O papel da escala experimental na capacidade operacional de troca iônica: Utilização do sistema NO_3^--SO_4^{2-} para avaliação do processo.

The role of the experimental scale in the operational ion exchange capacity: Use of the NO_3^--SO_4^{2-} system for process assessment.

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Abstract: The role of experimental scale size in the operational ion exchange capacity was investigated using the well-known NO_3^--SO_4^{2-} ion exchange system. To achieve our goal, breakthrough curves were obtained in a laboratory and a pilot fixed-bed column. The value of contact time remained the same for each scale, however, the liquid superficial velocity and resin bed height were different for the laboratory scale. The q_{opr} values calculated from the experimental data were 0.606 and 0.616 eq/L for the laboratory scale and 0.613 and 0.620 eq/L for the pilot scale, showing no significant differences. The MTZ representativeness decreased for the pilot scale, from 5.0% to 2.31%, nonetheless, this behavior did not influence the q_{opr} value. The results suggest that laboratory scale experiments can be used to collect q_{opr} values for ion exchange systems keeping the liquid contact time.

Palavras-chave: Pilot scale, laboratory scale; fixed bed experiments; operational capacity.

1. Introduction

Ion exchange is considered one of the best and most feasible methods for contaminants removal from water. To enable the use of any ion exchange resin for contaminants removal, is to understand about how the water chemistry and equipment variables affect the resin capacity. In general, the manufacturers provide engineering bulletins to permit engineers to calculate the operational capacity of the resin according to water chemistry, regeneration conditions, and equipment characteristics.

In the absence of engineering bulletins, an alternative is to obtain the capacity values from experimental columns simulating the conditions encountered in the industrial installations. This process should be conducted with careful attention to the experimental setup due to scale-up issues[1,2].

Ion exchange experiments performed on a laboratory scale cannot maintain the same liquid velocity and bed depth as the industrial columns for the same contact times. Due to these physical limitations, larger pilot systems are used to collect the desired data, keeping all variables unchangeable. Despite the advantage of unchangeable variables, operating pilot systems can be harder than small laboratory systems due to the more complex equipment involved, higher cost, and the higher water consumption to collect the desired data[1,2].

In this way, this study aimed to investigate the role of scale size on the experimental value of ion exchange capacity. To achieve our goal, we employed the well-known NO_3^--SO_4^{2-} ion exchange system on a strong base anion resin to investigate the mass transfer properties.

2. Methodology

2.1. Materials, reagents and analytical methods

The salts $NaNO_3$, Na_2SO_4, and NaCl were used to prepare all solutions. Before utilization, the salts were oven-dried at 120 °C for 6h. Demineralized water (< 0.5 µS/cm and $UVT_{254} > 99\%$) was used during all solution preparation.

The resin MA-20 used in the experiments was supplied by Samyang Company. The resin was washed three times with 10% wt. NaCl solution at 25°C, and 150 rpm for 90 min before their use.

The NO_3^- detection was performed by SMWW 4500-NO_3^- B method and SO_4^{2-} detection was made by SMWW 4500-SO_4^{2-} E method.

2.2. Fixed bed columns

The physical characteristics of the experimental columns used as fixed bed are presented in Table 1.

Table 1. Physical characteristics of columns used as fixed beds for the experiments.

Properties	Lab.	Pilot
Material	Glass	Acrylic
Internal diameter (mm)	10.3	74
Total cylindrical height (mm)	315	2000
Volume (mL)	25	8600
Area (m^2)	8.33×10^{-5}	4.3×10^{-3}

The desired feed solution was pumped to the laboratory fixed bed using a high-precision peristaltic pump. The solution passed through the resin bed was collected at the exit, and the NO_3^- and SO_4^{2-} concentrations were analyzed.

Figure 1 shows the representative flowsheet of the equipment used to acquire the breakthrough curves at the pilot scale. A centrifugal pump (P-01) was utilized to supply the desired demineralized water flow rate for the experiments. The volumetric flow rate of the pump was measured using an analogic rotameter (FL-01) and adjusted by valve (V-04). The NO_3^- and SO_4^{2-} were added to demineralized water using the P-02 metering pump. The static mixer (SM-01) was installed after the dosing point to ensure the solution homogenization. Sampling points before, and after the column were added to enable the sample collection and analysis.
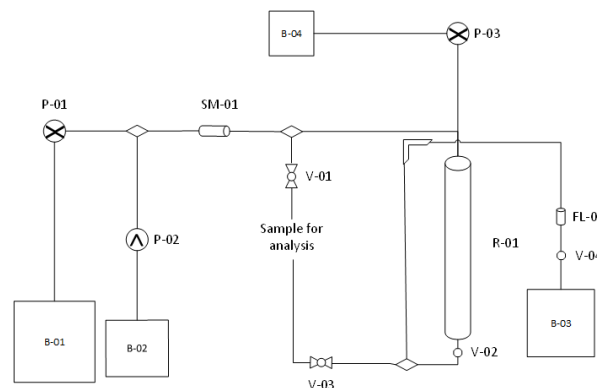

Fig. 1. Representative flowsheet of the ion exchange system used to perform the breakthrough curves at the pilot scale.

After the bed exhaustion, the resin was regenerated with 10% wt. NaCl solution applied at 4 BV/h. The brine step was followed by a slow and fast rinse using demineralized water at 4 and 40 BV/h, respectively. The regeneration parameters were the same in each scale.

2.3. Breakthrough curves and operational capacity

The experimental conditions related to the experimental breakthrough curves are shown in Table 2.

Table 2. Experimental conditions employed to acquire the breakthrough curves. Run 1: Virgin resin. Run 2: 1x 250g NaCl/L regenerated resin.

Parameter	Laboratory		Pilot	
	Run 1	Run 2	Run 1	Run 2
NO_3^- (meq/L)	1.80	2.13	1.68	1.73
SO_4^{2-} (meq/L)	2.08	2.25	1.72	1.74
R	1.15	1.06	1.03	1.00
V_R (mL)	16	16	3097	3140
Q (mL/min)	11	11	2293.33	2293.33
BV/h	41.25	41.25	44.43	43.82

The operational ion exchange capacity (q_{opr}), mass transfer zone height (MTZ), and useful bed height (H_u) were calculated using the state-of-the-art equations available in the literature[3].

3. Results and Discussion

3.1. Laboratory column evaluation

The scale criteria, recommended by Raghavan and Ruthven (1983) were evaluated to gather that the used column did not present problems regarding water channeling through the resin bed and walls effects[4]. The results and recommended values are shown in Table 3. The flow regime was investigated using the methodology recommended by Inglezakis and Poulopoulos (2006). For the proposed laboratory scale column, the calculated Peclet number was equal to 293, indicating that a plug flow regime can be assumed, and the axial dispersion can be disregarded for the system[5].

Table 3. Raghavan and Ruthven's (1983) for fixed bed columns.

Criteria	Calculated value
$Z/D \geq 5$	18.64
$D/d_p \geq 12 - 30$	17.91
$Z/d_p \geq 50 - 150$	333.9

The results suggest that the laboratory column was suitable for the experimental evaluation, avoiding fluid dynamics issues that can mask the mass transfer process[4,5].

3.2. NO_3^- and SO_4^{2-} behavior

Figure 2 shows the breakthrough curve for NO_3^- and SO_4^{2-} in the laboratory and pilot scale for Run 1. The breakthrough curve behavior for the other runs followed the same pattern shown in Figure 2.

The SO_4^{2-} ion leakage starts several minutes later than the NO_3^- leakage. This delay is due to the higher affinity of the resin for the SO_4^{2-} ions. After the depletion of the Cl^-, the initial ionic form of the resin, the SO_4^{2-} ion present in the incoming water, displaces the previously removed NO_3^- ion, leading to adimensional concentration values higher than 1.0. This phenomenon is well-known in the literature for non-selective resins and is called nitrate dumping[6-8].

The same behavior for NO_3^- and SO_4^{2-} was observed in the laboratory and pilot scale experiments, suggesting no scale influence on the chemistry of the process.
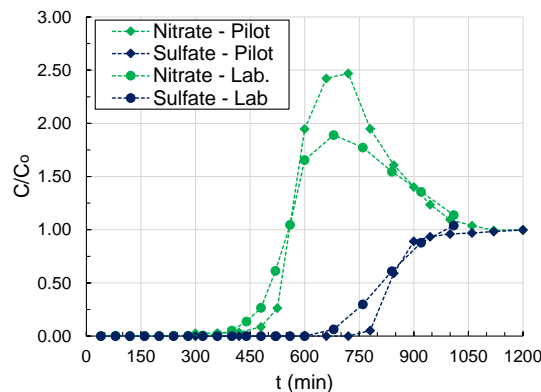

Fig. 2. Breakthrough curves for NO_3^- and SO_4^{2-} obtained in the laboratory and pilot column for Run 1.

3.3. Laboratorial and pilot scale comparison

The breakthrough curves obtained for the pilot scale column are shown in Figure 3 and the values of q_{opr}, MTZ, and H_u for these experiments are shown in Table 4. The pilot-scale values were compared to the values obtained in the laboratory scale in Run 1 and Run 2.

As seen in Figure 3, the behavior of the breakthrough curves in the laboratory and pilot scale were similar, showing the same width for the dumping peak. The maximum values for C/C_o in the pilot scale were slightly higher than the laboratory scale. Analyzing the slope of the curves is possible to see that the breakthrough curves obtained in the pilot scale column are slightly more inclined than the curves obtained in the laboratory scale. This fact indicates that the mass transfer was faster for the pilot-scale fixed bed[3-5].
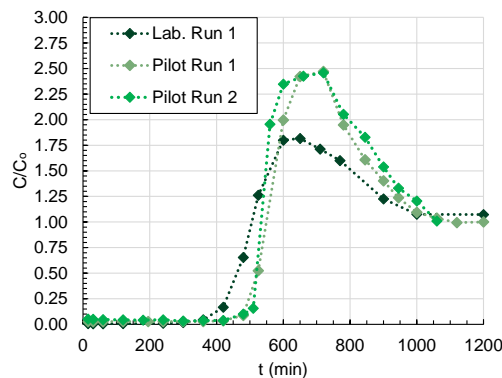

Fig. 3. Breakthrough curves for NO_3^- obtained in the pilot scale column and laboratory scale column.

Table 4. Operational capacity and mass transfer parameters calculated from laboratory and pilot scale breakthrough curves.

Parameter	Laboratory		Pilot	
	Run 1	Run 2	Run 1	Run 2
q_{opr} (eq/L)	0.606	0.616	0.613	0.620
t_b (min)	442.87	444.3	515.03	517.1
t_u (min)	426.36	420.53	490.75	489.6
t_t (min)	449.26	-	501.67	494.73
H_u (mm)	178.8	-	748.35	722.87
MTZ (mm)	9.6	-	16.65	7.48

The more effective mass transfer AT the pilot scale was confirmed by the analysis of the mass transfer zone compared to the total resin height. For the laboratory scale Run 1, the MTZ corresponds to 5.0% of the total bed height and in contrast, the MTZ value represents only 2.31% of the total bed height for the pilot scale Run 1. The decrease in MTZ representativeness can be attributed to the increase in the total bed height, making the process more effective from the mass transfer perspective. The NO_3^- leakage remained at 3% for the two scales.

Despite the improvement in the mass transfer, the q_{opr} value remained approximately the same for the two studied scales. The increase in the q_{opr} value for the pilot scale Run 1, compared to the laboratory scale Run 1, was equal to 1.14% while the increase for Run 2 was equal to 0.64%. These values indicate that the scale, or the liquid surface velocity, does not influence the q_{opr} value, and for the NO_3^- removal the most important variable is the contact time when operating at different scales[1,2,5].

The results obtained and discussed in this section suggest that the most important variable is the contact time for favorable ion exchange systems. This implies that the results obtained at the laboratory scale and keeping the pretended contact time can be used to project industrial equipment eliminating the need to carry out pilot-scale tests with the same values of contact time, liquid velocity, and resin height.

4. Conclusion

The scale study revealed that the chemistry of the well-known NO_3^--SO_4^{2-} system on strong base anion resin does not change with the process scale.

The values of q_{opr} and mass transfer parameters suggest that the scale did not influence the process in a significative way, where the q_{opr} values remained in the same magnitude order.

The results obtained in this study suggest that the most important variable for favorable ion exchange systems is the contact time between the solution and the resin, enabling laboratory experiments to get the experimental values of q_{opr} needed to project industrial systems. This fact implies that complex pilot systems keeping the same liquid velocity, contact bed time and bed height can be replaced by simpler laboratory-scale experiments.

Acknowledgements

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