Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 148 (2016) 779 – 786

Procedia Engineering

www.elsevier.com/locate/procedia

4th International Conference on Process Engineering and Advanced Materials

Adsorptive Resource Recovery from Human Urine: System Design, Parametric Considerations and Response Surface Optimization

Prithvi Simha[a,b], Paurush Banwasi[a], Melvin Mathew[d], M. Ganesapillai[c,*]

[a] Department of Environmental Sciences and Policy, Central European University, Nádor utca 9, 1051 Budapest, Hungary
[b] School of Earth, Atmospheric and Environmental Sciences (SEAES), The University of Manchester, M13 9PL, United Kingdom
[c] Mass Transfer Group, Department of Chemical Engineering, VIT University, Vellore – 632 014, India
[d] Chemical Engineering Division, SEMTE, Ira A. Fulton Schools for Engineering, Arizona State University, Tempe, Arizona

Abstract

Despite its high concentration, potential availability and hence, potential reusability of nutrients, human urine continues to be flushed away in our toilets. The poor management of nutrients in our built environment in lieu of the representative failures in our systems to safely handle, treat and assimilate these 'waste' resources has resulted in considerable environmental externalities. Adsorption systems that utilize agro–waste sourced carbon as an adsorption media have shown promise in recovering plant–required nutrients from urine. This study details the applicability of two continuously operated columns for stripping urea from urine for subsequent use as fertilizers. The first column was packed with prepared carbon at various bed heights (10–50 cm) and the second column had carbon immobilized over etched glass beads of various support sizes (1.5–2.5 cm). By using a Box–Behnken design and Response Surface Methodology (RSM), the system was optimized with the objective of maximizing column capacities. For the packed bed, maximum sorption of 0.116 $g.g^{-1}$ occurs at inlet flow rate of 6 $L.h^{-1}$, concentration of 100% and carbon bed depth of 30 cm; in the immobilized bed, the optimal parameters were identified as flow rate of 10 $L.h^{-1}$, 100% initial urea concentration and support size of 1.5 cm to yield capacity of 0.328 $g.g^{-1}$. Immobilization as a pre–treatment in column design was significantly advantageous in recovering higher amount of urea at lesser activated carbon input relative to the packed bed. RSM was found to be an effective tool for selecting the process parametric inputs, in describing their effects on the operation of the column and in maximizing the urea recovery.

Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: Column adsorption; Immobilization; Packed bed column; Activated carbon; Wastewater; Ecological sanitation

* Corresponding author. Tel.: + 91 97902 99447; Fax: +91 462 24 30 92.
E-mail address: maheshgpillai@vit.ac.in

Peer-review under responsibility of the organizing committee of ICPEAM 2016
doi:10.1016/j.proeng.2016.06.557

Nomenclature

a	Modified dose- response model constant
A	Area under Break through curve, (m^2)
b	Modified dose- response model constant
C_{ads}	Adsorbed urea concentration, ($g.L^{-1}$)
C_b	Breakthrough concentration, ($mg.L^{-1}$)
C_o	Inlet sorbate concentration, ($g.L^{-1}$)
C_t	Outlet sorbate concentration, ($g.L^{-1}$)
m_{total}	Total amount of urea fed to the column, (mg)
m	Total mass of adsorbent in the column, (g)
q_c	Column capacity, (mg)
q_E	Capacity at the exhaustion point, ($mg.g^{-1}$)
q_{eq}	Equilibrium uptake or maximum column capacity, ($mg.g^{-1}$)
q_o	Maximum solid- phase concentration of the solute, ($mg.g^{-1}$)
Q	Flow rate, ($mL.min^{-1}$)
R^2	Correlation coefficient
t_b	Breakthrough time, (min)
t_{total}	Total flow time, (min)
U_o	Linear velocity, ($cm.min^{-1}$)
v	Flow rate, ($mL.min^{-1}$)
V	Velocity, ($cm\ min^{-1}$)
Z	Bed height, (cm)
τ/texp	Time required for 50% of adsorbate break-through, (min)
X_i	Controlled input parameters for RSM
Y	Desired output for RSM
$\beta_0,\beta_i,\beta_{ij}$	RSM model constants

1. Introduction

As a metabolic process, excrement is ubiquitous to all living organisms; while this process coexists in harmony with the functioning of natural ecosystems and biogeochemical cycles for all other living organisms, this is however not true for human excretion. Feces and urine (90% nitrogen, 50–65% phosphorus and 50–80% potassium), despite being one of the most concentrated streams of macronutrients along the food chain [1], have been managed in our built environment in ways that have resulted in environmental externalities [2]. Conventional wastewater treatment continues to be representative of our failures in designing appropriate systems to handle, treat and safely assimilate these 'waste' resources. Further, what is even more significant is that our ideology towards their management has seen these resources classified as 'wastes' and we have placed emphasis on their disposal rather than their recovery and reuse. Human urine continues to be highly underestimated as a source of nutrients and instead, we have compensated our needs in supplementing soil fertility through the application of synthetic fertilizers [3–5].

It is promising to see that several recent studies have utilized the benefits of source–separation based urine diversion toilets in designing appropriate processes for resource recovery. In our previous studies, we have methodically investigated the applicability of renewable agro–waste sourced activated carbon in designing adsorptive recovery processes for human urine; in particular, microwave activation induced carbonized coconut shells displayed near compete separation of solid urea from aqueous urine solutions [6–8]. Studies were performed in batch as well as continuous columns to identify various input parameters that determine the urea recovery potential of the carbon [9]. Hence, the data gathered and experiences garnered over the course of these experiments make case for an interesting objective of process optimization.

Since there are several factors that need to be considered simultaneously along with interactions of these factors, a one–factor–at–a–time approach cannot be applied. Since our identified process variables are inter–

dependent, we look towards Response Surface Methodology (RSM) to distinguish and analyze these interactions. Two continuously operated adsorption columns were designed and experiments were performed by taking the advantage of a Box–Behnken design [10,11]: the first column wherein, the activated carbon was packed at various bed heights and; the second wherein, the same activated carbon was immobilized onto glass beads to provide a relatively greater surface to volume ratio for the sorption. The objective in optimization for both the engineered columns was to maximize the urea removal at minimum carbon usage. To capture this we set the column capacity as the output response variable. A hypothesis that we also seek to test through the application of the experimental data from both the columns into the RSM model–derived equations is that: immobilization of the carbon would be comparatively advantageous and result in higher column capacity.

2. Experimental

Human urine was collected from 30 volunteers over a 1 month collection period and utilized continuously; the collection was carried out using polyethylene flasks (1 L) and conditioned as described elsewhere [7]. Activated carbon was prepared from coconut shells (precursor) by microwave (180 W, 15 min) induced carbonization (500°C, 22°C.min^{-1}, 1 h) as detailed in our earlier studies [6–8]. To perform the resource recovery experiments on the collected urine, two columns of ϕ 4 cm and height 80 cm were designed and installed; column 1 was packed with the prepared carbon at various bed heights (10–50 cm) and column 2 had the carbon immobilized over etched (HF) glass beads of various support sizes (1.5–2.5 cm). Sorption experiments were performed in both columns as per the procedures detailed earlier [9].

Various process parameters control the potential recoverability of urea from human urine; however, since all the parameters are controllable and measureable, it is possible to optimize the response surface of the engineered columns. To do this, we look towards Response Surface Methodology (Design–Expert® V.9, MN, USA) as it allows numerical quantification of the direct and interactive relationships between the controlled input parameters (X_i) and the desired output (Y: response) [12]. A second–order equation was utilized with the objective of maximizing the column capacity (Y or q_c; g.g^{-1}) as shown below (Eq. 1, 2); β_0 represents the model constant, X_i the controlled independent parameters, β_i and β_{ij} the coefficients determined by non–linear regression of the model equation. Furthermore, a three–factorial, three–level rotatable Box–Behnken experimental design was used to efficiently select the experiments (17 runs each) to be performed over both the columns as well as to minimize the experimental error.

The input variables (factors) for column 1 were: initial concentration X_1 (20, 60 and 100 mg.g^{-1}), urine flow rate X_2 (2, 6 and 10 L.h^{-1}), and bed depth X_3 (10, 30 and 50 cm). Similarly, for column 2: initial concentration X_1 (20, 60 and 100 mg.g^{-1}), urine flow rate X_2 (2, 6 and 10 L.h^{-1}), and carbon support size X_3 (1.5, 2 and 2.5 cm). The statistical significance, goodness of fit and reliability of the model was checked by Analysis of variance (ANOVA) and Fischer–Test in Minitab® (V.15.1, State College, PA, USA) [11]. Consequently, following the validation, the obtained 3–D surfaces were visually interpreted to understand the dependency of the response on the controlled input factors.

$$q_c = \left(\frac{Q\,A}{1000}\right) = \frac{Q}{1000}\int_0^{t_{total}} C_{ads}\,dt \tag{1}$$

$$Y = \beta_0 + \sum_i \beta_i X_i + \sum_{ij} \beta_{ii} X_i^2 + \sum_{ij} \beta_{ij} X_i X_j \tag{2}$$

3. Results and Discussion

To begin with, the validity of the model was verified and the results of the statistical analyses are presented in Table 1. The model was able to take into account more than 90% of the variability in the experimental data for each response. As seen through R^2_{Pred}, models for both the columns exhibited good predictive capability. Since P–value is less than 5% it is safe to assume that at least one factor is statistically significant in determining the output response

[13]. Furthermore, from the test for lack of fit, the *P*–values were found to be low (< 1%) and we accepted the hypothesis that the model is adequate in describing the adsorption within both the columns.

$$Y = 0.094 + 0.032 \cdot X_1 - 0.012 \cdot X_2 - 5.875 \times 10^{-003} \cdot X_3 - 0.010 \cdot X_1^2 - 0.022 \cdot X_2^2 \quad (3)$$

$$Y = 0.210 + 0.076 \cdot X_1 + 0.050 \cdot X_2 - 0.042 \cdot X_3 - 0.053 \cdot X_1^2 - 0.041 \cdot X_2^2 + 1.500 \times 10^{-003} \cdot X_3^2 \quad (4)$$

Table 1. ANOVA, check of statistical significance and validity of the models for column adsorption

* Note: Values highlighted in black represent high influence; values in grey represent moderate influence

Source	Sum of Squares		*df*		Mean Square		*F* value		*Prob* > *F* *	
	Column 1	Column 2	1	2	Column 1	Column 2	Column 1	Column 2	Column 1	Column 2
Model	0.1059991	0.0140223	9	9	0.0117777	0.0015580	17.026789	65.404739	0.0005752	0.0000063
X_1	0.0462080	0.0083205	1	1	0.0462080	0.0083205	66.802148	349.28636	**0.0000795**	**0.0000003**
X_2	0.0200000	0.0011761	1	1	0.0200000	0.0011761	28.913672	49.372564	**0.0010335**	**0.0002066**
X_3	0.0137780	0.0002761	1	1	0.0137780	0.0002761	19.918629	11.591454	**0.0029254**	**0.0113707**
X_1X_2	0.0046240	0.0001440	1	1	0.0046240	0.0001440	6.6848410	6.0449775	0.0361809	0.0435512
X_1X_3	0.0000640	0.0000000	1	1	0.0000640	0.0000000	0.0925238	0.0000000	0.7698361	1.0000000
X_2X_3	0.0011560	0.0000003	1	1	0.0011560	0.0000003	1.6712102	0.0104948	0.2371274	0.9212773
X_1^2	0.0118274	0.0004316	1	1	0.0118274	0.0004316	17.098633	18.120019	**0.0043762**	**0.0037616**
X_2^2	0.0072516	0.0020148	1	1	0.0072516	0.0020148	10.483489	84.579421	**0.0142961**	**0.0000371**
X_3^2	0.0000095	0.0012711	1	1	0.0000095	0.0012711	0.0136959	53.360294	0.9101235	**0.0001621**
Residual	0.0048420	0.0001668	7	7	0.0006917	0.0000238		R^2	0.9563158	0.9882480
Lack of Fit	0.0048420	0.0001668	3	3	0.0016140	0.0000556		R^2_{Adj}	0.9001505	0.9731383
Pure Error	0	0	4	4	0	0		R^2_{Pred}	0.3010532	0.8119678
Cor Total	0.1108411	0.0141891	16	16				Adeq Precision	12.641577	23.708764
Std. Dev.	0.0263005	0.0048807						BIC	–62.20585	–119.4718
Mean	0.1632353	0.0707647						AICc	–33.87132	–91.13730
C.V. %	16.111995	6.8971107								
PRESS	0.0774720	0.0026680								
–2 Log Likelihood	–90.53798	–147.8040								

The slight discrepancy between the R^2 and R^2_{Adj} values points towards the inclusion of non–significant factors in the model [14]. To address this, the model was refined as per the results of Table 1 and the new model equations along with the regression coefficients are provided in Eq. 3 (column 1) and Eq. 4 (column 2). For column 1, X_1, X_2 are highly influential whereas X_3, X_1^2 and X_2^2 are moderately significant; for column 2, X_1, X_2, X_2^2 and X_3^2 are highly influential and X_3, X_1^2 assert moderate influence [15].

Table 2 enlists the experimental and predicted column capacities obtained for both the columns; as seen, the capacity varied from 0.026 to 0.107 $g.g^{-1}$ in the packed bed while it significantly higher and varied from 0.028 to 0.299 $g.g^{-1}$. Good agreement was seen between the theoretical predictions and the observed values indicating that the model equations were adequate in capturing the column capacity as a function of the input variables to the column (X_1, X_2, and X_3). Initial urea concentration varied through deionized water dilution of urine exerted the most significant effect over both the columns. Visualization of the experimental response as a function of the input factors to the column was done by plotting 2–D isoresponse contours that allowed graphical illustration of a constant column capacity in a two–factorial plain for all the three factorial combinations at their intermediate levels (Fig. 1).

As corroborated through the contour plots, higher inlet concentration (80–100%) is necessary to stimulate the column to overcome resistances in mass transfer (Fig. 1 (a,b)). However, the interaction of concentration with inlet

flow rate is markedly different for both columns; flow rate exhibits an inverse relationship at higher input values with column capacity in the packed bed (Fig. 1 (c)) whereas it is directly contributing towards higher capacity in the immobilized bed (Fig. 1 (f)). Interestingly, higher flow rate to the immobilized bed is favorable only when the carbon support size is low. Given the converse relationship between bed residence time of the sorbate and the inlet flow rate, higher flow rates resulted in poor adsorption as seen in run 5 (column 1) and run 9 (column 2). Moreover, smaller the size of the support beads, greater is the interaction of the urea in urine with the immobilized carbon on account of higher surface area to volume ratio (Fig. 1 (e)); Ko et al. [16] observed a similar correlation in their study of metal–char interaction.

Lastly, in order to perform numerical optimization for both the columns, the desirability function approach was followed to transform the column capacity (response) into desirability (d_j), a dimensionless entity; the model was setup in order to identify the values of the input variables that result in maximization of the column capacity. Desirability ranges from 0 to 1 with $d=0$ unacceptable and $d=1$ indicating that the model response is equal to that of the target value [13]. For the packed bed column adsorption, column capacity attains maximum of 0.116 $g.g^{-1}$ when inlet flow rate is 6 $L.h^{-1}$, concentration is 100% and the carbon bed depth is 30 cm. Similarly, for the immobilized carbon adsorption, the optimal parameters were identified as flow rate of 10 $L.h^{-1}$, 100% initial urea concentration and support size of 1.5 cm to yield a capacity of 0.328 $g.g^{-1}$. Based on the optimum capacities of both the columns, we also accept the hypothesis that immobilization had a significant impact on the urea recovery and performs better than the packed bed column.

4. Conclusions

The present study dealt with optimization of urea recovery from human urine passed through two adsorption columns. A comparative approach was followed using a Box–Behnken design and we concluded that RSM was well suited for our goal of maximizing the urea adsorption within the columns. RSM allowed identification as well as quantification of the direct and interactive effects of the controlled input parameters to the system. Immobilization as a pretreatment in column design was found to be advantageous as it resulted in higher amount of recovery at lesser activated carbon input. We find RSM to be very useful and effective in selecting the process inputs and in maximizing the desired output (column capacity) in adsorption systems for wastewater treatment and resource recovery.

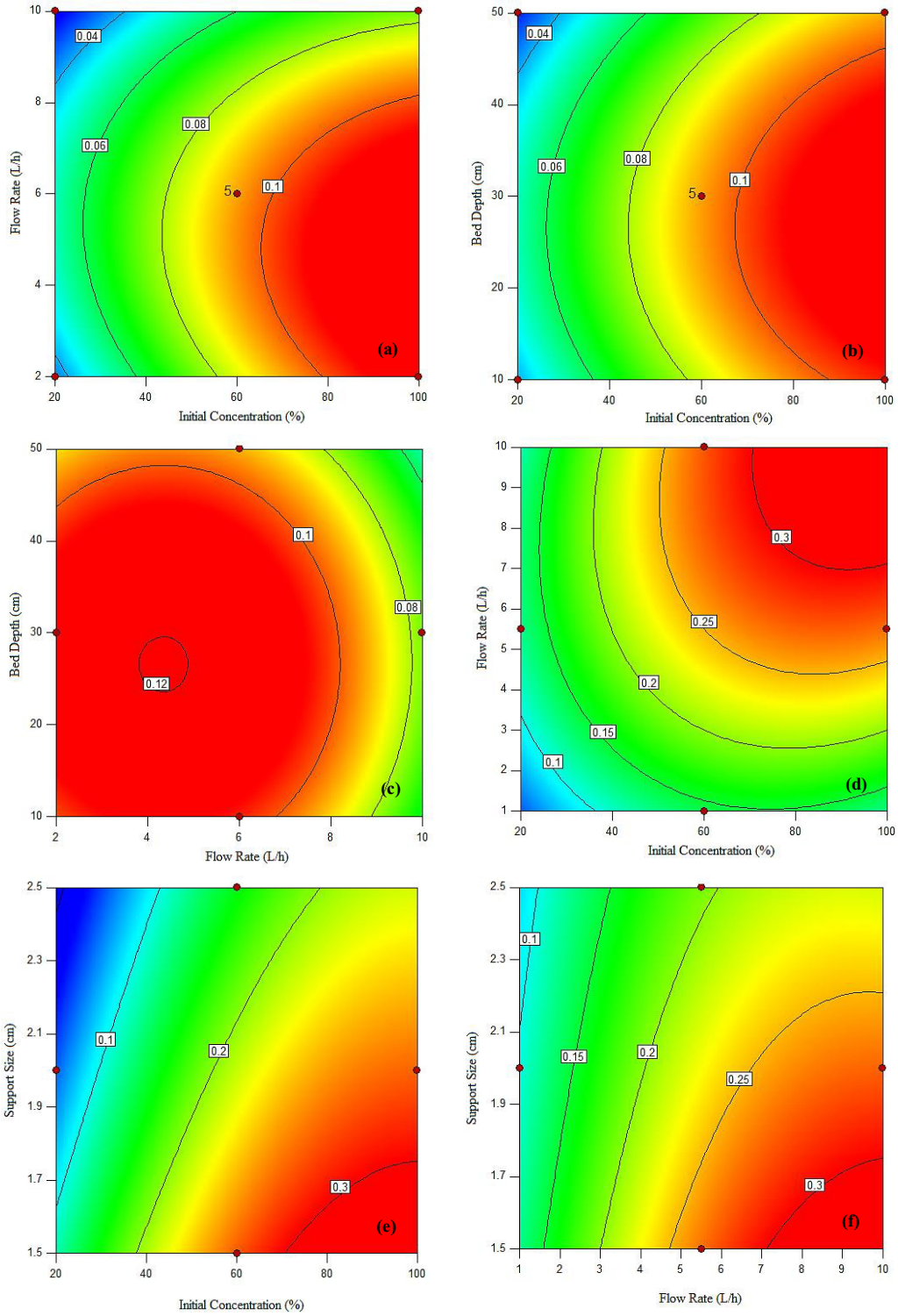

Fig 1: Isoresponse contour lines for urea adsorption and optimization in two different column designs

Table 2. Optimized experimental design and results for urea recovery from both adsorption columns

Run	Real Variables			Coded Variables			Response: Column Capacity (Y; $g.g^{-1}$)	
	X_1	X_2	X_3	X_1	X_2	X_3	Experimental	Predicted
Column 1: Packed Bed Adsorption								
1	100	6	10	+1	0	–1	0.107	0.105
2	60	6	30	0	0	0	0.094	0.094
3	60	6	30	0	0	0	0.094	0.094
4	20	6	50	–1	0	+1	0.026	0.028
5	20	10	30	–1	+1	0	0.030	0.024
6	60	6	30	0	0	0	0.094	0.094
7	20	2	30	–1	–1	0	0.035	0.036
8	60	10	50	0	+1	+1	0.033	0.037
9	60	6	30	0	0	0	0.094	0.094
10	100	6	50	+1	0	+1	0.096	0.093
11	100	2	30	+1	–1	0	0.106	0.112
12	60	2	50	0	–1	+1	0.064	0.061
13	100	10	30	+1	+1	0	0.077	0.076
14	60	2	10	0	–1	–1	0.077	0.073
15	60	6	30	0	0	0	0.094	0.094
16	20	6	10	0	0	–1	0.037	0.040
17	60	10	10	0	+1	–1	0.045	0.048
Column 2: Immobilized Bed Adsorption								
1	60	2	2.5	0	–1	+1	0.069	0.093
2	60	10	1.5	0	+1	–1	0.299	0.276
3	100	10	2	+1	+1	0	0.250	0.273
4	20	6	2.5	–1	0	+1	0.035	0.034
5	60	6	2	0	0	0	0.207	0.207
6	100	2	2	+1	–1	0	0.131	0.105
7	60	6	2	0	0	0	0.207	0.207
8	60	10	2.5	0	+1	+1	0.184	0.159
9	20	10	2	–1	+1	0	0.028	0.053
10	20	6	1.5	–1	0	–1	0.128	0.125
11	60	2	1.5	0	–1	–1	0.116	0.142
12	60	6	2	0	0	0	0.207	0.207
13	100	6	1.5	+1	0	–1	0.268	0.269
14	60	6	2	0	0	0	0.207	0.207
15	60	6	2	0	0	0	0.207	0.207
16	100	6	2.5	+1	0	+1	0.191	0.194
17	20	2	2	–1	–1	0	0.043	0.021

References

[1] H. Kirchmann, S. Pettersson, Human urine – Chemical composition and fertilizer use efficiency, Fertil. Res. 40 (1995) 149–154. doi:10.1007/BF00750100.

[2] G. Langergraber, E. Muellegger, Ecological Sanitation–a way to solve global sanitation problems?, Environ. Int. 31 (2005) 433–444. doi:10.1016/j.envint.2004.08.006.

[3] T. Karak, P. Bhattacharyya, Human urine as a source of alternative natural fertilizer in agriculture: A flight of fancy or an achievable reality, Resour. Conserv. Recycl. 55 (2011) 400–408. doi:10.1016/j.resconrec.2010.12.008.

[4] M. Winker, B. Vinnerås, A. Muskolus, U. Arnold, J. Clemens, Fertiliser products from new sanitation systems: their potential values and risks., Bioresour. Technol. 100 (2009) 4090–6. doi:10.1016/j.biortech.2009.03.024.

[5] M. Ganesapillai, P. Simha, S.S. Beknalkar, D.M.R. Sekhar, Low–grade rock phosphate enriched human urine as novel fertilizer for sustaining and improving agricultural productivity of Cicer arietinum, Sustain. Prod. Consum. 6 (2016) 62–66. doi:10.1016/j.spc.2016.01.005.

[6] M.G. Pillai, P. Simha, A. Gugalia, Recovering urea from human urine by bio–sorption onto Microwave Activated Carbonized Coconut Shells: Equilibrium, kinetics, optimization and field studies, J. Environ. Chem. Eng. 2 (2014) 46–55. doi:10.1016/j.jece.2013.11.027.

[7] M. Ganesapillai, P. Simha, A. Zabaniotou, Closed–loop fertility cycle: Realizing sustainability in sanitation and agricultural production through the design and implementation of nutrient recovery systems for human urine, Sustain. Prod. Consum. 4 (2015) 36–46. doi:10.1016/j.spc.2015.08.004.

[8] M. Ganesapillai, P. Simha, The rationale for alternative fertilization: Equilibrium isotherm, kinetics and mass transfer analysis for urea–nitrogen adsorption from cow urine, Resource–Efficient Technologies 1 (2015) 90–97. doi:10.1016/j.reffit.2015.11.001.

[9] M. Ganesapillai, P. Simha, K. Desai, Y. Sharma, T. Ahmed, Simultaneous Resource Recovery and Ammonia Volatilization Minimization in Animal Husbandry and Agriculture, Resource–Efficient Technologies (2016). doi:10.1016/j.reffit.2015.12.001

[10] K. Yetilmezsoy, S. Demirel, R.J. Vanderbei, Response surface modeling of Pb(II) removal from aqueous solution by Pistacia vera L.: Box–Behnken experimental design., J. Hazard. Mater. 171 (2009) 551–62. doi:10.1016/j.jhazmat.2009.06.035.

[11] I. Elksibi, W. Haddar, M. Ben Ticha, R. Gharbi, M.F. Mhenni, Development and optimisation of a non conventional extraction process of natural dye from olive solid waste using response surface methodology (RSM), Food Chem. 161 (2014) 345–52. doi:10.1016/j.foodchem.2014.03.108.

[12] M. Ganesapillai, M. Mathew, A. Singh, P. Simha, Influence of Microwave and Ultrasound pretreatment on Solvent Extraction of Bio–components from Walnut (Julgans regia L.) Shells, Periodica Polytechnica Chemical Engineering 60 (2016) 40–48. doi:10.3311/PPch.8480.

[13] J. Li, C. Ma, Y. Ma, Y. Li, W. Zhou, P. Xu, Medium optimization by combination of response surface methodology and desirability function: an application in glutamine production., Appl. Microbiol. Biotechnol. 74 (2007) 563–71. doi:10.1007/s00253–006–0699–5.

[14] P. Simha, M. Mathew, M. Ganesapillai, Empirical modeling of drying kinetics and microwave assisted extraction of bioactive compounds from Adathoda vasica and Cymbopogon citratus, Alexandria Eng. J. (2016). doi:10.1016/j.aej.2015.12.020.

[15] C. Li, J. Bai, Z. Cai, F. Ouyang, Optimization of a cultural medium for bacteriocin production by Lactococcus lactis using response surface methodology, J. Biotechnol. 93 (2002) 27–34. doi:10.1016/S0168–1656(01)00377–7.

[16] D.C.K. Ko, J.F. Porter, G. McKay, Optimised correlations for the fixed–bed adsorption of metal ions on bone char, Chem. Eng. Sci. 55 (2000) 5819–5829. doi:10.1016/S0009–2509(00)00416–4.