COLOUR REMOVAL FROM AQUEOUS SOLUTIONS. 
PART I. FLOTATION

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ABSTRACT

The removal of colours from aqueous solutions and/or dispersions has been studied by dispersed-air flotation, in a semi-batch flotation column. Three colours were used for the experiments: Basic Yellow 28 (acidic), Direct Black 22 (basic) and Disperse Orange 30 (dispersion colour). All three were effectively removed by flotation within 15 to 30 min. Sodium lauryl sulfate and dodecylamine were found to be effective as collectors in the removal of colour, which was also found to be related to the pH of the solution and the amount of collector added to it, with high collector dosages causing the process to become pH-independent.

Keywords: Flotation, flotation column, colour flotation, dodecylamine, sodium lauryl sulfate

INTRODUCTION

Water, by itself, is colourless and clear. Therefore any colouring matter existing in it is obviously allochthonous. Some colouring comes from humic substances carried in natural waters, but usually water becomes coloured after being used in textile-colouring, printing, leather-treating, dye-producing or various other plants, becoming loaded with various dyes, as well as other materials.

Most dyes and pigments are considered either inert or non-toxic, although some are not totally innocuous (1). Their toxicity, as constituents of plant effluents, is not well defined (2). The effluent toxicity, in fact, may be due to constituents other than dyes, e.g. chlorides (3). However, some of these dyes may be bioaccumulated and their long-term effects on animal and human health are not yet known, especially since newer types of dyes are less biodegradable than their predecessors (4). Hence, their presence in wastewater is unwarranted, not only for aesthetic reasons. It is therefore desirable to remove as much of the colouring material from effluents, before these are discharged. This becomes important, too, in regions where water resources might be scarce or sensitive, leading to a necessity of domestic and semi-industrial, urban wastewater clarification for eventual reuse.

The common biological treatment processes are often ineffective in removing colour from effluents, although they are capable of reducing much of BOD and suspended solids (5). Various techniques are available for the treatment of aqueous streams, in order to eliminate dyes: coagulation followed by sedimentation, and adsorption are the widely used ones, but other techniques are often applied, e.g. UV photodecomposition (6) and ultrafiltration, among others. However, colour flocs are often of very low density and hence their settling velocity is very low, making the sedimentation process rather ineffective.

Flotation is being used as an alternative to sedimentation; it is able to remove almost totally the flocs and is also capable of lowering turbidity, too, especially if provision is made for fine bubbles, as e.g. in dissolved-air flotation. Other methods for generating gas bubbles are: electrolysis and the in situ generation of O2 by H2O2 decomposition, which has been applied to the treatment of textile wastewaters (7).

In this work, the removal of colours from solutions and dispersions by dispersed-air
Flotation in a flotation column was investigated. The selection of this technique was dictated by the need to determine an efficient process for wastewater treatment, capable of removing other constituents, which would also require the smallest possible floor space, so that it may be accommodated in plants located in densely-populated urban or suburban areas. Three particular dyes were chosen for the experiments (Figure 1):
- the first one, Basic Yellow 28 (BY; C.I. 48054) is a reddish-yellow dye, used for direct dyeing of silk and synthetic textiles;
- the second one, Direct Black 22 (DB; C.I. 35435) is a greenish black dye, used for silk and other textiles dyeing; and
- the third one, Disperse Orange 30 (DO; C.I. 11119) is a reddish-orange dye used for acetic, triacetic or polyester textile dyeing.
All of them display a light fastness and their presence in the effluents either of dye-manufacturing or dye-consuming plants is highly undesirable.

**Basic Yellow 28 (C.I. 45048)**

![Basic Yellow 28](image)

**Direct Black 22 (C.I. 35435)**

![Direct Black 22](image)

**Disperse Orange 30 (C.I. 11119)**

![Disperse Orange 30](image)

**Figure 1.** Colours removed from solution by flotation (this work).
processing; otherwise, the lack of a stabilized froth results into a re-entry of the solute into solution.

These processes have been applied to several dyes. Shah and Lemlich (6) worked with a column, bubbling gas (N₂) through a solution of colour (Crystal Violet). Strictly speaking, this was not flotation, since the only thing that was achieved was a preliminary separation, with a concentration gradient being established along the column: a decrease down to 40% (w/w) of its original concentration was observed at the bottom of the column, whereas an increase up to 80% (w/w) of the initial concentration was found at the top of the column. Therefore, what was obtained was rather a kind of separation due to the limited self-hydrophobicity of the dye in question, but not a proper removal of the dye into an overlying froth, as would be expected in actual flotation. However, it was noticed that by increasing the column height the separation was enhanced; on the other hand, the increase in column diameter had an adverse effect; this was probably due to the intense internal circulation that is established inside columns (9). Several other species, related to dyes and colours, have also been treated by flotation or solvent sublation, e.g. lye (10), Kraft liquor (11,12), lignin and others. Table 1 presents a selective list of references related to the flotation and/or solvent sublation of dyes.

Interestingly, although flotation is not a new process, nor its use in colour removal recent, there is no mention about it in a recent review of techniques for dye wastewater treatment (1). It seems that more work is required before flotation may become an “accepted” alternative to sedimentation or adsorption.

**EXPERIMENTAL APPARATUS AND PROCEDURE**

Flotation experiments were performed in a laboratory-scale column, having an inside diameter of 4.0 cm and a height of over 50.0 cm (Figure 2). A cylindrical ceramic porous gas

<table>
<thead>
<tr>
<th>Colour/Dye</th>
<th>Coll. ¹</th>
<th>Gas</th>
<th>d₀ (cm)</th>
<th>h₀ (cm)</th>
<th>Process</th>
<th>Ref.</th>
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<td>Blue Direct 1</td>
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<td>60/90</td>
<td>F,S²</td>
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<td>F</td>
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¹ NaLS: sodium lauryl sulfate, BHDAC: benzyl hexadecyl dimethyl ammonium chloride, 2D2MABr: 2-dodecyl 2-methyl ammonium bromide, NaTDS: sodium tetradecyl sulfate, D: dodecyl hydrogen sulfate
Na salt; H: Hyamine 1622; N: nonyl phenol polyethylene glycol ether, HTABr: hexadecyl trimethyl ammonium bromide
² F: flotation; S: solvent sublation,
³ H₂O₂ generated
diffuser (with a range of pore diameters from 16 to 40 μm) was used as a gas sparger; the gas flowrate was monitored and controlled with a calibrated rotameter and the gas holdup - i.e. the volumetric percentage of gas retained in the gas-liquid dispersion - was for all experiments approximately 1% (v/v).

A small tube, located at the side of the column and just above the gas sparger, was used for withdrawing liquid samples with a syringe; its dead space was kept at a minimum, so as to avoid any sample contamination from the previous sample.

Sodium lauryl sulfate (NaLS; Merck approx. 90% grade), hexadecylamine (Fluka, pract. grade), dodecylamine (Merck, 98% synthesis grade), octylamine (Fluka, purissim. grade) and sodium oleate (NaOL; Riedel de Haan 90% grade) were used as collectors.

Stock solutions with 1000 ppm of colour were prepared daily and from these a batch of approximately 650 ml, with an initial colour concentration of 50 ppm, was used for each experiment. After the appropriate reagents were added to the colour solution, it was conditioned by agitation (200 rpm) for 15 min. Since amines were insoluble in water, they were added as ethanolic (EtOH) solutions, resulting in an effective EtOH concentration of the colour solution of 0.1% (v/v).

The flotation experiment was then initiated by opening first the air-regulating valve, which was previously set to the desired gas flow rate and then by pouring the dye solution into the column; the gas-liquid dispersion height was kept at 50.0 cm, thus maintaining the aspect ratio (i.e., the height-to-diameter ratio) to a value close to the 10:1 usually encountered in bubble and flotation columns.

During each experiment, small samples were withdrawn from the side sampler at various times; the samples were analyzed using a Hitachi U-2000 spectrophotometer to determine the amount of dye remaining in solution at the following λ_{max} for each colour: 440 nm (BY), 480 nm (DB) and 458 nm (DO). The removal of colour from solution (R%) was determined by its concentration at time t (C_{t}) and the initial one (C_{init}):

\[ R% = \frac{C_{t} - C_{init}}{C_{init}} \times 100 \]  

RESULTS AND DISCUSSION

Initial measurements of the optical absorbance of the dye at various pH values (Figure 3) showed that all colours remain practically stable over a wide pH range; an effective method of removing them over a wide pH range is therefore required.

Preliminary experiments indicated also that all three colours were not hydrophobic enough for collectorless flotation, yielding only less than 8% (w/w) removals.

Basic Yellow 28

All experiments were performed with solutions containing 50 ppm of Basic Yellow 28, corresponding to an initial concentration of 1.45x10^{-4} M.

Two collectors were used for the flotation of BY: sodium oleate (NaOL) for alkaline pH values and sodium lauryl sulfate (NaLS) for slightly acidic ones; these are anionic collectors widely used in the beneficiation of positively-charged mineral particles. Both reached the maximum of colour removal within 30 min (Figure 4).

The results obtained with NaLS indicate that the maximum removal is related to the amount of collector added to the solution; above a dosage of 20-30 ppm - which corresponds roughly to a collector:colour molar ratio of 0.5-0.6 (Figure 5) - all the colour is removed from solution. It also
seems (see Figure 4) that the removal of BY by NaLS is a first-order kinetic process. The exact mechanism responsible for the removal of BY is not known, hence a scheme for the apparent process is postulated.

Inside the flotation column used in these experiments, the liquid may be considered as well mixed (9); the gas, having a short residence time inside the dispersion (i.e., the time it remains inside the gas-liquid dispersion) of approximately 4 s (see Appendix 1), may be considered as flowing in plug-flow fashion. Hence, the colour removal may be compared to a first-order mass transfer process from a well-mixed liquid to a plug-flow gas. If \( V_L \) is the liquid volume and \( BY_{Lb} \) is the liquid-phase concentration of the colour, then the rate of colour depletion of the solution:

\[
N_{BY} = V_L \frac{dBY_{Lb}}{dt}
\]  

will be equal to the rate of colour "mass" transfer from the bulk of the solution to the liquid-gas interface:

\[
N_{BY} = k_L a (BY_{Lb} - BY_{Li})
\]  

(3) \( k_\text{L} \) is the liquid-side mass transfer coefficient, \( a \) is the total bubble surface available and the indices "b" and "i" refer to the (liquid) bulk and interface concentrations, respectively; this will also be equal to the rate of colour removal by the gas stream:

\[
N_{BY} = Q_G (BY_{Gout} - BY_{Gin})
\]  

(4) where \( BY_G \) refers to the gas-phase BY concentration, and the indices "out" and "in" refer to the outgoing and incoming gas-phase BY concentrations (it is assumed that the "bulk" gas-phase colour concentration is equal to the interfacial one, i.e., no gas-side mass transfer resistance exists).

In fact, the incoming gas stream BY concentration is nil, hence: \( BY_{Gin} = 0 \). On the other hand, if the gas-phase BY exit concentration \( (BY_{Gout}) \) is considered as being in equilibrium with the liquid-phase interfacial one \( (BY_{Li}) \), then the two concentrations may be related by Henry's constant \( (H)\):

\[
BY_{Gout} = H BY_{Li}
\]

(5) Therefore, the rate of BY removal may be written as:

\[
V_L \frac{dBY_{Lb}}{dt} = k_L a (BY_{Lb} - BY_{Li}) = Q_G BY_{Gout}
\]

\[
= \frac{1}{k_L a} + \frac{1}{H Q_G}
\]

(6) which may be written in a simpler form:

\[
\frac{dBY_{Lb}}{dt} = k BY_{Lb}
\]

(7) where:

\[
k = \frac{1}{V_L} \left( \frac{1}{k_L a} + \frac{1}{H Q_G} \right)
\]

(8) with \( k \) being the apparent mass-transfer coefficient.
Figure 4. Colour (Basic Yellow 28) removal by flotation as a function of collector concentration (ppm). (Top) Collector: sodium lauryl sulfate (NaLS); pH 5-6. (Bottom) Collector: sodium oleate (NaO1); pH 9.0. Initial colour concentration: 50 ppm (1.45x10^{-4} M); gas flowrate 96 cm³ min⁻¹. Points: experimental results; solid lines: model fitting (Eq. 13).

Equation 7 - which is similar to the one obtained by Wilson (22), but incorporates explicitly the mass transfer coefficient - describes the rate of disappearance of the colour from solution due to its removal into the gas stream. It may be integrated to yield the usual exponential decay:

\[ \text{BY} = \text{BY}_0 e^{-kt} \]  

(9)

with BY being the amount of aggregates left in solution after time t from the initiation of the gas flow.

In fact, what is removed from solution is not the colour itself, but the hydrophobic colour-collector aggregates. During conditioning time, BY comes into contact with the collector (C) and forms hydrophobic aggregates (BY-C) according to the following scheme:

\[ n\text{BY} + \text{C} \rightarrow \text{BY}_n\text{C} \]  

(10)

although the exact nature of the aggregate is not known, since it may involve water molecules as well, corresponding to a \( \text{BY}_n\text{C}_y(\text{H}_2\text{O})_z \) type. The value of the stoichiometry coefficient (n) seems from Figure 5 (top) to be about 1.7 to 2. The amount of BY-C being formed is limited by the
concentration of collector available, hence the restrictive role of the latter on the overall colour removal. Equation 9 may now be rewritten for the colour-collector aggregates:

$$BY - C = BY - C_0 e^{kt} \quad (11)$$

with $BY - C_0$ the initial aggregate concentration. If the initial colour ($BY$) concentration ($BY_0$) was only partially used to form the hydrophobic aggregates, then at time $t$:

$$BY = BY_{res} + BY - C = BY_{res} + BY - C_0 e^{kt} \quad (12)$$

where $BY_{res}$ is the amount of colour that will be left in solution after all the aggregates have been removed by flotation. Equation 1 may be written now (omitting the coefficient "100"):

$$R = 1 - \frac{C_t}{C_{init}} = 1 - \frac{BY}{BY_0} = 1 - \frac{BY_{res} + BY - C_0 e^{kt}}{BY_0} = \frac{BY_0}{BY_0} (1 - e^{kt}) = R_{max} (1 - e^{kt}) \quad (13)$$

Equation 13 predicts (and the results in Figure 4 confirm) that the removal of $BY$ will follow an inverse exponential form, and will
approach a maximum removal value $R_{\text{max}}$, which is be related to the amount of collector added to the colour solution before conditioning.

The experimental data were used to estimate $R_{\text{max}}$ by averaging the data of the horizontal section of each curve and the values of $k$ were obtained by least-squares fitting (Figure 5). The change in the values of $R_{\text{max}}$ follows a clear trend: as the amount of collector increases, so does the number of hydrophobic aggregates being formed, and since these are effectively removed by the gas bubbles, the process depends only upon the amount of BY aggregated with the available collector.

The change noticed in the values of the kinetic constant ($k$) is less easily explained. Here again, a trend may be seen: $k$ decreases as the collector dosage - hence the number of aggregates - increase, and this change is reversed when the amount of collector added exceeds that corresponding roughly to $R_{\text{max}}$. From Eq. 8, $k$ is seen to be a composite of parameters related to the chemical species (e.g. H) as well as operational ones (e.g. $V_L$, $Q_G$, $k_L$, etc.). Now, since $V_L$ and $Q_G$ have been kept throughout all these experiments constant, this change in $k$ must be attributed to H, a or $k_L$. Although the elucidation of the exact mechanism of this process is outside the scope of the present work, the following hypothesis may be postulated:

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**Figure 6.** Colour (Direct Black 22) removal by flotation with various amines as collector (16A: hexadecylamine; 12A: dodecylamine; 8A: octylamine). Collector concentration: (top) 4 ppm; (bottom) 8 ppm. Initial colour concentration: 50 ppm. Gas flow rate 56 cm$^3$ min$^{-1}$. 

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a) while the amount of collector added to the colour solution is less than that required for the aggregation of the totality of BY, a competition for collector causes the formation of intermediate aggregates, somehow deficient but still hydrophobic enough to be removed by the gas bubbles; whereas

b) when more collector is added to solution than the amount required by stoichiometry, then the mass transfer process is responsible for the migration from the liquid to the gas-liquid interface not only of the BY-collector aggregates but also of the residual collector as well, affecting the values of $H$, $a$ or $k_L$.

Results obtained with sodium oleate at alkaline conditions yield similar conclusions (Figures 4 and 5); in this case, it seems that a larger dosage of NaO1 than that tested is required for a complete removal of BY from solution; hence, the values of $k$ (Figure 5) are seen to be only decreasing, as was the case for NaLS in the collector-deficient region.

It seems, therefore, that sodium lauryl sulfate is more suitable for the treatment of this positively-charge colour.

**Direct Black 22**

All experiments were done with an initial Direct Black 22 concentration of 50 ppm, corresponding to $4.62 \times 10^{-5}$ M.

The optical stability of DB (Figure 3) is approximately constant over the pH range studied. However, a change occurred, with its hue becoming more “blue” than “brown” when the value of pH increased beyond 8.

Preliminary tests were performed with three amines (octylamine, dodecylamine and hexadecylamine), since the colour is initially negatively charged. The results at pH 4 (Figure 6; top) showed a substantial removal of DB within 10 to 15 minutes for the first two collectors. The performance of the longer-chain collector, hexadecylamine, improved as the collector concentration increased (8 ppm; Figure 6, bottom), reaching removals of over 80% (w/w), but after considerable time. Since dodecylamine seemed to remove DB more effectively than the other two amines, it was used in all further investigations with DB.

Experiments were performed for pH ranging from 4 to 8 and for collector concentrations ranging from 2 to 16 ppm, with a constant gas flow rate ($Q_g = 56$ cm$^3$ min$^{-1}$). At these conditions, maximum removals were reached within 15 to 30 minutes. Figure 7 shows some of the results, for pH 4 and 6: both pH and the collector dosage seem to affect the process. This is better illustrated in Figure 8, where $R_{max}$ is plotted against pH for the various dodecylamine concentrations.

Since pH influences the process only while the concentration of dodecylamine is below some

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**Figure 7.** Colour (Direct Black 22) removal by flotation with dodecylamine. pH 4. Initial colour concentration: 50 ppm. Gas flow rate $56$ cm$^3$ min$^{-1}$.  

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critical dosage, it may be inferred that DB "reacts" with some dodecylamine species, the amount of which depends both upon its concentration and the pH of the solution. Thus, while the dodecylamine dosage is below some critical level - corresponding in this case to 8 ppm, i.e. to a collector:colour molar ratio of approximately 0.9-1.0 - the amount of dodecylamine available to form the hydrophobic DB-dodecylamine aggregates is not sufficient for the removal of all DB. Above that critical dosage, the amount of dodecylamine available becomes sufficient, and this is true for all pH values.

The DB removals (Figure 7) indicated that Eq. 13 could again describe the process, hence $R_{\text{max}}$ and k values were determined for each experiment and these are plotted against the collector:colour molar ratio (Figure 9). The

Figure 7. Colour (Direct Black 22) removal by flotation with dodecylamine. pH 6. Initial colour concentration: 50 ppm. Gas flowrate 56 cm$^3$ min$^{-1}$.

Figure 8. Effect of pH on colour (Direct Black) removal by flotation. Initial colour concentration: 50 ppm. Gas flowrate 56 cm$^3$ min$^{-1}$.
results in this figure corroborate the hypothesis formulated above: above a critical dosage (approximately 1:1, on a molar basis), a terminal value in both $R_{\text{max}}$ and $k$ is reached. This may infer that the hydrophobic aggregates are formed by a 1:1 "reaction" of the following type:

$$\text{DB} + \text{RNH}_2 \rightarrow \text{DB-RNH}_2$$

The fact that a single hydrophobic species is involved may also be deduced from the fact that the value of $k$ is practically the same for all pH > 4, irrespective of the collector dosage.

The same trends were also observed with the other two amines tested (Figure 10): octylamine displayed an almost constant value of $k$, whereas in the case of hexadecylamine, the collector dosage was below the critical value (as expected from Figure 6).

Concluding, it was found that Direct Black 22 is also a colour that may be removed from solution by flotation; amines are effective for this purpose, with dodecylamine being the best of the three amines tested.
Disperse Orange 30

All experiments were done with an initial Disperse Orange 30 concentration of 50 ppm, corresponding to $1.11 \times 10^{-4}$ M. The optical stability of DO (Figure 3) was again found to be practically constant over the pH range studied.

Dodecylamine was again used as collector, with its concentration ranging from 4 to 16 ppm and for pH values from 4.0 to 10.0. The effect of collector concentration on the rate of removal depended on the value of pH, as well: at the lowest pH (4.0; Figure 11, top), the lowest dodecylamine concentration yielded poor results, but once this was raised to 8 ppm, removals improved, without any further collector concentration increase having any additional effect on colour removal. However, as the value of pH increased, a slightly different behaviour was noticed, with removals reaching a plateau for collector concentrations up to 8 ppm; when the latter increased further, no plateau was observed, and the removal for all higher concentrations followed approximately the same slow first-order kinetic scheme.

At the highest pH tested (10.0; Figure 11, bottom), a change was noticed, with each of the removal curves becoming distinct, corresponding to a particular kinetic constant, $k$. This may also be seen in the plot of the maximum removals and kinetic constants against the collector:colour concentration ratio (Figure 12); this plot shows that a much higher collector dosage than for the previous colours is necessary for the case of Disperse Orange. It also reveals a change occurring between pH 5 and pH 6: for pH ≤ 5, both $k$ and $R_{\text{max}}$ reach a kind of plateau for a ratio between 4 and 6 and then continue their respective change; for 7 ≤ pH ≤ 8, a different behaviour is noticed, with $R_{\text{max}}$ approaching a terminal value exponentially, whereas the values of $k$ decrease linearly until some steady value is reached; and finally for pH = 10, a completely different pattern for both $k$ and $R_{\text{max}}$ is seen, with $R_{\text{max}}$ steadily increasing while $k$ is steadily decreasing, indicating that at such high pH values a much higher collector (dodecylamine) dosage is necessary for the removal of Disperse Orange from solution. It is probable that these changes correspond to changes in the relative amounts of active and inactive dodecylamine species, brought by the change in the value of pH and the collector dosage, since for pH > 10 it is reported that neutral amine precipitates (23), therefore increasing amounts of collector would be required, so that enough of the active amine species is present in solution to form the necessary hydrophobic aggregates.
CONCLUSIONS

The presence of colours in wastewaters is not only aesthetically undesirable, but may also adversely affect secondary uses and/or wastewater treatment processes. It is therefore necessary to develop techniques for their removal from solutions. Three particular colours, a basic one (Basic Yellow 28), an acidic one (Direct Black 22) and a dispersion colour (Disperse Orange 30) have been used to investigate the effectiveness of dispersed-air flotation as such a process.

Various collectors were used to render the colours hydrophobic; sodium lauryl sulfate and sodium oleate were found to be effective, in the case of the acidic colour, with the former yielding faster colour removals. Dodecylamine was used for the flotation of both the dispersion and the basic colour. In all cases, the process of hydrophobic aggregate removal followed a first-order kinetic scheme.

The solution pH was also found to affect the colour removal, by altering the amount of active collector species available for the formation of the hydrophobic aggregates; however, this effect was related to the collector concentration, with high collector dosages rendering the process
practically pH-independent.

Finally, dispersed-air flotation - a process already proven capable of removing various effluent constituents, such as toxic metal ions - was found to be an effective process for the removal of colouring matter from aqueous solutions. The use of flotation columns, as in the present work, but operating in continuous mode, will provide the length of time of the order of 15 to 20 min necessary for the removal of the hydrophobic aggregates.

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NOTATION

\( a: \) gas-liquid interfacial (total bubble surface) area (cm\(^2\))

\( b: \) bulk

\( BY: \) Basic Yellow 28 concentration (mol cm\(^{-3}\))

\( BY-C: \) Basic Yellow 28-collector aggregate concentration (mol cm\(^{-3}\))

\( C: \) concentration (mol cm\(^{-3}\))

\( H: \) Henry's constant (-)

\( k: \) mass transfer coefficient (cm s\(^{-1}\))

\( k: \) composite or apparent mass transfer coefficient (min\(^{-1}\))

\( L: \) liquid

\( N: \) mass transfer rate (mol s\(^{-1}\))

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\( V: \) volume (cm\(^3\))

\( t: \) time (s, min)

\( \) condition at time \( t = 0 \)

\( i: \) interfacial

\( \) condition at time \( t \)

\( \) incoming

\( \) initial

\( \) outgoing

\( \) residual

REFERENCES


**APPENDIX 1**

*Estimation of the mean gas residence time.*

The mean residence time (τ) of a fluid (gas, liquid) flowing through any vessel may be estimated by the following equation (20):

$$\tau = \frac{V}{Q}$$

(A1)

where V is the volume of the vessel available to the flow and Q the volumetric flowrate of the incoming stream. In the case of the gas flowing through the present flotation column, the volume of the gas in the gas-liquid dispersion is given by:

$$V_G = \varepsilon_G V_{\text{disp}}$$

(A2)

where $V_{\text{disp}}$ is the volume of the dispersion and $\varepsilon_G$ is the gas holdup. For a column having an i.d. of 4.0 cm, a volumetric flowrate of the gas ($Q_G$) of 96 cm$^3$ min$^{-1}$ (as in the case of Basic Yellow flotation), a total dispersion height of 50.0 cm ($V_{\text{disp}} = 628.3$ cm$^3$) and for $\varepsilon_G = 1\%$ (as stated above):

$$\tau = \frac{\varepsilon_G V_{\text{disp}}}{Q_G} = \frac{0.01 \times 628.3}{96} = 0.065 \text{ min} \approx 3.9 \text{ s}$$

For lower gas flowrates, the mean residence time (τ) of the bubbles increases.

Alternatively, the mean velocity of the rising bubbles may be estimated, using the implicit equation of Fair *et al.* (21):

$$u_b = \frac{2gpr_b^2}{9\eta} \left[1 + \frac{0.34p_{\text{gas}} u_b}{12\eta} + \frac{1}{4} \sqrt{\frac{pr_b u_b}{2\eta}}\right]$$

(A3)

where $r_b$ and $u_b$ are the bubble radius (cm) and velocity (cm s$^{-1}$), respectively, $\rho$ is the medium (e.g. water) density (g cm$^{-3}$) and $\eta$ is the medium viscosity (Poise). For bubbles having a diameter of 1 mm (which is typical of these experiments) flowing in a water column ($\rho = 1$ g cm$^{-3}$, $\eta = 0.01$ Poise), the bubble rise velocity calculated using Eq. A3 is: $u_b = 12.9$ cm s$^{-1}$, which for the given column height results in an estimated residence time of 3.9 s, again.