develop models that are able to describe desorption kinetics for a variety of desorbents. The third objective was to verify efficient sorbent regeneration for the chosen desorbing agent by conducting isotherm experiments in order to quantify Cd bound by the previously desorbed peels.

2. Materials and methods

2.1. Materials

Dried peels of two different citrus varieties, processed Valencia orange peels (Alarma Consulting Corporation, FL) and waste grapefruit (*Citrus paradise*) peels from juice production (Peace River Citrus Products Company, FL), were ground and sieved to a 1–1.1 mm size diameter. Protonation of the peels was carried out in order to remove light metal cations such as Na or Ca, and to saturate binding sites such as carboxyl groups with protons, according to a modified procedure by Schiewer and Balaria [15]. The sorbent material was mixed with 0.1 M HNO_3 (20 g of peels/L) for 240 min on a magnetic stirrer, rinsed with nanopure water (approximately 18 Ω resistance), and dried for 720 min at 40 °C. The weight of the peels before and after protonation was recorded and weight loss was found to be negligible.

2.2. Adsorption isotherm

Adsorption isotherm studies were carried out by varying the initial metal concentrations from 0.089 to 8.89 mM (10 mg/L to 1000 mg/L). A 0.05 L solution of the desired cadmium (Cd^{2+}) concentration was prepared, using 89 mM (10,000 mg/L) AA (atomic absorption) standard solution of cadmium nitrate to prevent complexation. 0.05 g of the dried protonated citrus peels were put in contact with the prepared solutions in Erlenmeyer flasks placed on a rotary shaker for an equilibration time of 180 min. The pH was controlled and adjusted to 5.0 during the contact period, using 0.1 M NaOH. The samples were filtered on Whatman 40 ashless filter paper and the filtrate acidified with 10^{-3} L of concentrated (16 M) nitric acid, and stored (at 3 °C) for analysis on the Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 300).

2.3. Desorption studies

All desorption experiments were carried out using the batch process. Initial loading of cadmium onto the citrus peels was done by exposing 20 g of the dried protonated citrus peel to 1 L of 4.46 mM $Cd(NO_3)_2$ solution on a magnetic stirrer for 180 min (at pH 5). The amount of Cd loaded onto the citrus peels was 0.23 mmol/g for the grapefruit peels, and 0.305 mmol/g for the orange peels.

Cd^{2+} loaded orange peels were used for the desorption experiments with the desorbents NaCitrate, Na_2EDTA, and S,S-EDDS (desorption by Cd^{2+} complexation in solution), and Cd^{2+} loaded grapefruit peels were used for the desorption experiments with HNO_3, $NaNO_3$, $Ca(NO_3)_2$ as desorbents (desorption by ion exchange). Nitrate was chosen as the anion for that set of experiments since nitrate does not form complexes with Cd^{2+} under the studied conditions.

Kinetic studies were conducted in order to determine the desorption rate of the heavy metal from the citrus peels. The desorption studies were done by contacting 0.05 g of the loaded biomass with 0.05 L of the different desorbing agents at the chosen concentrations (0.001, 0.01, 0.1, and/or 1 M) on a rotary shaker. At different contact times (5–1440 min), the samples were immediately filtered on Whatman 40 ashless filter paper and stored for analysis. The data collected were modeled using different kinetic models.

2.4. Theoretical background

2.4.1. Adsorption isotherms

The metal bound per gram of biosorbent material was determined using the mass balance. If C_0 and C_f are the initial and final metal concentrations (mol/L), respectively, V is the suspension volume (L) and m is the mass of biosorbent material (g), then the metal bound q (mmol/g) can be calculated as:

$$q = \frac{V(C_0 - C_f)}{m} \tag{1}$$

The results were plotted as sorption isotherms (Langmuir, Freundlich, and BET) of the sorbate bound (q) versus the equilibrium concentration of the residual sorbate remaining in the solution (C_f).

The Langmuir adsorption model is valid for single-layer adsorption and assumes that all the binding sites are free sites. The Langmuir isotherm equation is:

$$q = q_{max} \frac{KC_f}{1 + KC_f} \tag{2}$$

where q_{max} is the maximum sorbate bound under the given conditions [mmol/g] and K [g/mmol] is a coefficient related to the affinity between the sorbent and sorbate.

The Freundlich isotherm model is the empirical equation:

$$q = kC_f^{1/n} \tag{3}$$

where k and n are the Freundlich constants.

The BET model represents sorption isotherms reflecting apparent multi-layer adsorption. It assumes that a number of layers of adsorbate molecules form at the surface. For low sorbate concentrations, where the first layer is not yet saturated, the model approaches the Langmuir equation. The BET isotherm is given by the equation:

$$q = \frac{Kq_{max}C_f}{(C_s - C_f)[1 + (K - 1)(C_f/C_s)]} \tag{4}$$

where C_s is the saturation concentration of the solute; K is a constant related to the energy of interaction with the surface and q_{max} is the moles of solute adsorbed per unit weight of adsorbent forming a complete monolayer on the surface.

2.4.2. Kinetic models

1st and 2nd order models are commonly used for adsorption, assuming that the adsorption rate is related to the difference between amount of metal bound at any given time versus the metal bound at equilibrium. To provide a model for desorption kinetics, which have so far not been modeled in the literature, the present work proposes to modify the commonly used kinetic models for adsorption and adapt them to desorption, with the remaining amount of metal bound being the rate-determining concentration. The desorption data obtained for the different desorbing agents were modeled according to a modification of the Lagergren zero-order, pseudo first and second order adsorption kinetic model. The modified models proposed in this paper consider the metal-biosorbent desorption reaction as the rate-limiting step. They regard the metal-saturated sites at the biosorbent surface as the reactant and are based on different assumptions of how the desorption rate depends on the quantity of these cadmium-filled binding sites.

The modified 0-order model assumes that the rate of desorption is constant, and independent of the quantity of the Cd^{2+} filled sites. It can be expressed as:

$$\frac{dq}{dt} = -k_{0,\text{des}} \qquad (5)$$

where q (mmol/g) is the remaining amount of metal bound to the biosorbent at any time t, dq/dt is the desorption rate, and $k_{0,\text{des}}$ the 0-order desorption rate constant (mmol g^{-1} min^{-1}).

The pseudo 1st-order model assumes that the rate of desorption is proportional to the number of Cd^{2+} filled sites and can be expressed as:

$$\frac{dq}{dt} = -k_{1,\text{des}}q \qquad (6)$$

where $k_{1,\text{des}}$ is the 1st-order desorption rate constant (min^{-1}).

The modified pseudo-2nd-order model assumes that the rate of desorption is proportional to the square of the number of Cd^{2+} filled sites and can be expressed as:

$$\frac{dq}{dt} = -k_{2,\text{des}}q^2 \qquad (7)$$

where $k_{2,\text{des}}$ is the 2nd-order desorption rate constant (g mmol^{-1} min^{-1}).

Stepwise numerical integration over time was performed for all three rate expressions according to the following equation:

$$q_{n+1} = q_n - \left(\frac{dq}{dt}\right)_n (t_{n+1} - t_n) \qquad (8)$$

where q_n is the amount of Cd remaining in peels at time t_n and q_0 is the initial amount of Cd in the peels (at time $t_0 = 0$), as determined from a prior adsorption step. From the equation we see that the amount of Cd^{2+} (mmol/g) found in the peels at time t_{n+1} will be the amount at time t_n minus the rate of desorption multiplied by the incremental time step.

2.4.3. Error analysis

Error analysis was done in order to evaluate the errors of the model predictions of both the isotherm and desorption kinetic models. The root mean square error (RMSE) was calculated with the equation:

$$\text{RMSE} = \sqrt{\frac{\sum_1^p (q - q_m)^2}{p}} \qquad (9)$$

where q is the experimental metal binding data, q_m is the model predictions of metal bound, and p is the number of data points. The parameters for kinetic models and isotherms were optimized using the solver function in Excel by minimizing the RMSE values.

3. Results and discussion

3.1. Adsorption isotherm

The optimization of Cd^{2+} desorption from loaded citrus peels began with characterizing the maximum amount of Cd^{2+} bound by grapefruit peels by creating a sorption isotherm for cadmium. These data were later used to compare to cadmium biosorption by previously desorbed peels, to determine whether regenerated peels were similarly efficient as fresh peels. The metal bound by the grapefruit peels as a function of the equilibrium cadmium concentration is shown in Fig. 1.

The data showed a steep initial increase in metal bound with increasing concentration. The slope of the curve gradually decreased and then showed a sharp increase beyond the metal
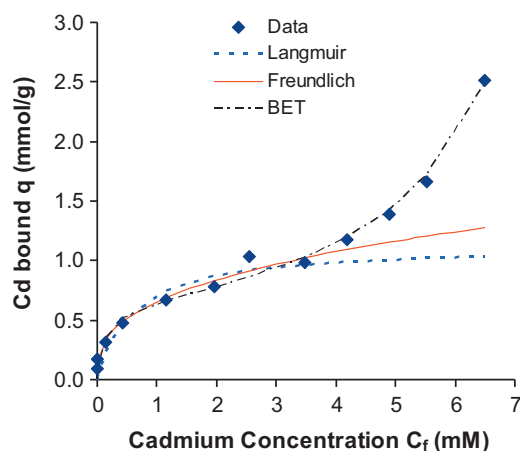

Fig. 1. Adsorption isotherm for cadmium binding by grapefruit peels (1 mm diameter) at pH 5. Data and predictions of Langmuir, Freundlich and BET isotherms. Langmuir and Freundlich model parameters were determined from data points up to 3.5 mM.

binding of 1 mmol/g (at the final metal concentration of 4.20 mM). The data showed a resemblance to the BET model. The Langmuir, Freundlich and BET models were fitted to the data by nonlinear parameter optimization using the Excel Solver function such that the RMSE was minimized. Since the Langmuir and Freundlich models did not fit well for the data at high concentrations, Table 1 shows not only model parameters obtained by fitting the model over the entire data range, but also model parameters obtained by fitting only to the data points up to 3.5 mM.

For those low cadmium concentrations ($C_f = 0.002–3.5$ mM), the Freundlich isotherm had the best fit (lowest RMSE value). However when considering all data points, the BET isotherm had by far the lowest RMSE value. The results obtained at low cadmium concentrations are in accordance with a similar study by Schiewer and Patil [6] on the use of pectin-rich fruit wastes as biosorbents, where the Freundlich and Langmuir isotherms both provided a good fit for adsorption of cadmium by different citrus peels at pH 5 and pH 3.

No conclusion could be drawn about the underlying mechanism responsible for the observed increase in Cd binding at higher concentrations, which resulted in a better fit of the BET model. Other biosorption studies concluded that multilayer sorption occurred when data followed a BET type isotherm [16,17]. In some cases, the BET isotherm and corresponding multilayer sorption was invoked even though the data did not follow a typical BET isotherm behavior (Langmuir – type plateau followed by isotherm becoming steeper as asymptotic value is approached) [18–20]. The authors of the present study are wary of over-interpreting results. Multilayer adsorption, which is commonly associated with the BET isotherm, would be highly unlikely due to a lack of binding sites for Cd^{2+} ions once the first sorbate–sorbent layer is formed. No cadmium precipitation was observed even at higher cadmium concentrations. Visual Minteq (Ver. 2.61) was used to calculate the equilibrium speciation and evaluate whether precipitation of Cd complexes could have occurred. The Minteq modeling showed that even at the highest cadmium concentration of 7 mM, over 97% of Cd was present as Cd^{2+}, with 2.4% of Cd present as $CdNO_3^+$ and virtually no hydroxides. No formation of precipitate would have occurred according to Minteq. A possible explanation for the sudden increase in Cd^{2+} bound observed after $C_f = 3.5$ mM is a change in the stoichiometry of the adsorption model from a 1:2 stoichiometry (where one divalent metal ion binds to two monoprotic sites) to a 1:1 stoichiometry (one divalent metal ion binds to one monoprotic site).

Table 1
Equilibrium parameters of Langmuir–Freundlich and BET isotherm models for cadmium bound by grapefruit peels at pH 5.

Isotherm	Model parameters						RMSE (mmol/g)
Langmuir	K (L/mmol)	1.7[a] 0.0027[b]	q_{max} (mmol/g)	1.13[a] 126[b]			0.092[a] 0.231[b]
Freundlich	k	0.66[a] 0.44[b]	n	2.83[a] 1.22[b]			0.053[a] 0.223[b]
BET	K (−)	51[a] 70[b]	q_{max} (mmol/g)	0.72[a] 0.63[b]	C_s (mM)	10.6[a] 8.68[b]	0.081[a] 0.073[b]

[a] Using only data with $C_f < 3.5$ mM to determine parameters.
[b] Using all data to determine parameters.

3.2. Desorption efficiency and kinetics

The desorption efficiency and kinetics studies for the selection of optimal elution conditions were done using varying concentrations of several desorbents based on their efficiency in Cd^{2+} removal from the citrus peels. For each desorbent and at each concentration, the desorption efficiency DE (%) was calculated as:

$$DE = \left(\frac{q_0 - q}{q_0}\right) \times 100 \qquad (10)$$

where q_0 is the amount of metal (Cd^{2+}) bound into the citrus peels before desorption and q is the amount of remaining metal bound after desorption (mmol/g).

The desorption efficiency and kinetics for the different concentrations of the selected desorbents HNO_3, $NaNO_3$, $Ca(NO_3)_2$ (desorption by ion exchange with competing ions "pushing" Cd^{2+} off binding sites) as well as Na-Citrate, Na_2EDTA, and S,S-EDDS (desorption by complexing agents "pulling" Cd^{2+} into solution) can be seen in Figs. 2 and 3, respectively. A logarithmic time scale was chosen to achieve a better resolution for the first 30 min, during which much of the sorption took place.

As seen in Fig. 2, the concentrations used were 1 M, 0.1 M, 0.01 M and 0.001 M for HNO_3, 1 M and 0.1 M for $Ca(NO_3)_2$, and 1 M for $NaNO_3$. For each desorbing agent, concentrations were lowered until less than 70% desorption was achieved in 30 min. Therefore, lower concentrations were investigated for the more efficient HNO_3 compared to the weaker desorbing agent $NaNO_3$. With the exception of $NaNO_3$ and 0.001 M HNO_3, all desorbent solutions were able to achieve 90–100% removal of cadmium from the citrus peels within 120 min or less.

HNO_3 at 1 M, 0.1 M and 0.01 M showed a fast desorption rate, achieving 90% removal within the first 60 min. Surprisingly, 1 M HNO_3 showed a slightly lower efficiency than 0.1 M and 0.01 M. This was most likely due to the fact that the high acid concentration damaged the overall structure of the citrus peels, also indicated by a discoloration of the solution. This was also noticed for 0.1 M HNO_3, which showed a reduction in efficiency after 240 min. The 0.01 M HNO_3 showed optimum performance, achieving 90% removal within the first 50 min without damaging the peels.

Overall, $Ca(NO_3)_2$ displayed a lower desorption rate than HNO_3. Even for 1 M $Ca(NO_3)_2$ desorption was lower than for 0.01 M HNO_3, i.e. concentrations for $Ca(NO_3)_2$ had to be about 100 times higher than HNO_3 concentrations to have the same effect. For the first 30 min, desorption was faster for 1 M $Ca(NO_3)_2$ than for 0.1 M $Ca(NO_3)_2$, after that, both concentrations showed similar results.

$NaNO_3$ was the weakest of the desorbing agents compared in Fig. 2, 1 M $NaNO_3$ performed similar as 0.001 M HNO_3, i.e. the concentration had to be a thousand times higher for $NaNO_3$ than for HNO_3.

Fig. 3 shows the kinetics and efficiency of the different complexing agents whose concentrations were 0.1 M and 0.001 M for EDTA, 0.001 M for S,S-EDDS and 0.1 M for Na citrate, based on previous studies on the desorption of cadmium or lead from algae, activated

sludge, and grape stalks using these complexing agents [12,13,21]. As seen in Fig. 3, all three complexing agents were highly efficient, achieving 100% desorption. Efficient desorption by EDTA was also noted for other agricultural waste materials [22]. With the exception of 0.001 M EDTA, they all showed fast kinetics, achieving 90% desorption within the first 50 min. Even after long exposure to the complexing agents, desorption remained at 100%, unlike observations for acidic desorption. Apparently, complexing agents did not damage the citrus peels.

3.3. Desorption models

The desorption kinetics of the different desorbents were modeled according to the zero, 1st and 2nd order models, whose
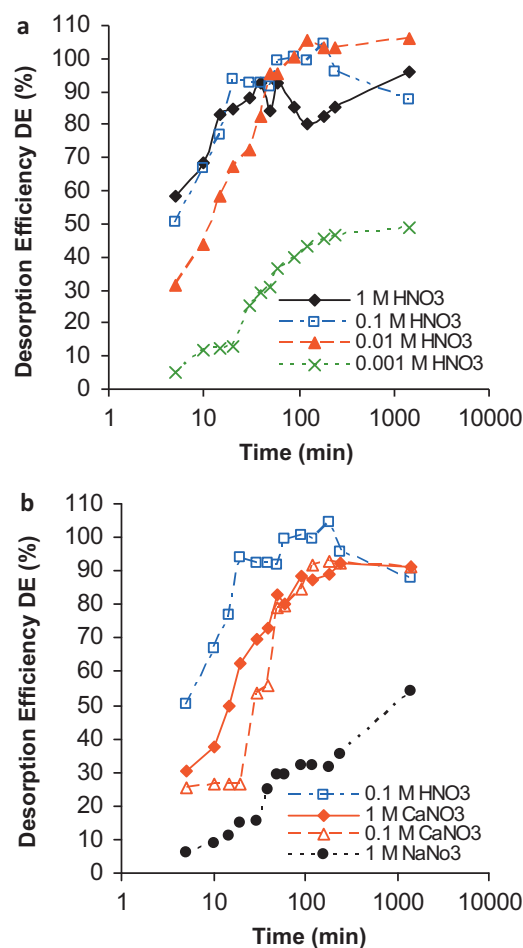
Fig. 2. Desorption kinetics using different desorbing agents for grapefruit peels with an initial amount of Cd^{2+} bound of 0.23 mmol/g. (a) Comparison of different concentrations of HNO_3. (b) Comparison of HNO_3, $Ca(NO_3)_2$, and $NaNO_3$.

Table 2
Parameters for 0, 1st and 2nd order kinetic models of selected desorbents for Cd elution from citrus peels.

Desorbent	Rate constant k			RMSE		
	Zero (mmol g^{-1} min^{-1})	1st (min^{-1})	2nd (g mmol^{-1} min^{-1})	Zero (mmol/g)	1st (mmol/g)	2nd (mmol/g)
HNO$_3$ 1 M[a]	0.0014	0.113	0.702	0.131	0.014	0.016
HNO$_3$ 0.1 M[a]	0.0018	0.103	0.672	0.132	0.005	0.019
HNO$_3$ 0.01 M[a]	0.0016	0.054	0.434	0.108	0.009	0.014
HNO$_3$ 0.001 M[a]	0.0007	0.005	0.029	0.031	0.024	0.016
Ca(NO$_3$)$_2$ 1 M[a]	0.0015	0.044	0.338	0.095	0.012	0.011
Ca(NO$_3$)$_2$ 0.1 M[a]	0.0015	0.026	0.196	0.074	0.016	0.024
NaNO$_3$ 1 M[a]	0.0005	0.003	0.022	0.028	0.024	0.030
EDTA 0.1 M[b]	0.0025	0.102	0.474	0.189	0.020	0.033
EDTA 0.001 M[b]	0.0015	0.063	0.088	0.080	0.060	0.011
SS,EDDS 0.001 M[b]	0.0020	0.041	0.228	0.136	0.019	0.021
NaCitrate 0.1 M[b]	0.0020	0.056	0.298	0.156	0.016	0.024

[a] Grapefruit peels with q_0 = 0.23 mmol/g.
[b] Orange peels with q_0 = 0.305 mmol/g.

parameters are shown in Table 2. The parameter k was determined by non-linear parameter optimization, with the root mean square error (RMSE) being minimized using the solver function in Excel. As described above, the experimentally determined initial amount of Cd^{2+} in the peels before desorption was used in the desorption model, i.e. q_0 = 0.23 mmol/g for the grapefruit peels with HNO$_3$, NaNO$_3$, Ca(NO$_3$)$_2$, and q_0 = 0.305 mmol/g for the orange peels with Na-Citrate, Na$_2$EDTA, and S,S-EDDS. The data used for fitting the kinetic models did not include the data points where severe disintegration occurred (the last data point at 1440 min for the desorption using 1 M and 0.1 M HNO$_3$), as disintegration of the peels is a secondary process that masks the actual desorption kinetics. As Fig. 4 shows, rate constants increased with increasing desorbent concentration, i.e. desorption was faster at higher concentrations (except for 1 mM for zero order kinetics, which however was not an appropriate model assumption for the data set). For 0.1 mM, the 1st and 2nd order rate constants were already maximal; it would therefore be financially wasteful to use higher concentrations. It may overall even be most beneficial to use the more economical 0.01 mM HNO$_3$ in spite of slightly lower rate constants.

0.1 mM EDTA was similarly efficient as 0.1 mM HNO$_3$, with 1st order rate constants $k_{1,des} \approx 0.10$ min^{-1}. Among the complexing agents, SS,EDDS was stronger (higher rate constant) than EDTA, which in turn was stronger than Na-Citrate at the came concentration.

The data in Table 2 show that the desorption kinetics data fit well to both the first and second order kinetic models, with RMSE of 0.01–0.05 mmol/g for the best fitting model, which is small compared to the initial cadmium bound of 0.23 mmol/g for grapefruit
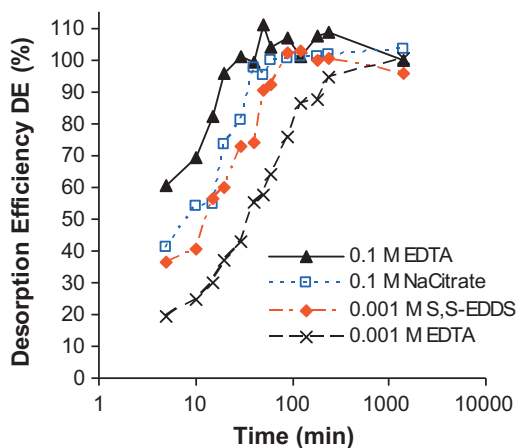
peels and 0.305 mmol/g for orange peels. With the exception of 0.001 M HNO$_3$, 0.001 M EDTA, and 1 M Ca(NO$_3$)$_2$, for which the 2nd order model fit best, all desorbents showed a slightly better fit for the first order model. The close fit of the two models may be either due to the fact that the selected concentrations of the reactant species (desorbents) are not in the rate-governing range, and initial excess of any of the reactants will give a mixed response or because the order of desorption is a fractional value between the first and second order [14].

A comparison of the different order models to the desorption data can be seen in Fig. 5 which shows the performance of all the three rate models for 0.01 M and 0.001 M HNO$_3$. Those were chosen as representative examples where the 1st order model fit well (as in most cases) and where the 1st order model fit was less satisfactory, which was the case for 0.001 M HNO$_3$ because of incomplete desorption. Current research focuses on alternative models for such cases.

3.4. Adsorption by regenerated peels

The success of citrus peel regeneration after desorption with 0.1 M HNO$_3$ and 0.1 M Ca(NO$_3$)$_2$ was also studied. Those desorbents and their concentrations were chosen as being favorable based on their cost, effect on the environment, desorption rate, efficiency, and the effect on the peels. The cadmium biosorption isotherms
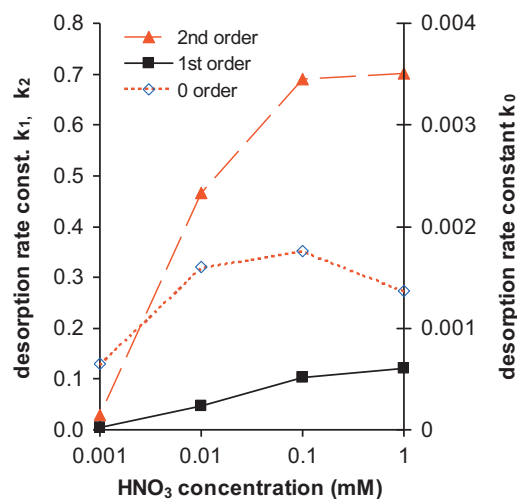
Fig. 3. Comparison of desorption kinetics using S,S-EDDS, Na-Citrate and EDTA for orange peels with an initial amount of Cd^{2+} bound of 0.305 mmol/g.

Fig. 4. Effect of HNO$_3$ concentration on zero, 1st and 2nd order rate constant for cadmium desorption from grapefruit peels with an initial amount of Cd bound of 0.23 mmol/g.
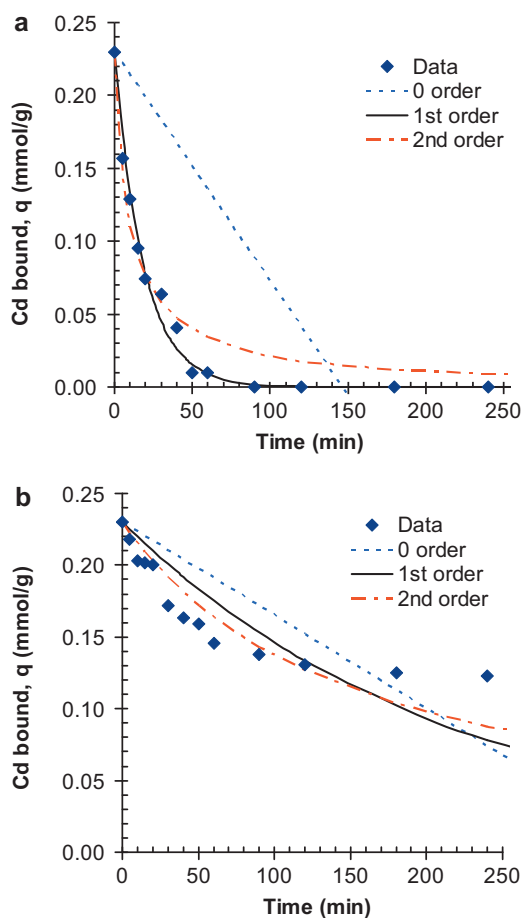
Fig. 5. Kinetics of cadmium desorption by HNO_3 for grapefruit peels with an initial amount of Cd bound of 0.23 mmol/g. Data and predictions of zero, first and second order model. (a) 0.01 M HNO_3 and (b) 0.001 M HNO_3.

by the previously loaded citrus peels after desorption using 0.1 M HNO_3 and 0.1 M $Ca(NO_3)_2$ can be seen in Fig. 6.

The cadmium bound by the peels in an adsorption step after desorption using 0.1 M HNO_3 was very similar to that of the original peels. On the other hand the cadmium bound after desorption using 0.1 M $Ca(NO_3)_2$ was much lower. This was most likely due to the fact that the two divalent ions cadmium and calcium are
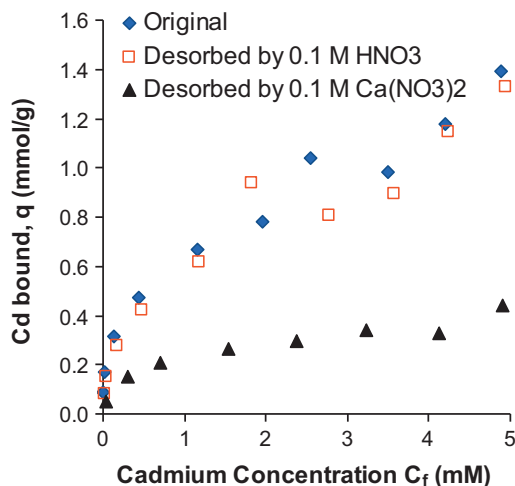
strong competitors for the same binding sites. Calcium has been shown to repress cadmium and zinc binding, respectively, by seaweeds in biosorption experiments where both metals were present at varying concentrations [23,24]. Preliminary results of ongoing experiments of the authors similarly show cadmium binding by citrus peels decreasing with increasing calcium concentration. While in the current study HNO_3 was used to be able to distinguish clearly between on the one hand competitive desorption by H^+ or other cations that "push" Cd^{2+} off the binding sites and on the other hand desorption by complexing agents which "pull" Cd^{2+} into the solution, in industrial applications other mineral acids such as HCl, which has a low cost and is of lower environmental concern than some other acids, may be used.

4. Conclusions

Several new models based on zero-, first- and second-order kinetics were adapted here to describe desorption kinetics. The models relate to the number of cadmium-filled binding sites as the rate-determining reactant. The first order kinetic desorption model fit data for Cd desorption from citrus peels well, except for those cases where desorption remained incomplete, namely 0.001 M HNO_3 and 1 M $NaNO_3$. The most promising desorbents were identified, considering criteria such as desorption effectiveness, desorption rate, cost, environmental effect and reuse-potential. Calcium salt was effective for desorption but slower than mineral acid and resulting in lower metal binding of Ca-regenerated peels compared to original or acid-regenerated peels. Mineral acids and complexing agents were fast and effective, achieving 90% desorption in less than 60 min. Since complexing agents are more expensive than common mineral acids, and 0.001 M acid was not an effective desorbent, 0.1 or 0.01 M acid were identified as the best desorbents. While HNO_3 was used in this study, other mineral acids such as the relatively harmless and cheap HCl are promising as industrial desorbents.

Fig. 6. Comparison of cadmium biosorption isotherms at pH 5.0 of protonated citrus peels and citrus peels desorbed with 0.1 M HNO_3 and 0.1 M $Ca(NO_3)_2$.

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