Mathematical Model Application for Phosphorus Removal and Recovery Prediction in Continuous Flow Fixed-Bed Columns

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Abstract: This work focused on modelling a demonstration scale ion exchange (IEX) process for phosphorus (P) removal and consequent recovery from tertiary wastewater. P was removed by a column packed with a hybrid anion exchanger (HAIX) and regenerated with sodium hydroxide (NaOH). The coefficients of the Thomas model were calibrated and then validated for P removal, while recovery with the NaOH solution was also calibrated and validated. The Thomas model adjusted well to the experimental data. This approach for the model setup can be used as a tool for designing, optimising and ultimately predicting potential P removal and recovery in existing WWTP, therefore estimating the economic advantage of such a process compared with traditional processes as well as revenue of P recovery.

Keywords: Phosphorus removal and recovery; ion exchange; mathematical modelling.

INTRODUCTION Ion exchange (IEX) adsorption columns are an excellent means to remove nutrients for tertiary treatment instead of resource hungry treatment units (e.g. biological). The ion exchange media has high affinity to remove the ions from the wastewater, that can then be recovered, therefore gaining economical value when compared with traditional methods (Martin *et al*., 2009). Dynamic adsorption occurs when a solution continuously flows through a fixed packed column (open system) filled with the adsorbent media (Xu *et al*., 2013). Modelling of breakthrough and saturation curves is important to describe experimental data and predict behaviour. Nevertheless, the mathematical complexity behind some models make them impractical, as a range of parameters are required from different experiments (Trgo *et al*., 2011). Consequently, different empirical models have been suggested.

This study aims at applying the empirical Thomas model (Thomas, 1944) to describe P removal from tertiary wastewater (WW) on a fixed-bed of a hybrid anion exchanger (HAIX). P Recovery was based on an empirical model. Calibration and validation were performed with 1 year of data.

METHODS Experimental research was conducted at Cranfield University with a demonstration scale ion exchange process. The column (93.9 cm) was filled with 25 kg of HAIX and treated 10 $m^3.d^{-1}$ of tertiary WW. It was regenerated with NaOH prior to recommencing treatment. The Thomas model is shown in Eq. 1.1 (C: Effluent concentration ($mg.ml^{-1}$); C_0: Influent concentration ($mg.ml^{-1}$); k_{th}: Thomas constant ($ml.min^{-1}.mg^{-1}$); q_0: Maximum adsorption capacity ($mg.g^{-1}$); m: Media mass (g); Q: Flow rate ($ml.min^{-1}$); t: time (mins)). The model was calibrated with autosampler data (30 min sampling intervals) and validated with data with from seven months of continuous sampling (less points per cycle). P mass in the regenerant after column regeneration is shown in Eq. 1.2 – $P_{recovery}$: P in the regenerant (g); P_{sim}: P simulated in the column; k and y: coefficient.

$$\frac{C}{C_0} = \frac{1}{1+e^{\left(k_{th} \cdot q_0 \cdot \frac{m}{Q} - k_{th} \cdot C_0 \cdot t\right)}} \tag{1.1}$$

$$P_{recovery} = k . P_{sim}^{y} \tag{1.2}$$

RESULTS AND DISCUSSION Calibration with varying C_0 and t resulted in a pair of k_{th} and q_0 coefficients from each run (independent data), presenting excellent fitting (Table 1.1 – partial result set shown due to page limitations). Applying the average model parameters (Fig. 1.1 (A)) in the model allowed to validate it with continuous sampling data. The area above the curves in Fig. 1.1 (A) (average, 95% confidence interval (CI)) represents the mass of P removed in the column, where the calibrated model can predict P removal with good accuracy (Table 1.1 – P_{obs} vs P_{sim}). Fig. 1.1 (B) and (C) represents the model validation of cycle 13 for continuous sampling, while the $P_{recovery}$ (calibration) model predicts most of the observed P in the regenerant (P_{NaOH}) within the 95% confidence interval, respectively. P_{sim} was overestimated compared to P_{NaOH} (not all recoverable), therefore the coefficients in Eq. 1.2 were calibrated to represent the simulation of $P_{recovery}$ in the regenerant (Fig. 1.1 (C)). MTZ depends on the BT, with lower times resulting in greater MTZs and consequently greater column saturation, independently of C_0 (Table 1.1).

Table 1.1 P column operating conditions, model parameters, model fitting and breakthrough (BT) curve parameters.

AS run	Operating conditions			Model parameters			BT curve parameters			
	C_0 ($mg.l^{-1}$)	Run (min)	P (g) NaOH	q_0 ($mg.g^{-1}$)	k_{th} ($ml.min^{-1}.mg^{-1}$)	RMSE	P_{obs} (g)	P_{sim} (g)	MTZ (cm)	BT (min)
2	5.73	1260	-	1.49	0.664	0.97	34.5	39.5	92.3	22
5	5.08	900	29.0	1.69	1.128	0.994	30.6	35.5	24.8	663
7	5.51	2580	35.2	2.20	0.597	0.987	56.3	48.1	67.9	714
10	5.28	1080	22.3	1.65	0.728	0.989	33.6	40.4	57.8	415
11	5.33	1200	30.7	1.50	0.570	0.983	32.3	43.0	80.4	172
16	4.91	1245	34.7	1.68	0.670	0.994	33.3	45.4	65.3	380
17	5.27	1125	33.3	2.16	0.889	0.977	39.6	41.5	42.7	613
Mean	***5.30***	***1281***	**-**	***1.75***	***0.74***	**-**	**-**	**-**	**-**	**-**

P_{NaOH}: P recovery observed in NaOH; P_{obs}: P removal calculated from observed data; P_{sim}: P removal calculated from model simulation with average coefficients; RMSE: Root Mean Square Error; MTZ: Mass transfer zone; BT: Breakthrough time 5%.C_0.

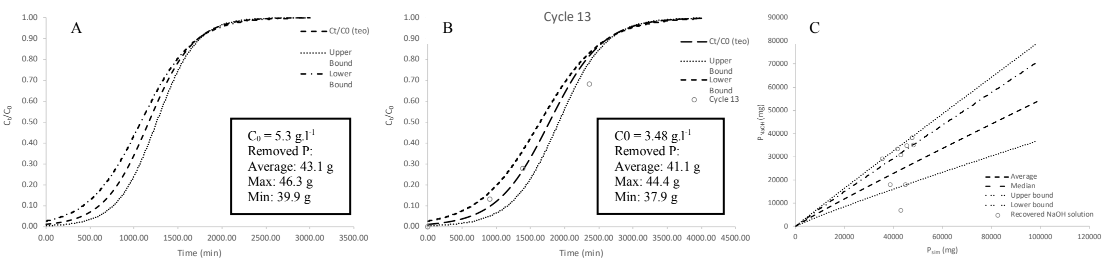

Figure 1.1 (A) Calibrated P curve with average values (C_0, k_{th}, q_0); (B) Validated cycle 13; (C) $P_{recovery}$ calibrated.

The Thomas model was calibrated with success with experimental data from a continuous flow fixed-bed HAIX column removing P from tertiary WW. P recovery range broadens when P_{sim} increases (Figure 1.1 (C)), therefore the model for longer columns (more media) will increase its confidence interval. This study shows that the

Thomas model calibrated with a multitude of runs, with a 95% CI, is a useful tool when designing, optimising and ultimately predicting P removal. Therefore, the coverage properties for the models estimating P removal from WW and potential $P_{recovery}$ in NaOH are improved, opposed to calibrating one single run or not considering a CI.

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