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# Oxygen transfer in a three-phase bubble column using solid polymers as mass transfer vectors

# Transferencia de oxígeno en una columna de tres fases utilizando polímeros sólidos como vectores de transferencia de masa

G. Quijano[1,2,a], M. Franco-Morgado[1,a], M.S. Córdova-Aguilar[3,b], E. Galindo[3], F. Thalasso[1*]

[1]*Departamento de Biotecnología y Bioingeniería, Centro de Investigación y de Estudios Avanzados del IPN (Cinvestav), Av. IPN 2508, Mexico D. F. 07360, Mexico.*
[2]*Laboratory for Research on Advanced Processes for Water Treatment, Instituto de Ingeniería, Unidad Académica Juriquilla, Universidad Nacional Autónoma de México, Blvd. Juriquilla 3001, Querétaro 76230, Mexico.*
[3]*Instituto de Biotecnología, Universidad Nacional Autónoma de México, Cuernavaca 62250, Morelos, Mexico.*
[a]*G.Q. and M. F-M. contributed equally.*
[b]*Present address: Instituto de Ciencias Aplicadas y Tecnología (ICAT), Universidad Nacional Autónoma de México, México D.F. 04510, Mexico.*

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## Abstract

Three solid polymers; Kraton, Elvax, and Desmopan, previously suggested to be used in three-phase reactors, were evaluated for their ability to enhance oxygen transfer in a bubble column. These vectors were first characterized, including; particle size distribution, specific surface area, density, void fraction and thermal stability. Oxygen transfer was then determined with a non-coalescing medium using polymer volume fractions from 0 to 75% in a 4 L bubble column operated at air flow rates ranging from 1 to 6 L/min. The results showed that in most of the cases, particles clusters were formed at the surface of the bulk water phase, which caused a decrease of the oxygen transfer capacity. Kraton, was the polymer vector more easily dispersible in the air/water bulk phase of the bubble column, and used at a proportion of 10% with an aeration flowrate of 2 L/min, it allowed an oxygen transfer enhancement by 90-100%, compared to a control with no vector. This enhancement was a result of constant collisions between vector particles and bubbles, decreasing their rising speed, while not altering their mean size, thus resulting in a significantly higher gas holdup and air/water exchange area.

*Keywords*: bubble size, gas holdup, interfacial area, non-aqueous phases, TPPB.

## Resumen

Kraton, Elvax y Desmopan, tres polímeros sólidos comerciales fueron evaluados como vectores de transferencia de oxígeno en una columna de burbujeo. Los vectores se caracterizaron en términos de distribución de tamaño de partículas, área específica, densidad, fracción de espacio vacío y estabilidad térmica. Posteriormente, se determinó la transferencia de oxígeno con un medio no coalescente, usando fracciones de volumen de polímero de 0 a 75% en una columna de burbujas de 4 L operada con flujos de aire de 1 a 6 L/min. Los resultados mostraron que, en la mayoría de los casos, conjuntos de partículas se formaron en la superficie de la fase acuosa, lo que causó una disminución de la transferencia de oxígeno. Kraton, fue el vector más fácilmente dispersable en la columna de burbujas, y utilizado en una proporción del 10%, con un flujo de aireación de 2 L/min, permitió una mejora de la transferencia de oxígeno por 90-100%, en comparación con un control sin vector. Esta mejora fue el resultado de colisiones constantes entre las partículas del vector y las burbujas, disminuyendo su velocidad, sin alterar su tamaño medio, lo que resultó en una mayor retención de gas y área de intercambio aire/agua.

*Palabras clave*: tamaño de burbuja, fracción de gas retenido, área interfacial, fases no acuosas, biorreactor de partición.

## 1 Introduction

Due to the low oxygen solubility in water (air/water partition coefficient of 31.5), oxygen transfer from a gaseous phase (commonly air) to an aqueous phase is a key issue in many biotechnological processes (Martínez-Hernández *et al*., 2020). Enhancement of oxygen transfer rates has usually involved either the increase in stirring or aeration rates or the

* *Corresponding author. E-mail*: thalasso@cinvestav.mx
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introduction of oxygen-enriched air streams, which significantly increase production costs (Nielsen *et al*., 2003). Other strategies have been tested, including the addition to the culture medium of surfactant or electrolyte compounds (Baz-Rodriguez *et al*., 2014; Rivas-Interián *et al*., 2019), but this approach is limited by the media composition required by the bioprocess. An alternative method, explored for more than 30 years, is the addition of an immiscible organic phase, also called mass transfer vector, with high affinity for oxygen (Deziel *et al*., 1999). The reactors provided with a mass transfer vector are commonly referred as two-phase partitioning bioreactors (TPPBs) and are able to support significant oxygen mass-transfer enhancements, compared with the same reactors without a vector (Galindo *et al*., 2000; Elibol *et al*., 2001; Clarke and Correia, 2008; Quijano *et al*., 2009a; Muñoz *et al*., 2012). However, under specific conditions, decreases in the mass transfer performance have also been reported after vector addition (Nielsen *et al*., 2003; Clarke *et al*., 2006; Clarke and Correia, 2008).

Liquid solvents such as hexadecane, perfluorocarbons, polydimethylsiloxanes and silicone oil have commonly been used as mass transfer vectors (Muñoz *et al*., 2007; Quijano *et al*., 2009b; Darracq *et al*., 2010). These liquid vectors have been selected for their high affinity for oxygen and a variety of poorly water-soluble compounds but also for their relatively low viscosity making them relatively easy to disperse in aqueous phases and thus facilitating mass transfer (Quijano *et al*., 2017). More recently, solid polymers made of copolymers of polyurethane, vinyl acetate and/or ethylene, among others, have also been used in TPPBs. These solid vectors gained a rising acceptance because of their lower cost, simple separation and recycling in the process (Daugulis *et al*., 2011).

In spite of significant progresses of TPPBs in the last 20 years, the mechanisms of mass transfer in such multiphasic systems continue to be discussed. Several authors hypothesized that the observed mass transfer enhancement of poorly-water soluble organic compounds in TPPBs, is due to the establishment of a high-performance gas/vector/water pathway (Muñoz *et al*., 2007). On the contrary, Pulido-Mayoral and Galindo (2004) observed that the addition of castor oil in a bioprocess reduced the Sauter mean diameter of air bubbles and suggested that the positive effect of vector addition was through an increase of the air/water surface area. This effect was also observed by Quijano *et al*. (2010a) who showed that the increase of oxygen transfer was mainly due to an increase of the air/water transfer rate, rather than the creation of a new gas/vector/water pathway.

However, both mass transfer phenomena might coexist and the positive effect of vectors on mass transfer might be attributed to either a modification of the multiphase dispersion favoring gas/water transfer or to the establishment of gas/vector/water transfer pathway in addition to the conventional gas/water transfer. Such main mechanisms of mass transfer enhancement driven by the presence of the vectors are applicable to several bioreactor configurations, including pneumatic reactors such as bubble columns (Dumont *et al*., 2006, 2013). The aforementioned underlines the need to further explore and understand mass transfer in TPPBs and especially with solid vectors, which has been scarcely reported.

A wide assortment of solid vectors has been used for biotechnological processes but currently, three solid vectors have been predominantly reported; Elvax, Kraton and Desmopan, because of their granulometry and low-cost, making them potentially interesting for such processes. Several authors have reported the application of these solid vectors for the degradation of xenobiotic compounds (Amsden *et al*., 2003; Rehman *et al*., 2007,2008; Littlejohns and Daugulis 2008,2009; Isaza and Daugulis, 2009). Rocha-Ríos *et al*. (2011) studied the use of Desmopan and Hernández *et al*. (2010) the use of Kraton, for the degradation of alkanes. Morrish and Daugulis (2008) used Kraton in a bioconversion process and Quijano *et al*. (2010b) used Desmopan in model yeast fermentation. Most of these works have been done in stirred tank reactors (STRs) or in airlift reactors but to the best of our knowledge, the use of solid vectors in bubble columns has not been reported previously.

The main objectives of this paper were to investigate the effect of Elvax, Kraton and Desmopan on the oxygen mass transfer in a bubble column and furthermore, to characterize the gas, liquid and vector phases dispersion under the conditions most favorable to oxygen transfer. These vectors were tested in a bubble column, since it is the simpler and however less studied reactor design (Hashemi *et al*., 2012).

## 2 Materials and methods

### 2.1 Solid vectors characterization

DesmopanTM (9370A, Bayer), KratonTM (G1657, Kraton Polymers) and ElvaxTM (470, Dupont) were selected as solid vectors. Desmopan, Kraton and Elvax are polyurethane, styrene/ethylene-butylene and ethylene vinyl acetate polymers, respectively. The three solid vectors were characterized in terms of particle size and density, void fraction and thermal stability. The mean vector particle size was determined from direct measurements of a sample large enough to obtain arithmetic mean with 5% error and 95% confidence interval, according to Montgomery (2005). Statistic results were analyzed with NCSS 2000 Statistical Analysis System software (Number Cruncher Statistical Systems, USA). From the arithmetic mean particle dimensions, the specific surface area of each solid vector was calculated assuming a cylindrical (Desmopan), spherical (Kraton) or meniscus (Elvax) shape.

The bed density of the solid vectors was determined volumetrically, and the void fraction was determined from the volume of water added to fill a known bed volume of vector. The density of each material was calculated by dividing the weight of the carrier used by its volume (total bed volume less volume of water added). Resistance of solid vectors to sterilization via autoclaving was performed by adding 5 g of each vector to 120 mL glass flasks containing either distilled water or Minimal Salts Medium (MSM) (Quijano *et al*., 2010b). The flasks were autoclaved at 121 °C for 25 min and polymer thermal stability was evaluated by visual observation of polymer melting. Additionally, the surface of the vectors was characterized by electronic scanning microscopy (JSM-6510LV, JEOL, Mexico).

## 2.2 Oxygen transfer

Oxygen transfer experiments were done in a glass bubble column (0.12 m internal diameter, 0.775 m total height, 8.75 L total volume), filled with 4 L of non-coalescing media (KCl 0.13M). The bubble column was aerated with a porous plate located at the bottom of the column and controlled by a rotameter. Experiments were done at 25°C, controlled by a heating blanket. Oxygen transfer from the air to the water phase was characterized through mass transfer coefficient ($K_La$) according to the dynamic method of Badino *et al*. (2000), using $N_2$ to displace dissolved oxygen. Briefly, $K_La$ was determined, from Eq. 1, where $C$ is the measured dissolved oxygen concentration (kg m$^{-3}$), $D$ is the oxygen diffusivity in water (m$^2$ s$^{-1}$), $\delta$ is the liquid film thickness (m), $a$ is the specific air/water exchange area, $C^*$ is the dissolved oxygen concentration in saturated water (kg m$^{-3}$), $K_L$ is the liquid film coefficient ($D/\delta$; m s$^{-1}$), and where $K_La$ is the product of $K_L$ and $a$.

$$\frac{dC}{dt} = \frac{D}{\delta} \cdot a(C^* - C) = K_L \cdot a(C^* - C) = K_La(C^* - C) \tag{1}$$

$K_La$ was determined in triplicate for each experimental condition; namely (i) Kraton, Desmopan and Elvax, (ii) 0, 10, 25, 50 and 75% (v/v) vector, considering vector bulk volume and (iii) air flow rates of 1, 2, 4 and 6 L/min (corresponding to 0.25, 0.5, 1.0 and 1.5 volume of air per volume of reactor per minute -vvm-, respectively). Dissolved oxygen was measured with a polarographic dissolved oxygen bench meter (HI2400, Hanna Instruments, Mexico). The dissolved oxygen meter was connected to a PC for data acquisition. The oxygen probe was placed at the top of the reactor. For each experimental condition, the $K_La$ observed was compared with the control $K_La$ recorded with no vector ($K_La_0$). Then, an enhancement factor ($E_f$) was obtained by means of Eq. 2:

$$E_f = \left(\frac{K_La}{K_La_0} - 1\right) \times 100\% \tag{2}$$

In addition to $K_La$, Oxygen Transfer Capacity (OTC), which is the oxygen transfer rate observed when no dissolved oxygen is present in the aqueous phase, was also determined according to Eq. 3:

$$OTC = K_La \times C^* \tag{3}$$

The gas volume fraction contained in the reactor; i.e. the gas holdup ($\varepsilon$), was determined volumetrically according to the method suggested by Vandu *et al*. (2004). However, during the experiments, clusters formed by floating vector particles were often observed at the surface of the reactor. This layer of vector particles was highly irregular and impeded the accurate measurement of $\varepsilon$.

## 2.3 Phases dispersion and bubble size

As it will be shown in the results section, the major oxygen transfer enhancement was observed under very specific conditions; i.e., 10% of Kraton, in the bubble column aerated at 0.5 vvm. In order to explore what parameter was causing that observed mass transfer increase, the phase dispersion and bubble size was further characterized, under these conditions, in a control experiment with no solid polymer, and with 10% Kraton. Bubble size was determined from images taken with a high-speed digital camera (5130 images/s, 512 X 512 pixels, Redlake Motion Pro HS4, Microsys Technologies Inc., USA) connected to a stereomicroscope (SZ1145ESD, Olympus, Mexico). Images were taken at medium height (18 cm from bottom) of the bubble column, with backlighting obtained with 0.7 m long optical fiber connected to a high intensity direct light 230V/50 Hz, Arc Xenon, 180W (SX200, Fort Imaging Systems, Inc., France). This procedure was adapted from Guevara-López *et al*. (2008). Images analysis was performed with Image J software (Image J 1.44i, NIH, Mexico) and allowed to determine the bubble surface mean diameter ($d_S$), the volume mean diameter ($d_V$), and the Sauter mean diameter ($d_{32}$), the latter being used to estimate the mean air/water interfacial area.

### *2.4 Statistical analyses*

Statistical analyses were performed with NCSS® software (Jerry Hintze, 2001). Analyses of variance ($\alpha$= 0.05) and Tukey-Kramer tests were performed in order to evaluate significant differences among the gas/liquid dispersion parameters described in section 3.4. Additionally, bubble size distribution was tested for normality, through the Kolmogorov-Smirnov test. To estimate the standard deviation of $d_S$, $d_V$, and $d_{32}$, an error propagation method was used, according to Ku (1966). The error in all experimental procedures was expressed as the standard error of the mean.

## 3 Results and discussion

### *3.1 Solid vectors characterization*

The three vectors investigated in this work were composed of regular cylinders (Desmopan), spheres (Kraton) or meniscus (Elvax). The three vectors were of white translucent color. Scanning electron micrographs (Fig. 1) show that Kraton and Elvax had a relatively rough surface while Desmopan exhibited a smooth surface. Table 1 shows the main characteristics of the three selected vectors, which were similar in particle size and surface area. The particles diameter was quite regular, with a coefficient of variation from 8 to 12%. Contrastingly the height of the particles was more variable, especially for Desmopan, with a coefficient of variation of 41%, and irregular cuts at each opposite face, probably due to the manufacturing process. Desmopan presented a density very close to water, while Elvax and Kraton presented a lower density. Bulk densities as well as the void fractions of the vectors were similar. When thermal resistance to sterilization was tested, no effect was observed for Desmopan and Kraton, while Elvax particles merged as a result of the partial melting during sterilization with both water and MSM. This suggests that Elvax may not be suitable for biotechnological processes which require axenic culture conditions. Besides the differences between thermal resistance characteristics, none of the other characteristics evaluated in this work, allowed to discard any of the three vectors.

### *3.2 Mass transfer experiments*

Oxygen transfer was quantified by $K_La$, in the bubble column, at each of the experimental conditions. Fig. 2 shows the enhancement factor (Ef) observed for each experimental condition. In this Figure, the conditions at which the vector distribution was considered homogeneous are indicated with arrows, the criterion being the absence of a layer of motionless particles at the surface of the liquid. In 33 of the total 48 conditions tested, these conditions were not met, and clusters of solid vectors particles were observed at the surface of the reactor. Particle clusters were observed with Desmopan under all conditions except one, and under all conditions with Elvax except 10% vector, 1.0 and 1.5 vvm and 25% vector, 1.5 vvm. Contrastingly, Kraton was homogeneously distributed under all conditions, with 10 and 25% of vector.

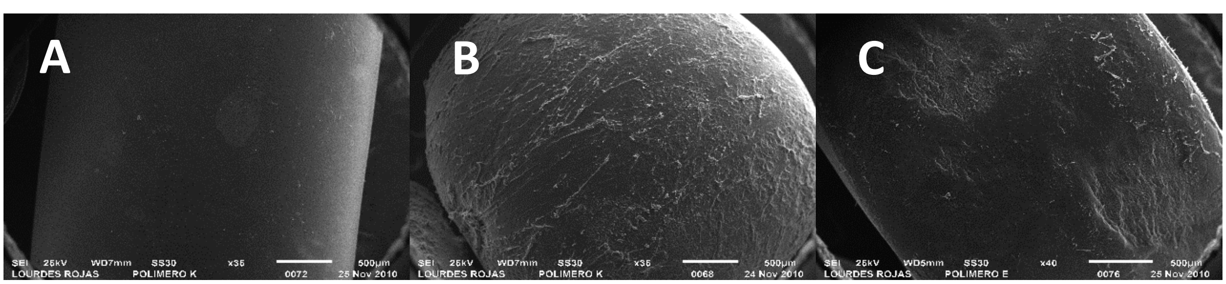


Fig. 1. Scanning electron micrographs of Desmopan (A), Kraton (B) and Elvax (C), white bars represent 500 $\mu$m.

Table 1. Main characteristics of the three solid vectors tested.

| | Desmopan | Elvax | Kraton |
|---|---|---|---|
| Shape | Cylinder | Meniscus | Sphere |
| Mean particle diameter (mm) | 2.71 ± 0.32 | 4.21 ± 0.32 | 3.15 ± 0.37 |
| Mean particle height (mm) | 3.22 ± 1.33 | 2.06 ± 0.43 | - |
| Mean surface area ($m^2/m^3$) | 2,209 | 1,960 | 1,927 |
| Material density ($kg/m^3$) | 1001 ± 0.81 | 835 ± 1.4 | 834±0.46 |
| Bulk Density ($kg/m^3$) | 446 ± 34.5 | 429 ± 46 | 408±28.1 |
| Void fraction (%) | 60 ± 1 | 60 ± 1 | 58 ± 0 |
| Thermal resistance | + | - | + |
| Cost[1] | 7.9 | 3.4 | 4.5 |

[1]In US dollars/L. Adapted from Quijano *et al*. [27], 10/03/2020 exchange rate.

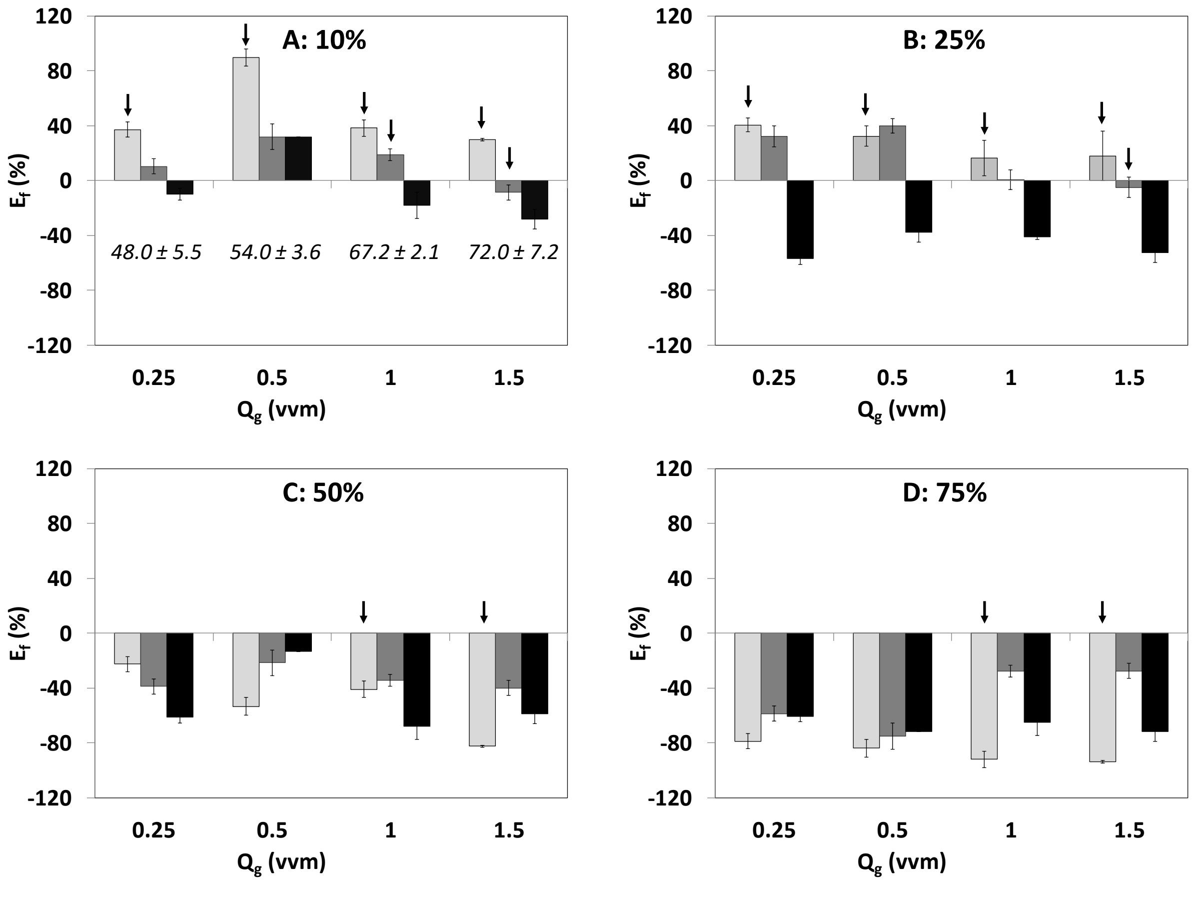


Fig. 2. $K_La$ enhancement factor observed with 10% (A), 25% (B), 50% (C) and 75% (D) of Kraton (■), Elvax (■) and Desmopan (■) in the bubble column, for aeration from 0.25 to 1.5 vvm. Inner values in italics (Figure 2A) give $K_La$ ($h^{-1}$) observed in the control experiment (no vector). Arrows indicate when vector distribution was homogeneous.

The reason why Kraton is more easily dispersible in a bubble column might be due to the spherical shape of the particles, which avoids straight angles to which other particles con stack on, on the contrary of Desmopan and Elvax. Thus, Kraton offers some guarantees that a good mixing is obtained at a vector percentage ≤ 25%, and at aeration flowrates ≤ 1.5 vvm, which seems to be a reasonable range for scaling up.

In terms of oxygen transfer, some positive $E_f$ were observed with 10% and 25% vector (Fig. 2A and 2B), compared with negative effects with all vectors and aeration flowrates, at 50 and 75% of vector (Fig. 2C and 2D). It should be noted that Desmopan had no positive effect on $K_La$ at any experimental condition, except for 10% vector and 0.5 vvm; i.e. one condition out of 16 tested. Elvax had a positive effect on $K_La$, only with 10 % vector at air flow rates below 1.5 vvm and with 25% vector at air flow rates below 1 vvm. On the contrary, 10% and 25% Kraton had a positive effect on $K_La$ at all air flow rates. The best $K_La$ observed was with 10% Kraton at 0.5 vvm air flow rate ($K_La$ of 102.5 ± 6.7 h$^{-1}$ and $E_f$ = 89.8 ± 6.4%). Overall, when cluster formation was observed, only 5 cases corresponded to a mass transfer enhancement (on average by 30%), while in 28 cases, cluster formation had a negative impact on mass transfer. In addition, since cluster formation seems to be a disorderly process, certainly not prone to scaling up, it was considered as an undesired phenomenon.

These results showed that the presence of a solid vector can enhance oxygen mass transfer in bubble columns, but only under specific operational conditions. Overall, no clear trend was observed regarding the impact of the air flowrate on mass transfer, and the results appear unpredictable. Nonetheless, when reducing the dataset to the cases of homogeneous distribution of Kraton (marked with downward arrows in Fig. 2), a clear trend was observed; i.e. optimal gas flowrate above which a decrease of oxygen transfer was observed. The overall complex behavior of our triphasic system is in accordance with the literature, as no clear consensus has been reached on the positive or negative effect of vectors on mass transfer (Dumont and Delmas, 2003). Quijano *et al*. (2010b) observed a significant enhancement of mass transfer with Desmopan in both Airlift and STR reactors, with $E_f$ of 255 and 90%, respectively. The same authors also observed a clear entrapment of the vectors in the upper section of the airlift reactor and it was suggested that such entrapment acted as an efficient air bubble disruptor, promoting mass transfer. For the STR, they observed also a significant enhancement of oxygen transfer and good vector dispersion. Thus, two effects of solid vectors on mass transfer were suggested in that previous work; (i) an effect of the suspended vector particles on gas dispersion with a potential increase of turbulence or bubble disruption as previously observed by several authors (Galindo *et al*., 2000; Zhang *et al*., 2006; Littlejohns and Daugulis, 2007), and (ii) an effect of entrapped vector particles on the gas phase dispersion (Quijano *et al*., 2010b). The differences between the results obtained with Desmopan in this work and the previous studies, highlight the fact that mass transfer improvement attributable to the presence of the solid vector is strongly dependent on the vector-reactor pair and the operational conditions. Indeed, the results obtained in this work, compared to those obtained by Quijano *et al*. (2010b), which both showed Desmopan entrapment in the upper section of the reactors, were contradictory in terms of mass transfer; i.e. negative effect in a bubble column (this work) but positive effect in an Airlift and a STR reactor (Quijano *et al*., 2010b). Thus, it seems that forced or channeled liquid recirculation had a positive impact on mass transfer with Desmopan, which might be not true with other solid vectors.

### 3.3 Mass transfer with 100% vector

In order to further investigate the potential effect of entrapped solid vectors particles on oxygen transfer, $K_La$ was measured in the bubble column filled with vector (100% vector, considering bulk vector volume) being then similar to a submerged filter. Fig. 3A shows the $K_La$ enhancement factors observed under these conditions. No significant $E_f$ was observed with Desmopan, except with an air flow rate of 1.5 vvm. On the contrary, a significant $E_f$ was observed with Kraton at all air flow rates and with Elvax, at air flow rate inferior to 1.5 vvm. Elvax showed $E_f$ of up to 250% at an air flow rate of 0.5 vvm. These results confirm the positive effect of static vector particle on gas dispersion, as it was previously suggested by Quijano *et al*. (2010b), at least for Kraton and Elvax vectors. It must be highlighted that no movement of the polymer particles was observed during $K_La$ determination, when the column was filled with 100% vectors. Since the presence of 100% vectors modified $K_La$, surface and mechanical effects likely promoted bubble coalescence and/or disruption phenomena, thus with antagonistic effects. For instance, Desmopan decreased $K_La$ at air flowrates ≤ 1 vvm, while it enhanced it at 1.5 vvm. In the case of Elvax, $K_La$ was increased at air flowrates ≤ 1 vvm, while and opposed effect was observed at 1.5 vvm. Interestingly, Kraton was the only vector able to increase $K_La$ under all air flowrates tested. However, the impact on $K_La$ also varied with the air flow rate. These results strongly suggest that the air flowrate was the parameter that mediated bubble coalescence or breakup, as well as the intensity of these phenomena.

From an engineering point of view, the potential positive impact of large vector percentages on $K_La$, is substantially reduced by a corresponding decrease of the liquid holding capacity of the reactor. Indeed, the use of 100% bulk volume of vector reduces the liquid holding capacity to the void fraction of the vector; specifically, from 58 to 60%. Thus, the oxygen transfer, per unit of reactor volume is reduced by the same factor. Fig. 3B shows oxygen transfer capacity (OTC), expressed per unit of reactor volume. No improvement of OTC was observed with any vector, compared with the control (no vector), except with Elvax, at an air flow rate of 0.25 and 0.5 vvm, which in this case represented an enhancement of 37 and 110%, respectively. These results suggest that a submerged biofilter packed with Elvax, might be a future potential application of solid polymers in bioprocesses, which should be further investigated. Indeed, the relatively low void fraction of Elvax (60%, Table 1) might be a significant bottleneck in this potential application, where a biofilm formation might generate interstitial clogging.

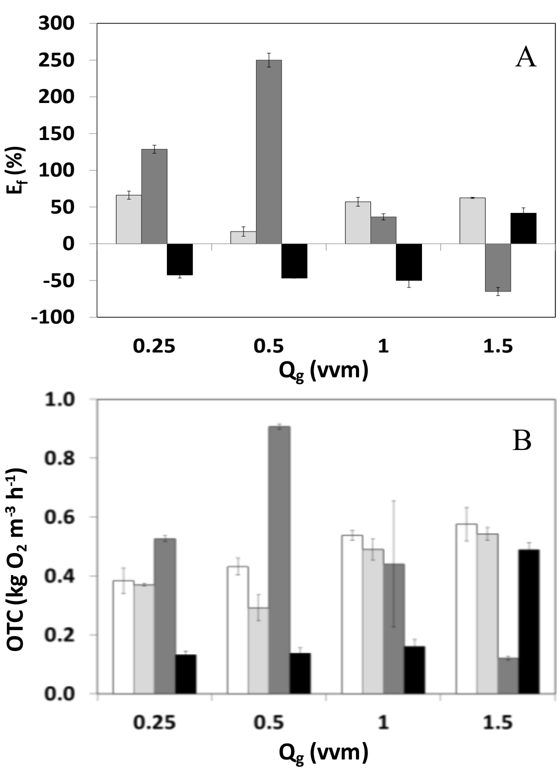


Fig. 3. (A) KLa enhancement factor observed in the bubble column operated as submerged filter (100% solid vectors) and (B) OTC expressed per unit of reactor volume. Control (□), Kraton (■), Elvax (■) and Desmopan (■).

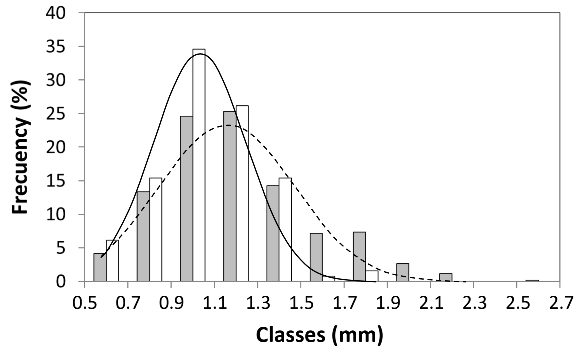


Fig. 4. Histogram of bubble diameter observed during control experiment with no Kraton (□) and in presence of 10% Kraton (■; n=300 each). Lines represent normal distribution for control (solid line) and Kraton (dotted line) experiments.

## *3.4 Phases dispersion and bubble size*

Motivated by the mass transfer enhancement observed with 10% Kraton under an aeration of 0.5 vvm, these conditions were further tested, through the characterization of phases dispersion and bubble size. The main results obtained with Kraton and during a control experiment without polymer, are presented on Table 2. As previously observed, a triplicate measurement of $K_La$ with Kraton confirmed that, under these conditions, the oxygen transfer was significantly enhanced, reaching a $K_La$ of 113 ± 6.4 $h^{-1}$ against 54.0 ± 3.6 $h^{-1}$ with no vector. Similarly, $\varepsilon$ increased by 153%, in presence of the vector. Furthermore, the bubble size distribution was determined and are presented on Figure 4. In both experiments, the bubble geometric diameters were normally distributed and not significantly different from each other ($p>0.05$), according to the Kolmogorov-Smirnov and the Tukey-Kramer tests, respectively. Therefore, under the experimental conditions tested in this work, Kraton had no significant effect on bubble size, which contradict what previously observed by Quijano *et al*. (2010b) and by Littlejohns and Daugulis (2007) with solid vectors in mechanically stirred tank reactor.

Overall, these results allow to unravel the main components of the gas transfer. First, from the measured bubble geometric diameters, the $d_{32}$ was determined, and no significant difference was found between control and Kraton experiments (Table 2). Next, combined with $\varepsilon$, the $d_{32}$ allowed to estimate the specific air/liquid area ($a$), according to Eq. 4, which on its turn, allowed to determine the liquid film coefficient ($K_L$), from the $K_La$ data.

Table 2 Mean characteristics of the air/water dispersion observed during control experiment and in presence of 10% Kraton, at an aeration rate of 0.5 vvm. Mean values ± one standard deviation of the mean are presented. Values in bold italic indicate significance difference between Control and Kraton (p<0.05).

| | Control | Kraton |
|---|---|---|
| Bubbles geometric mean diameter (d, mm) | 1.07 ± 0.24 | 1.21 ± 0.35 |
| Bubbles surface mean diameter ($d_S$, mm) | 1.10 ± 0.24 | 1.26 ± 0.37 |
| Bubbles volume mean diameter ($d_V$, mm) | 1.12 ± 0.25 | 1.31 ± 0.41 |
| Bubbles Sauter mean diameter ($d_{32}$, mm) | 1.17 ± 0.92 | 1.41 ± 1.59 |
| Gas holdup ($\varepsilon_g$, -) | 0.015 ± 0.003 | 0.038 ± 0.002 |
| $K_La$ ($h^{-1}$) | 54.0 ± 3.6 | 113.9 ± 6.4 |
| a ($m^{-1}$) | 76.9 | 161.7 |
| $K_L$ ($m \cdot h^{-1}$) | 0.702 | 0.704 |

$$a = \varepsilon \cdot \frac{6}{d_{32}} \quad (4)$$

The results showed that a was 76.9 and 161.7 $m^{-1}$, for the control and 10% Kraton experiments, respectively, which results in equal $K_L$ data of 0.70 for both experiments. Thus, under the experimental conditions tested, the increase of oxygen transfer was explained, only, by an increase of the gas holdup and subsequent increase of the gas/liquid surface area, not by the establishment of a high-performance gas/vector/water pathway. Observations from high speed digital images showed that in presence of Kraton, the air bubbles were temporarily slowed down or even stopped by collision with vector particles, which suggest an increased bubbles residence time. The average bubble residence time in the bubble column ($\theta_B$) was determined, from $\varepsilon$, the bulk volume of the reactor ($V_R$) and the aeration flowrate ($Q_g$) according to Eq. 5;

$$\theta_B = \frac{\varepsilon \cdot V_R}{Q_g} \quad (5)$$

Next, by dividing the height of the bulk liquid phase by the residence time, the mean bubble rising speed ($U_B$) in the reactor was obtained, for all aeration rates tested with 10% Kraton, and the results obtained are presented in Figure 5. Overall, the mean $U_B$ in the control reactor with no vector was 23.7 ± 9.9 cm $s^{-1}$, while in the reactor operated with 10% Kraton it was 9.3 ± 2.3 cm $s^{-1}$, thus confirming that 10% Kraton reduced the bubble rising speed by over 60%. It is worth noting that, from the mean bubble diameters, a theoretical free rising bubble speed, was also determined using the model developed by Park *et al*. (2017). This model gave a good prediction

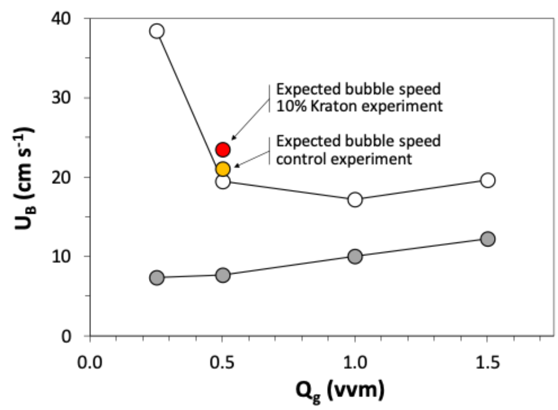


Fig. 5. Mean bubble rising speed determined from gas mass balance during control experiment with no Kraton (o) and in presence of 10% Kraton (●). Red and orange circles indicate theoretical bubble rising speed, as estimated from mean bubble diameter determined during 10% Kraton and control experiment, respectively (Park *et al*., 2017).

of the bubble speed in the control reactor, which allowed a closer estimation of the impact of Kraton on the bubble speed. Indeed, from the bubble diameter determined with 10% Kraton, a theoretical free rising speed of 23.5 cm $s^{-1}$ would have been observed, while the determined $U_B$ in the reactor was 7.68 cm $s^{-1}$: i.e. 3.1 time slower. These results indicate that the observed oxygen transfer enhancement in presence of Kraton, was caused by the collision of the rising bubbles with the polymer particles. This is not a new finding, since the multiples effects of solid particles on mass transfer has been previously reviewed by Mühlbauer *et al*. (2019) and, in particular, have shown that solid particles have a decreasing effect on bubble rising speed, as observed in the present work. To the best of our knowledge, this is the first time that this phenomenon is explicitely shown in a multiphasic reactor. A potential additional outcome is that any spherical particles of similar density and dimensions, might have similar effects, thus opening the way to the development of lower cost oxygen transfer enhancers.

## Conclusions

Solid vector particles can be an inexpensive and efficient way to improve oxygen transfer in bubble columns but only under precisely selected operational conditions. Kraton, was the polymer vector more easily dispersible in the air/water bulk phase of the bubble column. Also, Kraton, used at a proportion of 10% and with an aeration flowrate of 0.5 vvm, allowed to improve the oxygen transfer by 90-100%, compared to a control with no vector. It was shown that this positive impact was caused by collisions between bubbles and vector particles, which resulted in lower bubble rising velocity and higher gas holdup, without any amendment on the gas/liquid film. To the best of our knowledge, this mechanistical explanation has been previously documented in chemical reactor but never demonstrated in such a clear manner for two-phase partitioning bioreactors. Since Kraton is also thermally resistant during a sterilization process, its use in axenic culture might be foreseen. From these results, it is concluded that Kraton has a large potential as mass transfer promoter with a limited investment. According to a vector cost estimated to 4.5 US$ $L^{-1}$, the addition of 10% Kraton would represent an investment of 450 US$ per $m^3$ of bioreactor. This solid vector may certainly be recycled in most of the processes, even those requiring sterilization and may therefore be used on a long-term basis. More importantly, owing to its relatively low density, Kraton allows a significant increase of oxygen transfer with no increase of power input in bubble columns, being then a potential cost-effective enhancement strategy.

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