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Salicylic Acid Adsorption onto Sephabeads SP206 in View of its Purification by Thermal Parametric Pumping

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Abstract. Parametric pumping is a cyclic process that allows purification of industrial wastewaters without spending chemicals for regeneration and therefore avoiding a new pollution problem. The applicability of this technology to the purification of salicylic acid in liquid phase has been studied, salicylic acid being a phenolic compound with a high production in a world scale which is mainly linked to aspirin manufacture. The aim is to get at the same time a purified and a concentrated stream of salicylic acid, which allows recycling for the industrial process so contributing to achieve the concept of a zero-pollutant plant. Different operating conditions were accomplished in an automated pilot plant and experimental results were compared to those simulated by a previously developed package (Davesac et al., 2000). A satisfactory agreement is obtained with the linear driving force and axial dispersion model.

Keywords: parametric pumping, purification, salicylic acid

Introduction

There has been a growing concern for public health and environment over the last few decades. Methods such as aeration, biological degradation, chemical oxidation, photo-oxidation, solvent extraction and adsorption have been developed for the removal of organics from wastewater. Among them, solvent extraction and adsorption are the most commonly used. Solvent extraction is preferred when the solute concentration is relatively high, typically <1 wt.%. Adsorptive processes are able to concentrate solutes and are used in the purification of diluted wastewaters and they have the advantage that they are non destructive and recovery of organics through regeneration is possible. However, from an environmental point of view, they suffer from two important drawbacks: one is the need for a chemical regenerant, with the associated waste disposal problem; the other is the inefficiency of the fixed bed operation, since only a fraction of the adsorbent capacity is used really. Those drawbacks may be overcome by the operation of parametric pumping as a technology for the purification of wastewaters.

Parametric pumping is a separation cyclic process based on the coupling of periodic changes in equilibrium conditions with the flow direction in which the liquid effluent to be treated is pumped through the adsorbent bed. Changes on the equilibrium conditions are got by periodically changing an intensive variable such as temperature, pH, pressure, etc. The basis of thermal parametric pumping is the fact that equilibrium isotherms of a solute onto a certain adsorbent are strongly affected by temperature. The principles can be easily understood by comparing parametric pumping cyclic operation with the McCabe-Thiele diagram used in binary distillation. The detailed description of the methodology, first described by Wilhelm and colleagues (Wilhelm et al., 1966) may be found elsewhere (Simon et al., 1997), several authors having modeled this (Wankat et al., 1978; Chen et al., 1972; Ferreira and Rodrigues, 1995a, 1995b; Díez et al., 1998; Silva et al., 1999; Davesac et al., 1999).

Salicylic acid is a drug compound nowadays produced from phenol. Its synthesis involves the

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combination of several reactants and results in almost pure product after separation and purification. Although salicylic acid was once used as a painkiller it has been substituted by a derivative product, acetyl salicylic acid (aspirin), which reduces stomachaches effect of salicylic acid. Aspirin production must fulfill the needs of a market that only in the United States involves more than 10,000 tons of aspirin a year. On the other hand, salicylic acid concentrations above 800 mg/L after 6 hours post exposure are severely toxic and may be lethal (Balali-Mood, 1981). The separation, purification and concentration of salicylic acid must then be considered in this context.

Although activated carbons were conventionally used for the removal of variety of organics from wastewater they have a poor response to regeneration (Browne and Cohen, 1990; Cairo et al., 1982; Grant and King, 1990). Polymeric resins later started to be viewed as an alternative to activated carbon because of their variations in functionality, surface area, porosity, etc, which makes it possible to customize the resins for the selective removal of specific organic solutes (Kunin, 1977). Sephabeads SP206 is a synthetic adsorbent based on a styrene and DVB (divinylbenzene) copolymer. This resin has been successfully used for phenol and phenolic derivatives adsorption but scarce information is available on drug adsorption and transport within this or other polymeric resins.

The aim of the present work is to study the effect of operational variables of thermal parametric pumping technology on the purification of diluted wastewaters from a salicylic acid manufacture unit. At the same time it would be desirable the technology to concentrate salicylic acid to allow recycling of the concentrated stream for the industrial process and so contributing to achieve the concept of a zero-pollutant plant.

Experimental

Chemicals and Adsorbents

Salicylic acid ($C_7H_6O_3$) was purchased from Sigma-Aldrich (Spain) and work solutions were prepared with degassed and distilled water. Concentration of salicylic acid in solution was determined by measuring the light absorbance at a wavelength of 295 nm by means of a UV-visible spectrophotometer Jasco (model 7800, Japan).

The polymeric resin Sephabeads SP206 (Mitsubishi Chemical Corporation) was purchased from Resindion (Italy). Table 1 shows the physical characteristics of Sephabeads SP206 as supplied by the manufacturers.

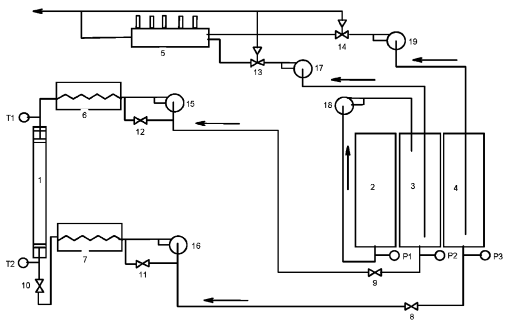
Parametric Pumping Operation

Design of any adsorption cyclic process requires studying equilibrium in details along with the studies of dynamics of the adsorbent beds for the solutes involved. Results about salicylic acid batch adsorption onto Sephabeads SP206 were previously obtained (Otero et al., 2004). Adsorption equilibrium data are shown in Table 1 together with the rest of parameters used for the simulations and the characteristics of the bed.

The automated pilot plant, which experimental set up is shown in Fig. 1, was used to carry out the salicylic acid purification experiments by recuperative parametric pumping. After saturation of the bed at the cold temperature ($T_c = 293$ K), the liquid solution is pumped through the bed of Sephabeads SP206 in upward flow (hot half-cycle at temperature $T_h = 333$ K) followed by downward flow pumping of the solution (cold half-cycle at temperature $T_c = 293$ K). This is repeated for several cycles and each cycle comprises one hot and one cold half-cycles. The top reservoir receives product when the solution is pumped through the column in

Table 1. Characteristics and parameters used for the simulations of the operated parametric pumping system.

Resin properties	Bed characteristics	Equilibrium data	Thermal parameters	Transport parameters
$\rho = 1190$ g L^{-1}	$L = 0.85$ m	$Q = 45.2$ mg g^{-1}	$Pe_{\mathrm{h}} = 100$	$Pe = 120$
$f_{\mathrm{h}} = 0.5$	$d = 0.09$ m	$K_L^{\infty} = 1.27 \times 10^{-8}$Lmg^{-1}	$\xi_h = 1.205$	D_m (293 K) $= 4.46 \times 10^{-8}$m^2 min^{-1}
$r_p = 2 \times 10^{-4}$ m	$\varepsilon = 0.4$	$\Delta H_L = -37190$ Jmol^{-1}	h_w =0.852 KJ/(m^2 min K)	D_m (333 K) $= 5.07 \times 10^{-8}$ m^2 min^{-1}
$\varepsilon_p = 0.607$				
$\tau = 2$				



Legend:
(1) Glass column G90-Amicon
(2) Feed reservoir
(3) Top reservoir
(4) Bottom reservoir
(5) Fraction collector Gilson
(6) –(7) Heat exchangers
(8)-(12) Two ways solenoid valves
(13)-(14) Three ways solenoid valves
(15)-(16) Peristaltic pumps Watson Marlow
(17)-(19) Peristaltic pumps Gilson
(T1)-(T2) Thermocouples (type K)
(P1)-(P3) Pressure transducers Schwaevitz (type P510)

Figure 1. Experimental setup of the parametric pumping pilot plant.

upward flow and the bottom reservoir when in downward flow. The system was operated in a recuperative mode, i.e., the temperature change was carried out by the solution itself, which is heated or cooled by means of thermostatic baths (Fig. 1). Direct mode implies that the temperature change is imposed through the column wall, but the recuperative mode is more appropriate for industrial purposes as this allows for larger diameter columns (Ramalho et al., 1991). The combination of both modes has also been studied (Ghasem, 2003) but, anyway, under appropriate conditions one can expect to get a concentrated solution at the top of the column and a free-solute effluent at the bottom, so thermal energy is used as regenerant.

The parametric pumping unit was operated in a semicontinuous way and the main aim was to obtain clean water as the bottom product and salicylic acid concentrated solution as the top product.

Runs under different experimental conditions were carried out to ascertain the effect of the cycle time, the flow rate and the ratio between bottom and top product volumes. Experimental conditions are shown in Table 2.

Effect of the Cycle Time. The effect of the cycle time on the system salicylic acid-Sephabeads SP206 has been studied by comparing runs 1, 2 and 3. The volume percolated in upward flow (hot half cycle) and downward flow was changed while the following conditions were set:

- Production $(V_B + V_T) = 8$ L
- Ratio $(V_B\ /\ V_T) = 0.6$
- Flow-rate (Q_c and Q_h) $= 200$ mL min^{-1}

Effect of the Flow-Rate. This effect was ascertained by comparing the runs 1, 4 and 5, which were carried out at different fluid flow-rates, both upward and downward the column. The following conditions were fixed:

- $\phi_{\mathrm{B}} + \phi_{\mathrm{T}} = 0.4$
- $\phi_{\mathrm{B}}/\phi_{\mathrm{T}} = 0.6$

Effect of the Ratio Between Fractions of Volume Reservoir Obtained as Bottom and Top Product (ϕ_{B}/ϕ_T). In order to find out the influence of the ϕ_{B}/ϕ_T, runs 1, 6 and 7 were compared. This ratio

Table 2. Experimental conditions used for the different parametric pumping runs carried out in recuperative mode.

Run	C_F (mgL^{-1})	T_{amb} (K)	t_h (min)	t_c (min)	Q_h (mL min^{-1})	Q_c (mL min^{-1})	ϕ_T	ϕ_B	Q (π/ω) (L)	Q_{TP} (mL min^{-1})	Q_{BP} (mL min^{-1})
1	101	298	85.00	100.00	200	200	0.25	0.15	20	62.50	31.58
2	108	298	35.00	50.00	200	200	0.30	0.50	10	166.67	66.67
3	106	298	110.00	125.00	200	200	0.2	0.12	25	47.62	25.00
4	109	298	56.60	66.60	300	300	0.25	0.15	20	96.77	48.65
5	114	300	106.25	125.00	160	160	0.25	0.15	20	49.38	25.00
6	109	300	75.00	100.00	200	200	0.15	0.25	20	42.86	52.63
7	104	300	95.00	100.00	200	200	0.35	0.05	20	77.78	10.53

was changed for each of these three runs while setting the following:

- $\phi_B + \phi_T = 0.4$
- Average time of cycle = 185 min

Simulation of Experimental Parametric Pumping Runs

A package previously developed in LSRE (Davesac et al., 2000) was used for the simulation of this cyclic operation under different experimental conditions (Table 2). Two models were implemented in the package: an equilibrium model with axial dispersion (Model I) and a Linear Driving Force model with axial dispersion (Model II). Both models include equations for mass balance in a volume element of the column, energy balance in the column and Langmuir adsorption equilibrium isotherm. Model II also considers the mass-transfer resistance inside the particle described by the LDF approximation.

Discussion

The histories of top and bottom concentrations for the parametric pumping experiments show that during the hot half-cycle, the salicylic acid in the bed is desorbed and so the top concentration increases; then, during the cold-half cycle, it is possible to adsorb more salicylic acid so a less concentrated stream is collected as bottom product. Operating conditions were studied to ascertain the system response. The effect of the cycle time, the flow-rate and the ratio between bottom and top product volumes may be seen in Figs. 2–4 respectively.

The Model I and Model II predictions are very similar for the top concentrated product but not for the bottom purified one. On the whole, the LDF model (Model II) predictions are in better agreement with experimental results. The LDF approximation used in Model II seems to be adequate to describe intraparticle mass transfer for the cyclic process here considered. It may be seen in Figs. 2–4 that the LDF model explain the parametric pumping operation for the system salicylic acid/water/polymeric adsorbent SP206 to a great extent, except for small disparities related to deviation of the equilibrium results from the Langmuir model (Otero et al., 2004).

A comparison between runs 1, 2 and 3 shows that not only bottom purification but also top concentration are favored by longer cycle times. A long cycle time allows improving of interphase mass transfer and the operation to be closer to the equilibrium conditions so better results are attained.

Lower flow-rates imply longer cycle times, which allow for better separation ratios and a higher purification level. The flow-rate does not influence the ratio of velocities of thermal and concentration waves. In this system the thermal wave is much faster than the concentration wave. However, a minimum flow-rate is required to guarantee thermal breakthrough up to the level of the feed temperature in each half-cycle. According to the results presented in Fig. 3, operating conditions of run 5, for which the flow-rate is lower than for runs 4 and 1, give better separation results. The flow-rate (run 5) is able to maintain a difference of temperature enough to cause separation and the effect of longer contact between the phases is favorable.

The ratio ϕ_B/ϕ_T affects the volume of top and bottom reservoir which is percolated through the column, so, the larger this ratio is the larger is the top concentrated reservoir volume which is percolated downward

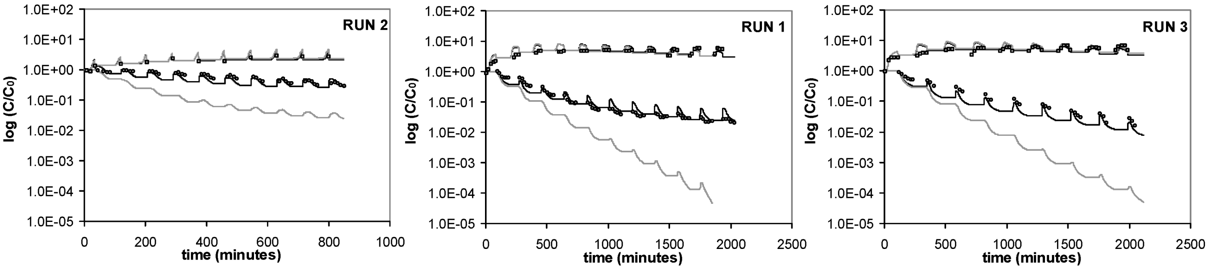


Figure 2. Experimental results and model predictions (—) Model I, (—) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the cycle time (RUN 2: 85 min; RUN 1: 185 min; RUN 3: 230 min).

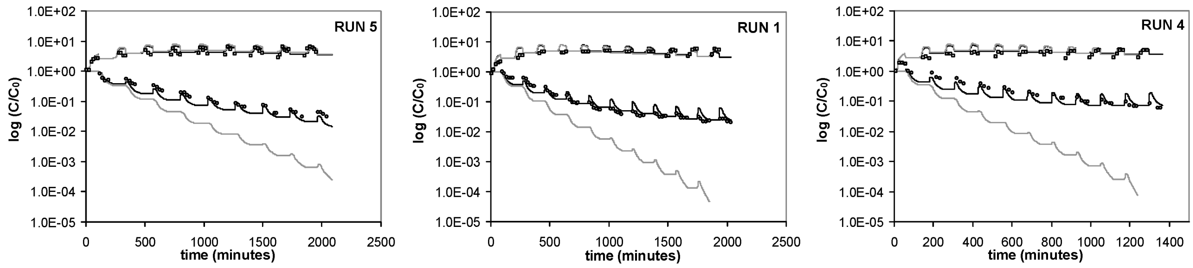


Figure 3. Experimental results and model predictions (—) Model I, (—) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the flow-rate (RUN 5: 160 mL min^{-1}; RUN 1: 200 mL min^{-1}; RUN 4: 300 mL min^{-1}).

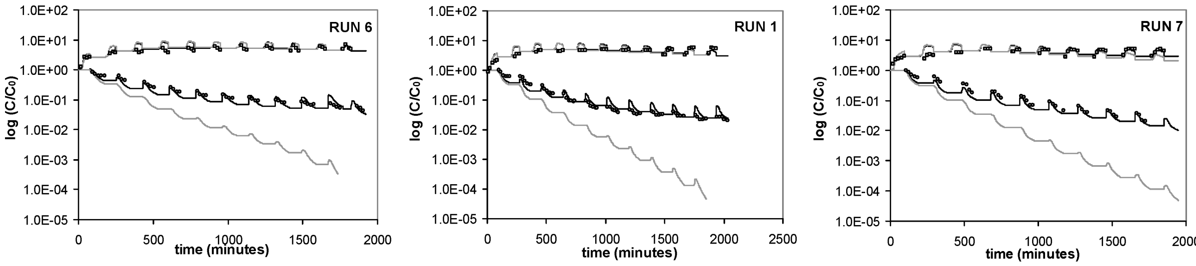


Figure 4. Experimental results and model predictions (—) Model I, (—) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the ratio ϕ_B/ϕ_T (RUN 6: 5/3; RUN 1: 3/5; RUN 7: 1/7).

flow and the smaller the purification with respect to the starting concentration. Run 7 then results in a higher purification level than runs 6 and 1 although less bottom product is got.

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Nomenclature

ΔH_L	enthalpy of adsorption from Langmuir fitting (J mol^{-1})
C_F	feed phenol concentration in the liquid-phase (mg L^{-1})
D	bed diameter (m)
D_m	molecular diffusivity of the solute (m^{2}min^{-1})
f_h	humidity factor (g dry resin/g resin)
h_w	global wall heat transfer coefficient (KJ m^{-2} s^{-1} K^{-1})
K_L^∞	equilibrium constant corresponding to the Langmuir model (L mg^{-1})
L	length of the bed (m)
Pe	mass Peclet number
Pe_h	thermal Peclet number
Q	constant in the Langmuir isotherm model (mg g^{-1}) related to the adsorptive capacity
Q_c	flow-rate of the fluid in the column during the cold half-cycle (mL min^{-1})
Q_h	flow-rate of the fluid in the column during the cold half-cycle (mL min^{-1})
Q_{TP}	flow-rate of the top product removing (mL min^{-1})
Q_{BT}	flow-rate of the bottom product removing (mL min^{-1})
r_p	radius of the particle of the adsorbent (m)
t_c	cold half-cycle time (min)
t_h	hot half-time (min)
T_c	absolute temperature of the fluid pumped to the column during the cold half-cycle (K)
T_h	absolute temperature of the fluid pumped to the column during the hot half-cycle (K)
V_B	volume withdrawn as bottom product per cycle (L)

V_T volume withdrawn as top product per cycle (L)

Greek Symbols

ε porosity of the bed
ε_p porosity of the adsorbent
$Q(\pi/\omega)$ reservoir displacement volume (L)
ϕ_B fraction of the Q (π/ω) that is withdrawn as bottom product
ϕ_T fraction of the Q (π/ω) that is withdrawn as top product
ρ specific gravity (g L^{-1})
τ tortuosity of the adsorbent
ξ mass capacity parameter
ξ_η heat capacity parameter

References

Balali-Mood, M., "Effects of Forced Alkaline Diuresis on Salicylate Distribution and Elimination Following Overdosage," Ph.D thesis, University of Edinburgh, pp. 132–270 (1981).

Browne, T.E. and Y. Cohen, "Aqueous-Phase Adsorption of Trichloroethene and Chloroform onto Polymeric Resins and Activated Carbon," *Ind. Eng. Chem. Res.*, **29**, 1338–1345 (1990).

Cairo, P.R., J.T. Coyle, J.T. Davis, H.M. Neukrug, I.H. Suffet, and A. Wickland, "Evaluating Regenerated Activated Carbon Through Laboratory and Pilot-Column Studies," *J. Am. Water Works Assoc.*, **74** (2), 94–102 (1982).

Chen, H., J. Rack, J. Stokes, and F. Hill, "Separation via Continuous Parametric Pumping," *AIChE J*, **18**, 356–361 (1972).

Davesac, R.R., L.T. Pinto, F.A. Silva, L.M. Ferreira, and A.E. Rodrigues, "A Package for Thermal Parametric Pumping Adsorptive Processes," *Chemical Engineering Journal.*, **76**, 115–125 (2000).

Díez, S., A. Leitão, L.M. Ferreira, and A.E. Rodrigues, "Adsorption of Phenylalanine onto Polymeric Resins: Equilibrium, Kinetics and Operation of a Parametric Pumping Unit." *Separation and Purification Technology***13**, 25–35 (1998).

Ferreira, L.M., and A.E. Rodrigues, "Adsorptive Separation By Thermal Parametric Pumping. Part 1: Modeling and Simulation," *Adsorption* **1**, 213–231 (1995a).

Ferreira, L.M., and A.E. Rodrigues, "Adsorptive Separation by thermal Parametric Pumping. Part 2: Experimental Study of The Purification of Aqueous Phenolic Solutions at Pilot Scale," *Adsorption*, **1**, 233–252 (1995b).

Ghasem, N.M., "Combined Mode Operation For Thermal Parametric Pumping," *J. Chem. Technol. Biotechnol,* **78**, 666–669 (2003).

Grant, T.M., and C.J. King, "Mechanism of Irreversible Adsorption of Phenolic Compounds by Activated Carbon," *Ind. Eng. Chem. Res.*, **29**, 264–271 (1990).

Kunin, R., "Polymeric Adsorbents for Treatment of Waste Effluents," *Polym. Eng. Sci*. **17**, 58 (1977).

Otero, M., C. Grande, and A. Rodrigues, "Adsorption of Salicylic Acid onto Polymeric Adsorbents and Activated Charcoal," *Reactive and Functional Polymers (in press)*.

Ramalho, R., C. Costa, G. Grevillot, and A. Rodrigues, "Adsorptive Parametric Pumping for The Purification of Phenolic Effluents.", *Separations Technology*, **1**, 99–107 (1991).

Simon, G., G. Grevillot, L. Hanak, T. Szanya, and G. Marton, "Theoretical Study of Adsorptive Parametric Pumping and Swing Chromatography With Flow Reversal," *Chem. Eng. Sci.*, **52**, 467–480 (1997).

Silva, F.A., J.A.C. Silva and A.E. Rodrigues, "A General Package for The Simulation of Cyclic Adsorption Processes," *Adsorption*, **5**(3), 229–244 (1999).

Wankat, P., "Continuous Recuperative Mode Parametric Pumping," *Ind. Eng. Chem. Fund.*, **12**, 372–380 (1978).

Wilhelm, R., A.W. Rice, and A.R. Bendelius, "Parametric Pumping, a Dynamic Principle For Separating Mixtures," *Ind. Eng. Chem. Fund*, **5**(1), 141–144 (1966).