



## Recovery of carboxylic acids from actual effluent by using sequential cationic-anionic adsorption steps at semi pilot scale

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### ABSTRACT

This work presents for the first time an exhaustive experimental assessment at semi-pilot scale for the sequential use of cationic-anionic adsorption columns for recovering carboxylic acids (CAs) from a real fermentation broth. The consecutive steps were dedicated to *i*) remove cations limiting the CAs interaction with the functional group of the anionic resin, and *ii*) adsorb CAs onto the anionic resin, respectively. The experimental broth was obtained from anaerobic co-fermentation of urban biowaste (UBW-broth). Breakthrough (BT) tests were firstly performed with the cationic column containing the strong-acid resin Lewatit® S2568H. This allowed both to assess the single process and to prepare 60 L of decationised UBW-broth to be used in the BT-tests with the anionic column (containing the weak-basic resin Lewatit® A365). Both columns were assessed (at 25°C) under packed and expanded bed modes, by feeding at different rates the actual UBW-broth or synthetic solutions. Main study innovative outputs were: 1) 100 % of the CAs occurring in UBW-broth were recovered with the proposed system; 2) best performances were obtained under expanded bed mode of operation, allowing to use 100 % of the installed capacity; 3) the affinity of other organic matter else than CAs resulted weaker than  $\text{Na}^+/\text{NH}_4^+$  and  $\text{CAs}/\text{PO}_4^{3-}/\text{Cl}^-$  in both cationic and anionic columns, respectively (i.e. low adsorption performances generally reported are due to inorganic cations/anions presence); 4) a very preliminary economic analysis carried out on the basis of the obtained data indicates overall costs ranging 0.58–1.49 EUR/kg of CAs (depending on the process configuration).

### 1. Introduction

In the framework of circular economy stands the valorisation of organic matter through the biotechnological production of carboxylic acids (CAs), i.e. the carboxylate platform. The appeal on this platform resides on the possibility of exploiting a largely employed and economic technology (the anaerobic fermentation carried out by open mixed cultures) for producing molecules with numerous potential applications. Indeed, CAs can be employed as precursors of valuable products such as esters, ketones and polyhydroxyalkanoates (PHAs), among others [1,2].

The valorisation of urban biowastes (UBWs) and agro-industrial side streams through the production of CAs which in turns allows the obtainment of PHAs and esters have been explored lately [3–5]. Several

promising technologies were reported for recovering CAs from fermentation broths, e.g.: nanofiltration/reverse osmosis [6], electro-dialysis [7], spontaneous separation by acidification [8] or liquid-liquid extraction [9]. Type of produced CAs, obtained titers and desired final product guide the choice of the proper technique. Whereas spontaneous separation can be performed with medium chain length CAs (that have low water solubilities), resin adsorption is useful for recovering CAs in alcohol solutions and for successive esterification. In particular, the esterification of the produced CAs requires their separation from the aqueous fermentation broth: since water is a byproduct of esterification reaction, CA recovery in an organic solvent (e.g. ethanol) would unbalance the esterification equilibrium to products, resulting in improved reaction yields [5].

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To this purpose, the application of an anionic resin was first reported elsewhere (adsorption yield of ca. 30 %) [10]. However, higher performances are required in the perspective of developing an economically feasible process. Low performances are obtained with actual fermentation broths when the inorganic ions competitions are not considered, namely: *i*) when directly applying the anionic resin adsorption step, so the occurring strong cations ( $\text{Na}^+/\text{NH}_4^+$ , mostly arising from fermentation pH-control) are associated with the CAs and will hinder their adsorption to the weak amines; or *ii*) when attempting to optimise CAs adsorption step by adjusting the pH (adding inorganic acids/bases) for CAs deprotonation (supposedly to be adsorbed) and/or resin protonation (supposing to adsorb), so the adsorption yields are instead lowered since the added strong ions ( $\text{Na}^+$  or  $\text{Cl}^-/\text{PO}_4^{3-}/\text{SO}_4^{2-}$ ) compete with or for the weak amines specific sites. Such competition effects were observed on several reported batch tests performed with cationic and anionic resins [11–14]. *Notarfrancesco et al.* demonstrated that the reason of the low adsorption yields are those competitive ion-interactions by predicting the CAs adsorption isotherms for different resins and actual broths using two methods: 1) a simple sequential calculation recipe considering that CAs are adsorbed as when using a synthetic solution of just CAs and water except for the moles of  $\text{Na}^+/\text{NH}_4^+/\text{Cl}^-/\text{PO}_4^{3-}$  occurring in the actual broth that diminish the CAs adsorption in a proportion 1:1, and 2) developing a simple homogenous ion equilibrium model that accurately predict the  $\text{Cl}^-/\text{PO}_4^{3-}$  and CAs adsorption isotherms by giving the actual broth initial composition as input ( $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ , CAs and pH). The work also proposed the use of a strong cationic resin for adsorbing  $\text{Na}^+/\text{NH}_4^+$  (releasing CAs that can then be adsorbed) before applying an anionic resin adsorption step, using tertiary amine or bifunctional high exchanging resins: this results in complete recovery of the CAs occurring in the fermentation broth [15].

Notwithstanding these evidences, the study using cationic and anionic adsorption columns is needed in order to: *i*) definitely confirm the mentioned ions competition mechanisms by means of a different experiment (i.e. breakthrough tests), and *ii*) obtain accurate as well as representative breakthrough curves data allowing considerations on the process scale-up at its maximal potentiality. Regarding this last, the prediction of breakthrough (BT) curves has a relevant role for upscaling and design the operational units. Many works have been reported on the development of mathematical models for such prediction, e.g. fixed bed columns models were studied by *Farias et al.* for adsorbing bisphenols A [16] and by *Bringas et al.* for selectively recovering nickel and copper [17]. However, axial dispersion effects and the consequent deviation from ideal flow is highly specific for each pilot/industrial adsorption column conformation, e.g. resin sieves/screeners plates among others. Thus, these effects must be studied case by case for each industrial unit or at downscaled mimicking plant, namely: the models are semi-empirical where kinetic and dispersion factors are tuned so as to fit the BT-curves [18]. All above mentioned, this work focuses on experimental demonstrations which are then supported by conventional formulae describing the BT-curves without fitting requirements.

The main goal of the present work was to assess and optimise CA recovery using sequential cationic-anionic resins at semi pilot scale columns and using a real CAs-rich broth arising from the anaerobic co-fermentation of biological system sludge and the organic fraction of municipal solid waste. The specific aims of this study were to: *a*) assess cation and anions adsorption processes to evaluate the affinity - in each case - of other organic compounds else than CAs ( $\text{COD}_{\text{Other}}$ ), as well as to evaluate the chance of coupling the recovery of other ions too ( $\text{NH}_4^+$  or  $\text{PO}_4^{3-}$ ); *b*) optimize the feeding linear velocity in cation and anion adsorption columns, using packed or expanded beds configuration; and *c*) verify the feasibility of applying our recently reported desorption & regeneration procedures at bench scale [15] and evaluate the repeatability of adsorption-desorption cycles (process robustness).

## 2. Material and methods

### 2.1. Resins, reagents and fermentation broth

According to previously reported results [15], the strong cationic resin Lewatit®S2568H (CatRes; having sulfonic functional groups) was used for pre-treating the actual fermentation broth, while the weak anionic resins Lewatit® A365 (AnRes; with tertiary and quaternary amines functional groups) was used for recovering the CAs. Resins' datasheets were reported elsewhere [19,20]. Both resins were kindly provided by Lanxess-Italy, while all the required reagents were purchased from Sigma-Merck.

The UBWs-broth used in the study was provided by prof. Majone research group (University of Rome “La Sapienza”) in the framework of RES URBIS EU-project [3]. It was generated in a pilot acidogenic fermenter located at the wastewater treatment plant of Treviso (Italy), at the conditions reported elsewhere [4]. The actual broth was processed for suspended solids removal directly at the pilot plant facility. In details, UBWs-broth was centrifuged, filtered at 0.2  $\mu\text{m}$  using a ceramic rotating filter (JUCLAS - Italy) and stored at 4 °C before using. The UBWs-broth had a pH level of  $5.75 \pm 0.01$  and contained (mM):  $2078 \pm 200$  of  $\text{COD}_{\text{Tot}}$  (i.e. total value, colorimetric method),  $348 \pm 2$  of CAs,  $44.0 \pm 2.8$  of  $\text{Cl}^-$ ,  $5.8 \pm 0.2$  of  $\text{PO}_4^{3-}$ ,  $683 \pm 206$  of  $\text{COD}_{\text{Other}}$  (i.e. other organic matter else than CAs, defined in Eq. 9 - Sections 2.4),  $34.78 \pm 2.06$  of  $\text{NH}_4^+$ ,  $323.61 \pm 6.88$  of  $\text{Na}^+$  and  $358.58 \pm 6.89$  of ionic strength [15]. Regarding CAs composition, it mainly contained (on % molar bases): acetic ( $52.5 \pm 1.9$ ), propionic ( $7.6 \pm 0.2$ ), butyric ( $15.6 \pm 0.4$ ), valeric ( $7.1 \pm 0.0$ ) and hexanoic ( $11.7 \pm 1.2$ ) acid.

### 2.2. Experimental set-up

Two identical semi-pilot exchange columns were set up for cations (CatCol) and anions (AnCol) extraction (Fig. 1). Each system had a

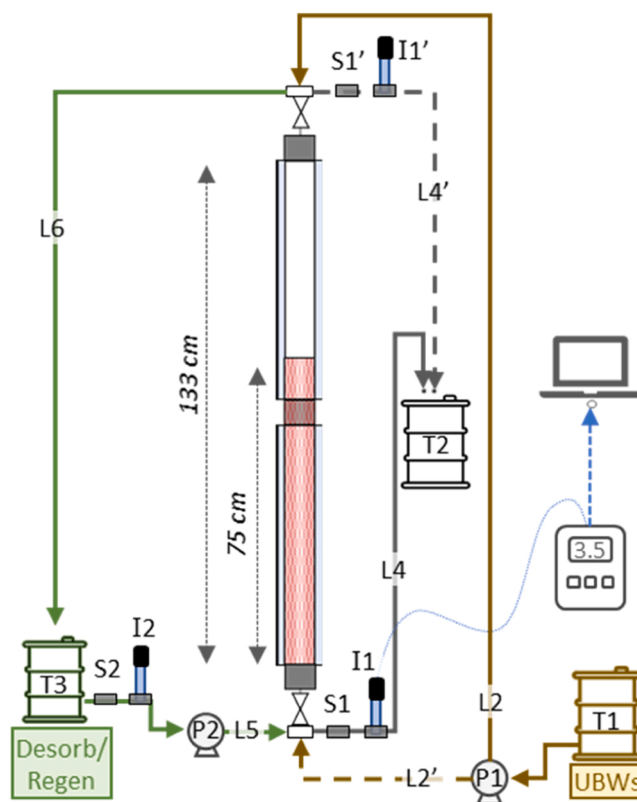


Fig. 1. Columns experimental set up for adsorption (feeding the CA-rich broth UBWs) and desorption/regeneration (Desorb/Regen) steps.

jacketed Plexiglas column (2.7 cm internal column diameter,  $d_{col}$ , and 133 cm height,  $h_{col}$ ) meaning a total volume ( $V_{Col}$ ) of 761.5 mL. Each column system included two peristaltic pumps (P1 and P2), two three-way sample valves (S1/S1' and S2), pH and conductivity probes (I1/I1' and I2) as well as three 5 L Pyrex bottles with magnetic stirring (T1, T2 and T3) containing the CAs-rich broth, the desorption/regeneration solution and the exhausted liquid (Fig. 1). All experiments were carried out at  $25 \pm 1$  °C by connecting the columns' jackets to a water bath with a recycling system. The columns, already containing deionised water, were filled with 171 g<sub>dry</sub> of Lewatit® S2568H or 160 g<sub>dry</sub> of Lewatit® A365 and the supplier's start-up procedures were followed. Briefly: 1) resins were soaked with water (1 hour); 2) backwashed with fresh deionised water fed through line L2' to let the beds expand and to let the hydraulic size classification occur (1 hour); and 3) let beds to settle and drain to within 10 cm of the top of the bed. CatCol and AnCol nominal bed volumes ( $BV_{nom}$ ) were defined from the resulting packed bed heights ( $h_{bed}$ , 97 and 75 cm for the CatCol and AnCol, respectively) and the  $d_{col}$ .

Adsorption tests were conducted in either packed or expanded bed mode by using pump P1 to feed the UBWs-broth (contained in T1) either through the columns top or through the bottom by using line L2 or L2', respectively. The columns effluent flowed first through the sampling valve S1 (or S1'), then through the pH/conductimetry probe I1 (or I1') and was finally discharged through line L4 (or L4') into the reservoir bottle T2.

The desorption tests were carried out using the peristaltic pump P2 to feed a basic or acidic solution (contained in T3) through the bottom of the columns (line L5). Then, the effluent was *i*) monitored using sampling valve S1' as well as the pH-sensor I1' and collected in T2 or *ii*) recycled through line L6 and then monitored using S2 as well as I2.

Adsorption and desorption feeding flow rates ( $F$ ) were periodically controlled at the discharge points of L4, L4' or L6. Furthermore, the in-line pH/conductivity measurements during the breakthrough tests were digitalised and recorded all along the experiments by means of a webcam and a simple MATLAB algorithm.

### 2.3. Experimental approach

All experiments were designed by considering recommended operating conditions reported in CatRes and AnRes datasheets, namely: exhaustion, regeneration and rinse linear velocity ranges as well as regenerant reagent and its concentration [19,20]. Besides, pattern flow tests and residence time distribution analyses were periodically carried out to control packing quality and dispersion in both columns operated in packed and expanded bed modes. To this end, the well-known procedure described elsewhere [21] were followed, namely: 1) step input type experiments were carried out by feeding HCl and NaOH 0.1 M as non-reactive tracers for the CatCol and AnCol, respectively; 2) mean residence time and the variance were calculated from the obtained curves; and 3) bed porosity ( $\epsilon$ ) and axial dispersion coefficients ( $D/uL$ ) were calculated from previous results.

#### 2.3.1. Broth pre-treatment with the CatCol

Adsorption BT tests were carried out by feeding the UBW-broth from the top of the CatCol, i.e. operating in a conventional packed bed mode. This allowed to: *i*) determine the adsorption affinity of other organic compounds else than CAs ( $COD_{Other}$ ) onto the CatRes, *ii*) study the feasibility of integrating the recovery of  $NH_4^+$  separated from  $Na^+$ , and *iii*) optimise the feeding rates of the adsorption process by assessing the used percentage of the installed adsorption capacity at the time of BT ( $t_{BT}$ ),  $Y_{CatRes;BT}$  (defined in Section 2.4).

Before starting each BT-test, the speed of pump P1 was set-up and the column temperature was regulated (column jacket) together with the temperature of the feed (statically incubated overnight at 25°C). The water inside the column was levelled by lowering the discharge point of the line L4 (2–4 cm above the resin level) and the initial resin bed height was recorded. Then, the BT-test was started, the feeding rate was

regularly controlled and liquid samples were taken periodically through S1 for later analysing the concentration of CAs,  $NH_4^+$ ,  $Na^+$ , total chemical oxygen demand (COD) and other organic material else than CAs ( $COD_{Other}$ ; calculation reported in Section 2.4). While the first flow-through volume of approximately 600 mL was discarded as it was diluted with water previously retained in the column, the following volumes were collected until the resulting pH of the accumulated liquid was 1.46 (the BT point). Successively, the effluent was accumulated in reservoir B2 (the decationised broth was useful for later AnCol tests) and the adsorption was conducted until CatRes saturation.

A second set of BT tests was then carried out with the CatCol in expanded bed mode using a synthetic solution simulating the UBW-broth (Sim\_UBW-broth), i.e. containing all inorganic ions and CAs at the same concentration occurring in it. The CatCol was started to be fed with deionised water at the desired experimental rate through line L2'. As soon as the expanded bed height was stabilised, the feed bottle B1 was replaced by the one containing the simulating solution. The process was monitored as described before, but samples were taken periodically through S1'. These tests allowed to assess the CatCol adsorption in expanded bed mode by evaluating the  $Y_{CatRes;BT}$  at the different  $F$  and comparing the obtained results with those belonging to the previous experiments in packed bed mode.

At the end of each BT test (i.e. when resin was completely saturated) the remaining UBWs-broth/Sim\_UBW-broth inside the CatCol was discharged through valve S1 and the regeneration procedure was started by sequentially flowing (ca. 34 mL/min) through line L5: *i*) 0.6 L of deionised water for discharging the remaining UBW-broth inside the column, *ii*) 2 L of HCl 6 % for regenerating the column, and *iii*) 2.5 L of deionised water for washing the column (i.e. until the conductivity was that of the deionised water,  $<10 \mu S$ ).

#### 2.3.2. CA recovery with the AnCol

While pre-treating 100 L of UBW-broth with the CatCol for generating a homogenous volume stock of decationised UBW-broth, preliminary adsorption breakthrough tests were carried out with the AnCol. A synthetic solution was used, containing all anions occurring in the decationised UBW-broth (CAs,  $PO_4^{3-}$  and  $Cl^-$ ) at the corresponding concentrations (hereinafter called Sim\_Decat\_UBW-broth). The tests were carried out at different feeding rates using packed (8–188 mL min<sup>-1</sup>) and expanded (20–71 mL min<sup>-1</sup>) bed modes. This allowed to compare the performance of both modes by assessing for each test the used percentage of the total AnRes capacity installed at the BT-point ( $Y_{AnRes;BT}$ , defined in Section 2.4). Two  $Y_{AnRes;BT}$  vs.  $F$  curves were determined, one for each adsorption mode. Start-up and monitoring procedures were the same described previously for the CatCol. At the end of each BT-test (i.e. when the AnRes was saturated) the remaining Sim\_Decat\_UBW-broth was discharged through valve S1 and then the regeneration procedure was started by sequentially flowing (35 mL/min) through line L5: *i*) 0.6 L of deionised water for removing the CA-rich solution remaining inside the column, *ii*) 2 L of NaOH 1 M for simultaneously desorbing the CAs and regenerating the AnRes (i.e. until the pH in I1 was 13 as in the fed NaOH solution), and *iii*) 2.5 L of deionised water for washing the AnCol (i.e. until the conductivity in the exit was that of the deionised water,  $<10 \mu S$ ).

A second set of experiments was carried out by feeding the actual decationised UBW-broth (34–51 mL min<sup>-1</sup>) to the AnCol working in expanded bed, the best performing set-up according to preliminary results. These experiments allowed to: *i*) assess the adsorption of  $COD_{Other}$  onto the AnRes, *ii*) study the feasibility of integrating the recovery of  $PO_4^{3-}$  separated from CAs and  $Cl^-$ , and *iii*) optimise the adsorption process by determining the corresponding  $Y_{AnRes;BT}$  vs.  $F$  curve. Importantly, in the framework of RES URBIS research project [3], the recovered CAs represented the raw material for Dr. Carlo Pastore group (CNR-Bari) studying the esterification for producing bio-solvents (e.g. ethyl acetate, ethyl butyrate, etc.). Thus, not all the BT tests with UBW-broth were conducted until AnRes saturation; much of them were conducted up to

40–70 % of resin saturation. This allowed to minimise the total volume required for each BT-test and so to maximise the CA recovery from the total available volume of decationised UBW-broth. When adsorption tests were finished, the desorption and regeneration steps were started. Differently from previous BT-tests using Sim\_Decat\_UBW-broth, the desorption procedure was modified in the interest of desorbing and rendering the CAs accessible to the consecutive esterification step [5, 15], namely using: *i*) ethanol 96 % as solvent (instead of water); *ii*) H<sub>2</sub>SO<sub>4</sub> as anion desorber (instead of NaOH); *iii*) lower volumes of more concentrated desorption solutions to obtain higher CA titer in ethanol. Hence, at the end of the adsorption tests the remaining UBW-broth was discharged through valve S1 and the desorption/regeneration procedure was started by sequentially flowing (35 mL/min) through line L5: *i*) 0.6 L of EtOH for removing the CA-rich solution remaining inside the column, *ii*) 1 L of H<sub>2</sub>SO<sub>4</sub>-ethanol solution 1 M for desorbing the CAs and inorganic anions, *iii*) 2.5 L of NaOH 1 M for regenerating the AnRes (i.e. when the pH in I1 was the same as that in the virgin NaOH solution), and *iv*) 2.5 L of deionised water for washing the column (i.e. when the conductivity in the exit was that of the deionised water).

Finally, a third set of experiments were carried out using the expanded bed set-up and the Sim\_Decat\_UBW-broth. Adsorption-desorption cycles were carried out using the same procedures described for the tests with the actual UBW-broth. This allowed to assess different hypothesis about the causes on the differences found between the  $Y_{AnRes, BT}$  vs.  $F$  trends obtained in the previous experiments carried out in expanded bed mode using the simulating (Sim\_Decat\_UBW-broth) or the actual decationised UBW-broth.

#### 2.4. Data treatment and analytical procedures

Total fed analytes ( $m_{Fed,n}$ ) in the breakthrough tests were evaluated by using the corresponding experimental feeding rate ( $F$ ), concentration in the feed ( $C_{Feed,n}$ ) and experimental time ( $t$ ):

$$m_{Fed,n}(t) = F * C_{Feed,n} * t \quad (1)$$

where  $n$  can be total cations, total anions, total CAs, COD or COD<sub>Other</sub>.

Total analytes coming out the column ( $m_{out,n}$ ) were calculated as

$$m_{out,n}(t) = F * \int_0^t C_{out,n}(t) * dt \quad (2)$$

The analytes remaining inside the system not adsorbed ( $m_{rem,n}$ ) were calculated as

$$m_{rem,n}(t) = C_{Feed,n} * (V_{dead1} + V_{dead2}) + C_{Feed,n} * (V_B - V_{Res}) * Y_{Res,n}(t) + C_{out,n}(t) * (V_B - V_{Res}) * (1 - Y_{Res,n}(t)) + C_{out,n}(t) * (V_{Col} - V_B) + C_{out,n}(t) * V_{dead3} \quad (3)$$

where  $V_{dead1}$  and  $V_{dead3}$  are the feeding and out-line dead volumes, respectively;  $V_{dead2}$  is the liquid volume over the resin ( $V_{dead2} > 0$  only in packed bed mode);  $V_B$  and  $V_{Res}$  are the expanded resin bed and its specific volumes. These and the resin utilization capacity ( $Y_{Res,n}$ ) allowed to calculate the remaining analytes in the saturated and not saturated fractions; and  $V_{Col}$  is the empty column total volume which allowed to calculate the volume of liquid contained over the expanded bed ( $V_{Col} - V_B$ ) and thus the residual analytes in it.

The resin utilization capacity was calculated as

$$Y_{Res,n}\%(t) = (m_{Ads,n}(t)/Q_{Res}) * 100 \quad (4)$$

Where  $Q_{Res}$  is the CatRes or AnRes total adsorption capacity installed in the corresponding column.

Therefore, the analytes adsorbed were calculated as

$$m_{Ads,n}(t) = m_{Fed,n}(t) - m_{out,n}(t) - m_{rem,n}(t) \quad (5)$$

using the following iteration: 1)  $m_{Fed,n}$  and  $m_{out,n}$  were calculated using

the experimental results, 2) an  $Y_{Res,n}$  value was supposed, 3)  $m_{rem,n}$  was calculated using Eq. (3) and the experimental data, 4)  $m_{Ads,n}$  was calculated using Eqs. (5), 5)  $Y_{Res,n}$  was calculated using Eq. (4) and compared with the supposed value in step 2. This iteration was repeated until the supposed and calculated  $Y_{Res,n}$  agree.

The adsorption yield was calculated as

$$Y_{Ads,n}(t) = (m_{Ads,n}(t)/m_{Fed,n}(t)) * 100\% \quad (6)$$

Feeding time was also expressed as bed volumes (BV) or as tau ( $\tau$ ) as follows

$$BV = F * t / BV_{nom} \quad (7)$$

and

$$\tau = (m_{Fed,n}(t) - V_{dead1} * C_{0,n}) / Q_{Res} \quad (8)$$

The analytical procedures used in the present work were those recently reported [15], where the COD<sub>Other</sub> was already defined as:

$$COD_{Other} = COD_{Tot} - COD_{CAs} - COD_{Cl^-} \quad (9)$$

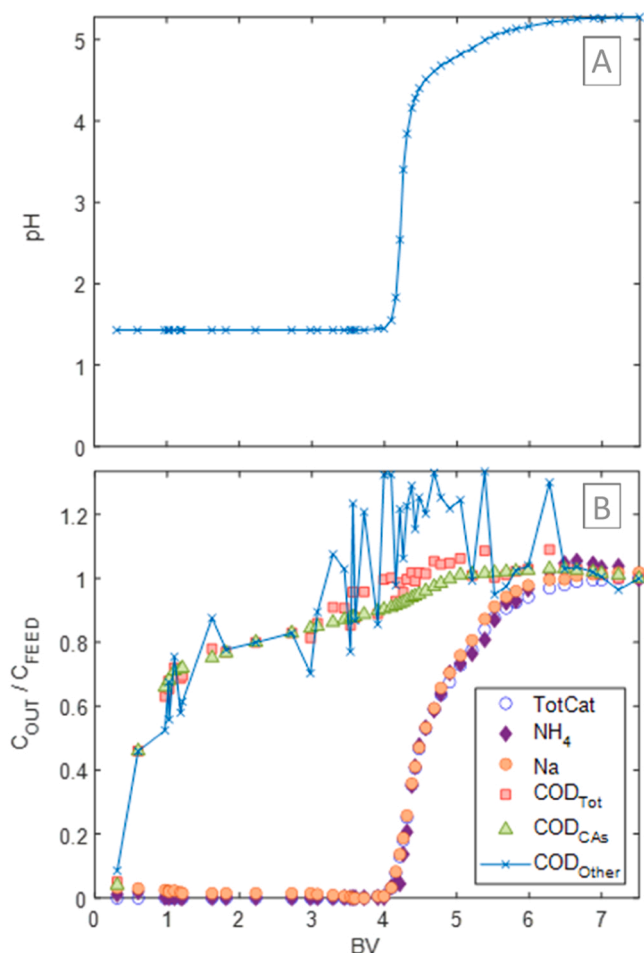
$COD_{Tot}$  represents the total value obtained from the colorimetric analyses of each sample, whereas  $COD_{CAs}$  and  $COD_{Cl^-}$  represent the equivalent contributions from CAs and Cl<sup>-</sup>, respectively, calculated by considering their stoichiometric oxidation.

### 3. Results and discussions

#### 3.1. Broth pre-treatment with the CatCol

The actual UBW-broth was pre-treated by operating the CatCol in conventional packed bed set-up. Indeed, the generation of the homogeneous stock of decationised UBW-broth (to be used later in the AnCol adsorption studies) was obtained during the CatCol adsorption process optimization study. To this aim, breakthrough tests were carried out by feeding the UBW-broth at different flow rates. The preliminary flow pattern analyses indicated a good quality of the packing. Indeed, the average packed bed porosity along the experimentation chronology with the CatCol ( $\epsilon_{CatCol} = 0.34 \pm 0.04$ ) resulted similar to that calculated from the resin densities reported in the commercial datasheet ( $1 - d_{bulk}/d_{real} = 0.37$ ). Besides, the obtained average axial dispersion coefficient ( $D/u.L$ ) showed low-intermediate dispersion effects in the CatCol (Sup. material, Table S1) and the resulted low standard deviations (representing 11–17 % of the average) evidenced the repeatability on the packing.

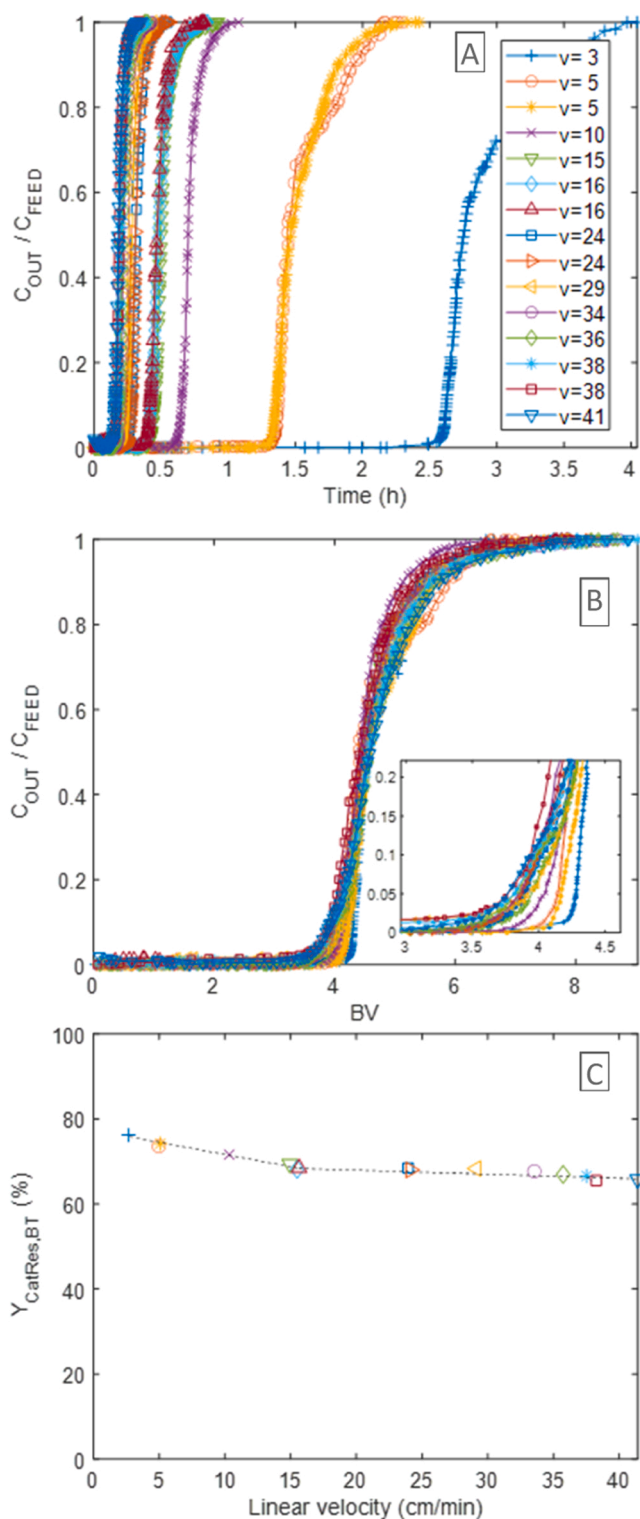
The first breakthrough tests were used to study the behaviour of cation adsorption, namely: *i*) adsorption affinity of other organic matter onto the CatRes, and *ii*) study the feasibility of integrating the recovery of NH<sub>4</sub><sup>+</sup> separated from Na<sup>+</sup>. Fig. 2A illustrates the outlet pH-level and Fig. 2B shows the corresponding normalised concentration profiles during a test performed at low flow rate. In all tests the cation (NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>) adsorption made the outlet pH-level to be low (1.43–1.55), whereas the CAs (COD<sub>CAs</sub>), Cl<sup>-</sup> (COD<sub>Cl</sub>) and COD<sub>Other</sub> started to exit from the beginning of the batch experiments and following almost identical concentration trends. This last confirmed their lack of affinity with the CatRes. COD<sub>Other</sub> showed a noisy trend since each value point includes all the uncertainties of the measured values with which they were calculated. Besides, the COD<sub>Other</sub> and COD<sub>Tot</sub> curves achieved values higher than 1 at  $3.2 \leq BV \leq 6$ . This was ascribed to the adsorption of a COD<sub>Other</sub> fraction acting as cations: such weak cations were then displaced (i.e. when the bed started to be saturated) by the stronger NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> that finally occupied those specific adsorption sites, and so  $C_{out}$  resulted higher than  $C_{Feed}$  during that gap. The COD<sub>Cl</sub> trend was not included in Fig. 2B since Cl<sup>-</sup> represented a minor fraction of the COD<sub>Tot</sub> (<1 %) and behaved identically to COD<sub>CAs</sub>, but it was considered for calculating the COD<sub>Other</sub> trend reported. Moreover, both NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> cations resulted to have very similar concentrations trends. This was



**Fig. 2.** CatCol breakthrough test carried out in packed bed mode by feeding the UBW-broth at 5.1 cm/min. Outlet profiles of pH levels (A) and normalised analytes concentration (B).

assigned to the fact that  $\text{NH}_4^+$  occurred at low concentration ( $\sim 30$  mM, i. e. 10 times lower than that of  $\text{Na}^+$ ), this making both cations breakthrough points to be very close to each other. However, it is known that sulfonated resin selectivity of  $\text{NH}_4^+$  over  $\text{Na}^+$  ranges 1.2–1.4 [22]. Thus, the application of two sequential CatCol would allow recovering  $\text{NH}_4^+$  separated from  $\text{Na}^+$ .

For the process optimization analysis as well as for generating a pre-treated homogenous volume, the breakthrough point for the UBW-broth decationisation was defined at 5 % of the feeding total cation concentration, i.e. the point at which pH-levels of the outlet stream and of the accumulated pre-treated broth were  $< 1.57$  and ca. 1.46, respectively. The obtained BT-curves at different feeding flow rates ( $15\text{--}237$  mL  $\text{min}^{-1}$ ) are presented in Fig. 3A, whereas Fig. 3B shows the same curves as a function of the fed BV. Fig. 3C, reveals the resulting resin utilization capacity at the different feeding rates (expressed as linear velocities). All tests were performed until resin saturation ( $988 \pm 17$  meq), which corresponded to  $\text{BV} > 6$  or  $\tau > 1.3$  (Sup. material, Fig. S1). Such CatRes adsorption capacity (equivalent to  $5.78 \pm 0.10$  meq/g<sub>DR</sub>) is in agreement with the previously reported value for  $\text{NH}_4^+$  and  $\text{Na}^+$  adsorption isotherms ( $5.33 \pm 0.03$  meq/g<sub>DR</sub>) [15]. The experimental set-up and operating procedures (including CatRes regeneration) resulted robust as it can be observed from the highly repeatability of BT-curves for the conditions carried out in double or triplicate (5, 15–16, and 24 cm/min). BT points were achieved at  $3.5 < \text{BV} < 4.3$  or  $0.65 < \tau < 0.80$  (Sup. material, Fig. S1). It was not possible to test higher feeding rates ( $> 237$  mL/min) since the resulting column pressure would have reached the upper limit value for the semi-pilot



**Fig. 3.** CatCol breakthrough tests carried out in packed bed mode by feeding the UBW-broth at different linear velocities. Responses: normalised total cation concentration in the outlet along time (A) and fed BV (B); (C) resulting CatRes utilisation capacity ( $Y_{\text{CatRes,BT}}$ ) at the different feeding linear velocities.

plant (2.5 atm). Considering all the breakthrough tests, the pilot column pre-treatment allowed to obtain ca. 60 L of an effluent portion almost completely deprived of cations and with the same concentration of CAs originally present in UBWs-broth. Briefly, the decationised UBW broth had a pH level of  $1.49 \pm 0.08$  and contained (mM):  $1396 \pm 29$  of COD,  $324 \pm 9$  of CAs,  $36.0 \pm 5.6$  of  $\text{Cl}^-$ ,  $5.8 \pm 0.5$  of  $\text{PO}_4^{3-}$ ,  $196 \pm 35$  of

$\text{COD}_{\text{Other}}$ ,  $0.23 \pm 0.09$  of  $\text{NH}_4^+$ ,  $2.30 \pm 5.78$  of  $\text{Na}^+$  and  $19.90 \pm 5.78$  of ionic strength (calculated by considering the mentioned ions). Such values resulted highly similar to those reported in our previous work, slight variations were ascribed to homogenisation and storage effects [15].

While generating a homogenous volume of decationised broth, the preliminary anion recovery experiments with the AnCol (using lab-prepared solutions) showed that working on expanded bed mode would allow exploiting 100 % of the installed resin exchange capacity (Sup. material, Fig. S3 D). Besides, it was realised that such operating mode would potentially tolerate working with a broth not necessarily filtered at  $0.22\text{--}0.45\ \mu\text{m}$ : the hydraulic classification inside the column would allow retaining the CatRes while the fine suspended solids would pass through without the occurrence of clogging problems. Despite this strategy might represent an economic advantage it was not possible to test it by using the actual broth since: 1) it was already fine filtered at the generating facility as described in Section 2.1; and 2) the treatment in expanded bed mode could generate a slightly different decationised broth whereas the aim was to obtain the higher possible volume of an homogeneous decationised broth. Nevertheless, the CatCol performance in expanded bed mode was assessed by employing a lab-prepared solution simulating the actual broth, this allowed to study the process with less axial dispersion effects. Indeed, the preliminary fluid-dynamic analysis indicated that axial dispersion coefficient for expanded bed mode resulted negligible in all tests ( $D/u.L = 0.0087 \pm 0.0001$ ). Accordingly, the obtained BT curves at different feeding rates ( $33\text{--}81\ \text{mL min}^{-1}$ ) were almost a step function as it can be observed in Fig. 4A and the breaking points resulted at  $5.9 \leq \text{BV} \leq 6.7$  (Fig. 4B) or  $0.8 < \tau < 1$  (Sup. material, Fig. S2). The expanded bed mode would allow the amount of adsorbed cations per batch to be increased by up to 25 % as compared to the packed bed mode, as shown by the obtained higher resin utilisation capacities, which resulted 100 % for the slowest feeding condition (Fig. 4C).

The prediction of BT curves has a relevant role for upscaling and design the operational units. However, axial dispersion effects and the consequent deviation from ideal flow is highly specific for each industrial adsorption column conformation, e.g. resin sieves/screeners plates among others. Thus, these effects must be studied at the occurrence for each industrial unit or at downscaled mimicking plant. In this latter case, also the LUB (Length of Utilised Bed) method could be used for upscaling. Importantly, the application of the simple model [18] (neglecting axial dispersion and using general mass transfer correlations) was sufficient for accurately predicting the BT points of the previous experimental expanded bed curves (Fig. 4A) with errors below 7 % (Sup. material, Fig. S3).

### 3.2. CA recovery with the AnCol

Preliminary anion adsorption tests were carried out using a lab-prepared solution (simulating the decationised broth) while a homogeneous volume of pre-treated actual broth was being generated using the CatCol in packed bed mode (Section 3.1). This allowed to verify that also the AnCol experimental set-up resulted robust and with high repeatability. The preliminary flow pattern analysis for the packed bed mode indicated a good packing quality and repeatability throughout the tests ( $\epsilon_{\text{AnCol}} = 0.39 \pm 0.05$ ). Such average porosity resulted like that calculated from the resin densities reported in the commercial datasheet ( $1 - d_{\text{bulk}}/d_{\text{real}} = 0.35$ ). Also in this case, the obtained axial dispersion coefficients ( $D/u.L$ ) were higher for packed bed than for expanded bed mode (Sup. material, Table S2). The robustness and repeatability of the experimental set-up remained confirmed by the  $D/u.L$  low standard deviations obtained as well as by the obtained BT-curves in packed (Sup. material, Fig. S4 A) and expanded bed (Sup. material, Fig. S5 E) modes using the laboratory prepared solution. Remarkably, as occurred with the CatCol, the tests evidenced that in packed bed mode the axial dispersion do not allow to exploit all the installed capacity, i.e.  $Y_{\text{AnRes,BT}}$

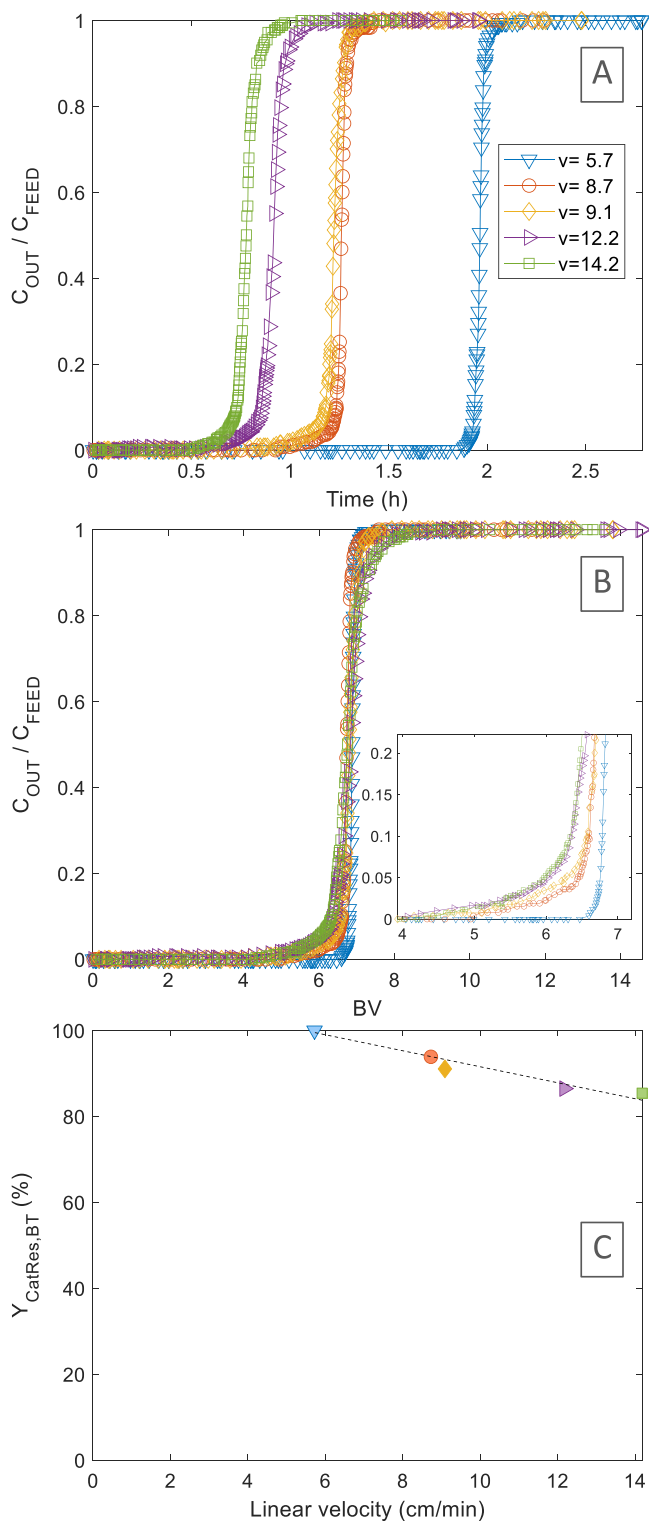


Fig. 4. CatCol breakthrough tests carried out in expanded bed mode by feeding the Sim\_Decat\_UBW-broth at different linear velocities. Responses: normalised total cation concentration in the outlet along time (A) and fed BV (B); (C) resulting CatRes utilisation capacity ( $Y_{\text{CatRes,BT}}$ ) at the different feeding linear velocities.

< 80 %, even at linear velocities lower than 2.5 cm/min (Sup. material, Fig. S3 D). Differently, the expanded bed configuration allowed to obtain  $80 \% < Y_{\text{AnRes,BT}} < 100 \%$  at linear velocities  $< 9$  cm/min, achieving almost 98 % at 3.5 cm/min (Sup. material, Fig. S4 H). Hence, CAs recovery from the actual decationised UBW-broth was assessed

using only the AnCol in expanded bed mode, this allowing to maximise the total CAs recovery useful for esterification assessments (not shown) within the overall research project [3].

First BT tests with the actual decationised UBW-broth were used to study the trends of pH, CAs, COD and COD<sub>Other</sub> as well as Cl<sup>-</sup> and PO<sub>4</sub><sup>3-</sup>. Fig. 5A illustrates the outlet pH-level and Fig. 5B shows the corresponding normalised concentration profiles during a test performed at the lowest flow rate. In all tests the anion adsorption (CAs, PO<sub>4</sub><sup>3-</sup> and Cl<sup>-</sup>) increased the pH level in the liquid up to 8.57–9.40, whereas the COD<sub>Other</sub> started to get out after 1 BV, this confirming their lack of affinities also with the AnRes. Neither the Cl<sup>-</sup> nor the PO<sub>4</sub><sup>3-</sup> concentration trends were included for the figure clarity sake since their stronger affinities with AnRes and their low concentration in the feeding broth implied BT-points far beyond significant limits. From this, both PO<sub>4</sub><sup>3-</sup> and Cl<sup>-</sup> anions could be potentially separated from CAs; i.e. the recovery of PO<sub>4</sub><sup>3-</sup> (an extra added value) could be easily integrated for improving the overall process economy.

The obtained BT-curves at different feeding flow rates are shown in Fig. 6A, whereas Fig. 6B shows the same curves as a function of the BV fed. The experimental set-up and operating procedures resulted robust as it can be observed from the highly repeatable BT-curves obtained for the conditions carried out in duplicate (6.3, and 7.1 cm/min). Aiming to maximise CA recovery from the 60 L decationised UBW-broth (they represented the raw material for an external research group studying the production of ethyl acetate, ethyl butyrate, etc [3].), only three BT tests were performed until resin saturation (1210 ± 42 meq), corresponding to BV > 13 (Fig. 6B) or  $\tau > 1.5$  (Sup. material, Fig. S6). Such AnRes

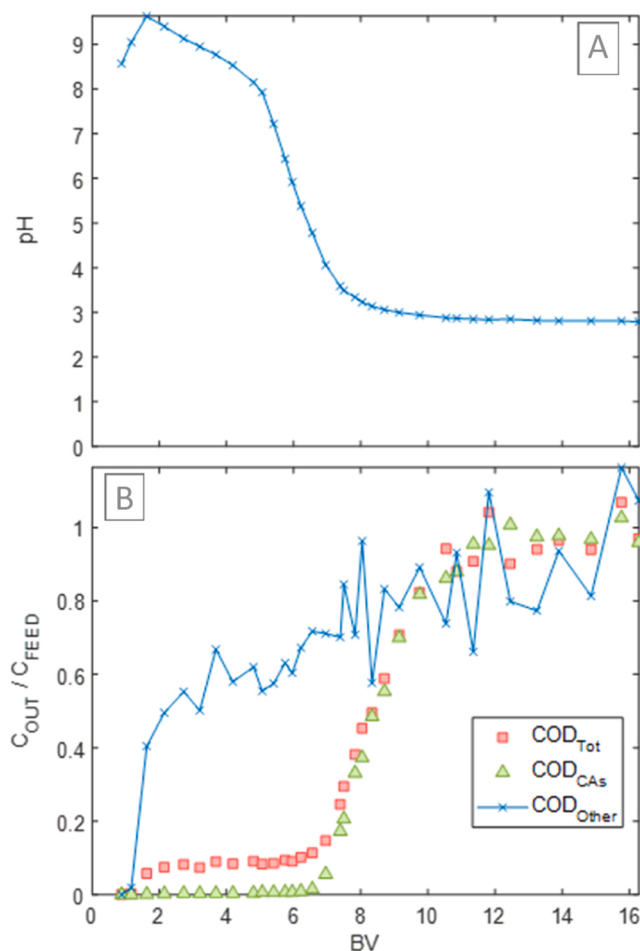


Fig. 5. AnCol breakthrough test carried out in expanded bed mode and by feeding the decationised UBW-broth at 6 cm/min. Outlet profiles of pH levels (A) and normalised analytes concentration (B).

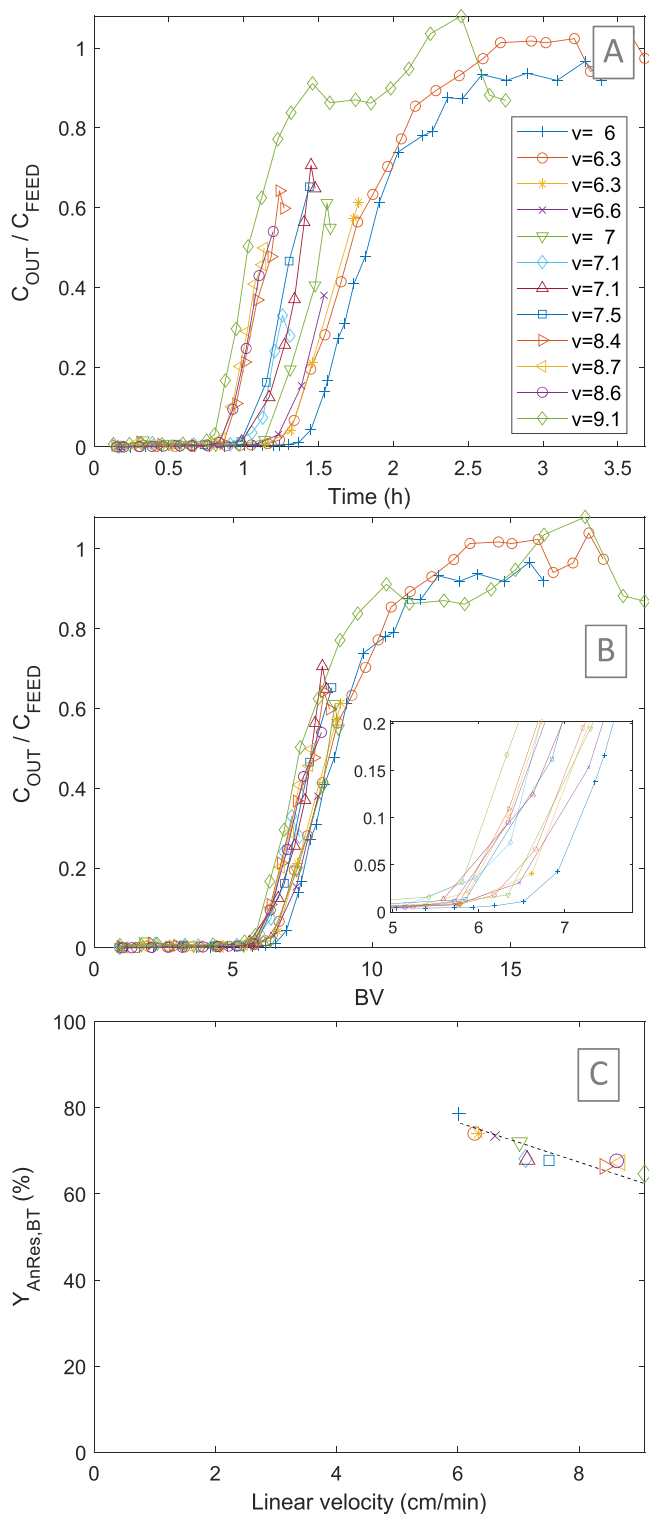


Fig. 6. AnCol breakthrough tests carried out in expanded bed mode by feeding the decationised UBW-broth at different linear velocities. Responses: normalised total anions concentration in the outlet along time (A) and fed BV (B); as well as AnRes utilisation capacity ( $Y_{AnRes,BT}$ ) at the different feeding linear velocities (C).

adsorption capacity (equivalent to  $7.56 \pm 0.26 \text{ meq/g}_{DR}$ ) is in agreement with the previously reported adsorption isotherms for the total anions of the same broth ( $q_{Tot,UBW2} = 2.83 * 365.8^{0.16} = 7.57 \text{ meq/g}_{DR}$ ) and for the acetic acid of a lab prepared water solution ( $q_{CAs} = 3.51 *$

$365.8 \cdot 10^{126} = 7.38 \text{ meq/g}_{\text{DR}}$  [15]; this confirming the effectivity of the ion equilibrium model predicting the isotherms and that decationised CAs-rich broth behaves as synthetic solutions, respectively. The rest of the BT-tests were conducted until  $C_{\text{Out,An}}/C_{\text{Feed,An}}$  was 40–70 %, this still allowing to evaluate the resin utilisation capacity ( $Y_{\text{AnRes,BT}}\%$ ) at different feeding rates. The BT-points were achieved at  $5.5 < \text{BV} < 7.5$  BV (Fig. 6B) or  $0.55 < \tau < 0.80$  (Sup. material, Fig. S6) and the  $Y_{\text{AnRes,BT}}\%$  ranged 66–82 % (Fig. 6C). Besides it would result on economically unfeasible performance ( $Y_{\text{AnRes,BT}} < 60\%$ ), it was not possible to test higher feeding rates ( $>52 \text{ mL/min}$ ) since the resulting AnRes height would have overcome the top of the column and thus resin would have been lost.

Regarding desorption, in this study at semi-pilot scale, it was not only aimed at recovering all CAs but also at obtaining concentrated CAs in ethanol solutions that would improve the performances of *i*) the adsorption process (less ethanol used) and *ii*) the esterification process (higher conversion). To this purpose, lower solvent volume and more concentrated NaOH solution (1 M instead of 0.5 M) were used. But, unlike previous report on desorption tests using stoichiometric quantities of basified ethanol at flask-scale [10,15], precipitation was observed. This was assigned to the fact that sodium carboxylates have low solubility in ethanol (5 g/L or 45.4 mM for sodium butyrate) whereas the proposed adsorption-desorption process allows to obtain the carboxylates at concentration equal to that in the original broth (for the case of sodium butyrate:  $348 \text{ mM} \cdot 15.6\% = 54.3 \text{ mM}$ ) or even slightly higher. Despite such precipitation phenomenon could result of interest for easily recovering the carboxylate salts granules, it was necessary to change the desorption mode strategy since the overall research project included the CAs esterification. Thus, to recover the CAs already solubilised in ethanol, a  $\text{H}_2\text{SO}_4$ -ethanol solution (1 M) was fed (instead of Na-ethanol) and recycled until constant concentration was obtained (Fig. 7A). Contemporary measurements of the pH in lines L6 and S2 were carried out so as to end the process when same values were achieved (Fig. 7B). This procedure allowed recovering 100 % of the adsorbed CAs in ethanol solutions containing 37–47 g/L of CAs. The final titer depended on AnRes utilisation capacity obtained for the different feeding experimental conditions. Besides CAs desorption, also the production of esters was observed since it was triggered due to  $\text{H}_2\text{SO}_4$  catalytic activity potentiated by the retro-mixing effects. In this work such early esterification was considered positive for the integrated project, but it could also be avoided by practicing passthrough desorption instead of recycling (data not shown). Although the low obtained concentration factor (1.48–1.88 the CAs initial concentration), the adsorption steps allowed to change the solvent (water to ethanol) and leave the CAs available for esterification. Total adsorption-desorption-regeneration cycles performed during the whole research activity (with simulating solutions and actual fermentation broth) accounted 55, without observing any AnRes detriment along them.

Notably, it is disadvantageous to generate salt by-products during desorption and regeneration of resin, namely: after desorption with  $\text{H}_2\text{SO}_4$ -ethanol, resin was regenerated with NaOH-water solution, leaving the adsorption site in OH form and generating  $\text{Na}_2\text{SO}_4$  as by-product. Whereas this problem could be avoided for the CatCol step by replacing it with a bipolar membrane electro dialysis (separating the cations  $\text{Na}^+/\text{NH}_4^+$  as well as rendering CAs free and prompt to be adsorbed), it remains an actual problem for the proposed AnCol step. In this regard, *Cabrera et al.* reported the effective implementation of  $\text{CO}_2$ -expanded alcohols for recovering adsorbed CAs without the consequences of generating salts by-products during desorption and regeneration [23]. Yet, CA recovery by sequentially applying cationic-anionic resins still represent a better adsorption configuration than that proposed by *Cabrera et al.* In that process the direct CA adsorption with a strong anionic resin suffers from 1) inorganic cations interferences ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ) which result in prompt break-through; and from 2) the low CAs titers in

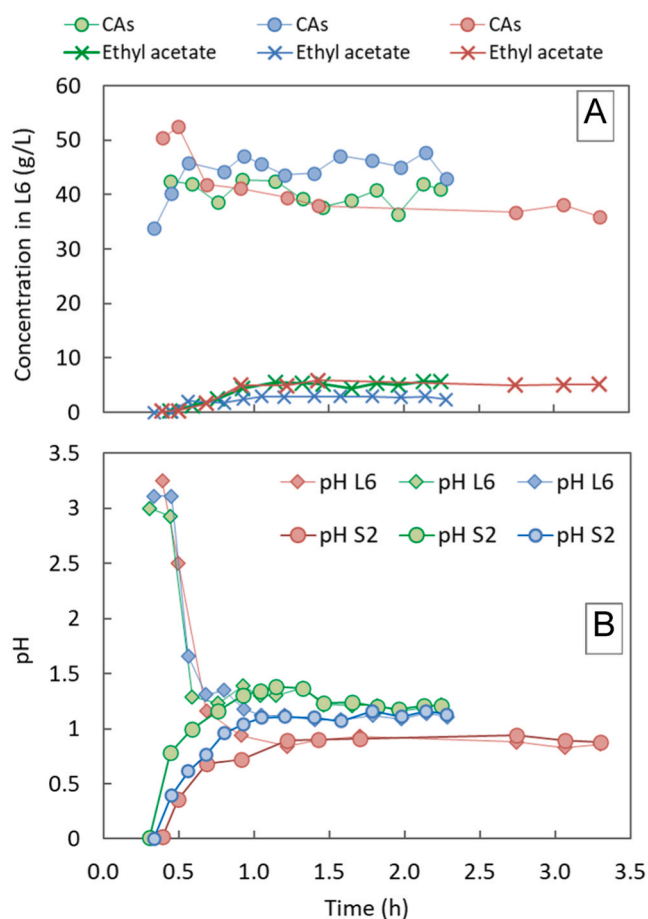


Fig. 7. CAs desorption process for three representative batches. Concentration profiles of CAs and esters in the recycling line L6 (A) and pH levels in line L6 and S2 (B).

desorption eluent as matter of the few adsorption sites contained in strong type resins; both facts evidenced on a recently reported work [24]. However, the innovative recovery of CAs with  $\text{CO}_2$ -expanded alcohols is also theoretically applicable for weak or bifunctional anionic resins, like those used by *Notarfrancesco et al.* [15]. Therefore, the novel desorption strategy using  $\text{CO}_2$ -expanded alcohols [24,25] was preliminary assessed in batch tests since the already set-up semi pilot AnCol does not allow to work under significant pressure ( $P < 0.5 \text{ bar}$ ). Briefly, AnRes was firstly saturated with a laboratory prepared solution simulating the decationised UBW-broth. Thereafter, desorption with  $\text{CO}_2$ -expanded ethanol ( $25^\circ\text{C}$ , 2 bar  $\text{CO}_2$ , 2 h) allowed to recover 25 % of the adsorbed CAs. Such preliminary outcome is in line with previously reported results using the strong resin type 1 Dowex Marathon MSA [23].

As previously discussed, it is important to predict BT points to be able to scale up the process. Also for the case of the AnCol the application of the simple model (without dispersion [18]) resulted accurate enough for predicting the BT points of the experimental curves obtained for expanded bed mode (Fig. 6), with percent errors ranging 2–18 % (Sup. material, Fig. S7).

Notably, no adsorption control experiment was done using directly the anion exchange column without the previous cation exchange or by feeding a broth without  $\text{PO}_4^{3-}/\text{Cl}^-$ . However, the benefits related to the employment of the cationic pre-treatment had been already demonstrated in our previous work reporting the competitive ion-equilibrium model that predicts CAs adsorption isotherms at different contents of  $\text{Na}^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and CAs: Fig. 5 in that work shows the negative effects of  $\text{Na}^+$  concentration on the CAs adsorption isotherms [15]. Moreover,



such model was ratified by the experimental data reported in the present work, namely: 1- the hypothesis of COD<sub>Other</sub> being an interferent of CAs adsorption was definitely refuted since the early BT-point obtained for the COD<sub>Other</sub> (Fig. 5B) confirmed that it has a lower resin affinity than CAs; 2- the total adsorbed anions in those tests carried out until the resin saturation matched with the nominal installed capacity (determined from previously numerically discussed isotherms); and 3- it was possible to accurately forecast the time of CAs BT-points for different experimental feeding rates by means of formulae that included the isotherm predicting model. Regarding the last two bullets, in case of feeding the same broth but just partially decationised (at pH 5 instead of 1.49 as in the experiments presented) the resin adsorption capacity (q) would be reduced by ~80 % and so directly proportional earlier BT-points would be obtained.

### 3.3. Preliminary costs assessment

Regarding the process overall economy, a preliminary assessment was carried out for a hypothetical plant producing 10 k ton/y of CAs, corresponding to 13 % of the Italian market if considering a global market of 13.4 M USD/y [26] and an average price of 1300 USD/ton [27]. To this aim: 1) the hypothetical CatCol and AnCol were designed by using the LUB method and conservative feeding rates; 2) resins lifetime was considered as reported elsewhere (30 % of the bed renewed each year) [28]; 3) only resins, reagent and final solvent evaporation energy costs were estimated (using industrial prices), whereas 4) CAPEX (columns, tanks, pumps, piping, etc.) was not considered at this preliminary stage since an industrial plant with 30 year life span won't have any significant influence on the final cost as recently reported elsewhere for different ion-exchange adsorption plants for recovery CAs ( $\leq 10\%$ ) [29], for sodium gluconate decationisation (~3 %) [30] and for recovering itaconic acid (11 %) [31]. The resulted estimations (shown in Sup. Material, section S3) indicate that NH<sub>4</sub><sup>+</sup>/Na<sup>+</sup> separation with the CatCol would cost 0.39 EUR/kg\_CAs and CAs recovery with the AnCol would cost 1.10 EUR/kg\_CAs, totalizing 1.49 EUR/kg\_CAs. However, the CatCol step could be replaced by a bipolar membrane electrodialysis (see Section 3.1) which does not requires chemical reagents but just the energy for separating cations from anions (0.1–0.3 kWh/mol, [32,33]), this diminishing cost to 0.19 EUR/kg\_CAs. Furthermore, CAs could be desorbed by using CO<sub>2</sub>-expanded ethanol (i.e. saving all the H<sub>2</sub>SO<sub>4</sub> used for desorption and limiting NaOH utilisation to the inorganic anions desorption requirement), this reducing AnCol cost to 0.39 EUR/kg\_CAs. Taking together, both hypotheses would allow a limited total recovery cost of 0.58 EUR/kg\_CAs. A recent techno-economic analysis, which compared weak-base with conventional strong-base resins, indicated a lower CAs recovery costs of ca. 0.1 EUR/kg\_CAs [29]. However, despite being an innovative approached analysis, it needs adjustments since: i) it does not consider inorganic cations and anions interferences in CAs adsorption (CatCol pretreatment dedicated to rendering CAs adsorbable must be included in evaluation); and ii) the employed procedure for determining adsorption isotherms and resin capacities overestimates them, e.g. the anionic resin DOWEX 77 (also called Amberlite FPA77) adsorption capacity from datasheet is 4.5 mmol/gDR (as the values reported elsewhere for other resins with tertiary amine functional group [15]) and not 8 mmol/gDR as reported in that work.

Overall, the high performances and robustness of the process are very encouraging in the perspective of applying the process at industrial scale. The obtained curves of resin capacity utilisation vs linear feeding rate would allow practicing such scale up. Yet, despite the many practiced adsorption-desorption cycles, the process should be tested in industrial environment (TRL 6–7) for the required to confirm evidence reported in this work. In this regard, the future pilot-scale plant should be able to work under pressure so as to test CO<sub>2</sub>-expanded alcohol desorption.

## 4. Conclusions

Breakthrough experiments conducted using semi-pilot scale columns and an actual fermentation broth confirmed that the application of a cation adsorption pretreatment (for separating Na<sup>+</sup>/NH<sub>4</sub><sup>+</sup>) allows recovering almost 100 % of the CAs occurring in a real fermentation broth in a consecutive anion adsorption column filled with weak basic resin. Moreover, despite there were no control experiments where the broth was directly fed to the anion exchange column without the previous cation exchange (or by feeding a broth without PO<sub>4</sub><sup>x-</sup>/Cl<sup>-</sup>), the breakthrough experiments allowed to validate the clue CAs adsorption mechanistic issues previously reported from the modelling of experimental isotherms determined in batch test at flask-scale. In particular it was confirmed that other organic compounds else than CAs (COD<sub>Other</sub>) have a weaker affinity than CAs and so they do not interfere on their adsorption. Hence, the low CAs adsorption yields generally reported are due to strong inorganic cations/anions presence and not due to the presence of COD<sub>Other</sub> neither to the broth's pH level which modification does not bring benefit to the resin-CAs interaction. This conclusion is supported by the perfect matches observed in the anion exchange column between a) total adsorbed anions and nominal installed capacity as well as b) the experimental BT-points at different feeding rates and those predicted with the CAs isotherms model including the Na<sup>+</sup>/NH<sub>4</sub><sup>+</sup>/PO<sub>4</sub><sup>x-</sup>/Cl<sup>-</sup> negative effects. Besides, operating the columns in expanded bed mode drastically diminishes the axial dispersion: breakthrough curves can be accurately predicted for cationic (error < 7 %) and anionic (error < 18 %) columns by using previously reported isotherms and the simple formulae described in conventional engineering books. Finally, a preliminary economic analysis indicates production cost (ranging 0.58–1.49 EUR/kg of CAs depending on the process configuration) that are very encouraging for considering further assessments at higher scale.

### CRedit authorship contribution statement

**Fabio Fava:** Supervision. **Maurizio Mancini:** Writing – review & editing, Supervision. **Andrea Negroni:** Writing – review & editing, Resources, Investigation. **Joana M.B. Domingos:** Resources, Investigation. **Gonzalo Agustín Martínez:** Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Formal analysis, Data curation, Conceptualization. **Sarah Notarfrancesco:** Investigation. **Elena Morselli:** Investigation. **Lorenzo Bertin:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2024.114089](https://doi.org/10.1016/j.jece.2024.114089).

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