Effects of impurities on oxygen transfer rate in the electroflotation process

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In this work, three different types of impurities: soybean oil, surfactant and diatomaceous earth were doped to simulate the impurities in wastewaters issued from edible oil refinery plant. The effects of the impurities on the oxygen transfer rate were investigated in an electroflotation cell. The volumetric mass transfer coefficient was studied for a batch mode involving different values of the current density for different impurities concentrations. The capacity of oxygenation and the corrective alpha factor were also studied. Models which relate the volumetric mass transfer coefficient to the current density and the concentration of the impurities were established. The results showed that the presence of impurities significantly reduce the volumetric mass transfer coefficient $K_{L,a}$.

Keywords: Electroflotation, Transfer of oxygen, Soyabean oil, Surfactant

Oxygen transfer or aeration is the most important and indispensable operation unit for the treatment of wastewater. Several techniques were developed to improve the efficiency of this process and to minimize the energy cost. The electroflotation is one of the recent processes used for the separation of the suspended matter and the aeration of the liquid solution during the treatment.

Electroflotation is one of the electrochemical processes which was proposed by Kuhn in 1974 for solid-liquid physical separation system. It is a simple process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. The electrochemical reactions at the cathode and anode are respectively hydrogen evolution and oxygen evolution reactions. The chemical reactions taking place at the cathode and the anode are given as follows:

Anodic oxidation:

$$2H_2O \rightarrow O_2^- + 4H^+ + 4e^- \quad \ldots (1)$$

Cathodic reduction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad \ldots (2)$$

The performance of an electroflotation system is reflected by the pollutant removal efficiency and the power and/or chemical consumptions. The pollutant removal efficiency is largely dependent on the size of the bubbles formed. For the power consumption, it relates to the cell design, electrode materials as well as the operating conditions such as current density, water conductivity, etc.

Electroflotation technique has three principal advantages. First, dispersed gas bubbles formed from electrolysis are extremely fine and uniform, (with average bubble diameter around 20 $\mu$m). Second, varying current density gives the possibility of varying any gas bubble concentration in the flotation medium. Third, selection of appropriate electrode surface and solution conditions permits to obtain optimum results for a specified separation process.

Electroflotation techniques are highly versatile and competitive with settling tank techniques that require much land. Indeed, this process is also more competitive than other flotation techniques such as dissolved air flotation and dispersed air flotation.

The objective of the present study is to evaluate the performance of aeration in wastewater by electroflotation process. In fact, the effect of some impurities on the oxygen transfer coefficient in an electroflotation cell has been investigated and the results are reported.

Theory

To determine the volumetric mass transfer coefficient, $K_{L,a}$, several techniques have been proposed. Most measurements in aeration systems may be divided into two groups: physical and chemical methods. Among physical methods, the
well-known method is the desorption of an oxygen saturated solution with nitrogen \textsuperscript{13,14}.

Many chemical methods such as oxidation of glucose \textsuperscript{15}, stannous chloride \textsuperscript{16}, and ethanol \textsuperscript{17} have been proposed. In the present work, the sulphite oxidation method which is the most widespread technique for determining the volumetric oxygen transfer coefficient and the interfacial area per unit of volume \textsuperscript{18,19} has been reported.

For clean tap water the double Film Theory of Lewis and Whitman is considered \textsuperscript{20}. For gases of low solubility, such as oxygen in water, Lewis and Whitman assumed that the gas side resistance is negligible and that the gas transfer may be determined from considering the liquid side resistance only:

$$\frac{dC}{dt} = K_L a (C^* - C) \quad \cdots (3)$$

where \(\frac{dC}{dt}\) is the rate of change of concentration with time.

Equation (4) can be readily integrated to yield the following expression for \(C\) as a function of time:

$$C = C^* - \left(C^* - C_0\right) \exp\left(-K_L a t\right) \quad \cdots (5)$$

where \(C_0\) is the initial dissolved oxygen concentration at \(t = 0\). A nonlinear regression analysis based on the Gauss–Newton method is recommended by ASCE (American Society of Civil Engineers) to fit Eq. (5) to the experimental data using \(K_L a\), \(C^*\) and \(C_0\) as three adjustable model parameters\textsuperscript{21}.

The volumetric mass transfer coefficient must be corrected to a standard reference temperature of 20°C by using the Arrhenius relationship:

$$K_{L,a}(20°C) = K_{L,a}(T) \theta^{(20-T)} \quad \cdots (6)$$

A generally accepted value of the temperature correction factor, \(\theta\) is 1.024\textsuperscript{22}.

The alpha factor (\(\alpha\)) is the ratio of the volumetric mass transfer coefficient in waste water to that in clean tap water, it is expressed as\textsuperscript{23}:

$$\alpha = \frac{K_{L,a}(\text{waste water})}{K_{L,a}(\text{tap water})} \quad \cdots (7)$$

The capacity of oxygenation (CO) presents the mass of oxygen that can be transferred by the aeration system per m\(^2\) and per hour to hopeless dissolved oxygen concentration water.

$$CO = K_L a \left(C^* - C_0\right) \quad \cdots (8)$$

**Experimental Procedure**

The electroflotation cell (Fig. 1) was used in the present study for batch mode. It was a rectangular column fabricated out of plexiglas material. Its length was 5.8 cm, width 6.7 cm and height 71.5 cm. It was provided with two electrodes: titanium coated with ruthenium oxide anode and a stainless steel cathode. These two electrodes are connected to a DC current generator which enables the variation of current density. The gap between anode and cathode was maintained at 5 mm to minimize the ohmic loss. The cathode compared to the anode was perforated and occupied the top position. This perforation allows the evacuation of bubbles produced at the anode.

**Determination of volumetric mass transfer coefficient**

The volumetric mass transfer coefficient, \(K_{L,a}\), was measured using the unsteady state method with an oxygen probe (DO meter WTW DurOx 325) placed mid-way in the electroflotation cell. The oxygen concentration was reduced to zero by adding 150 g/m\(^3\) of sodium sulphite (\(\text{Na}_2\text{SO}_3\)) and 2 g/m\(^3\) of cobalt ions.

$$2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4$$

**Preparation of solution**

In this study, commercial soybean oil (SO) from refining plant SORAHUILE (Tunisia), surfactant: Benzyl dimethyl hexa decylammonium chloride (BDHACl) from Fluka products of pure quality

![Fig. 1 — Schematic diagram of the experimental set-up.](image)
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(>97%) and diatomaceous earth (DE) from Oil-DRI (USA) were doped to simulate the impurities in wastewaters. For each test run, the cobalt chloride and the impurity were simultaneously added to the liquid phase and agitated to allow uniform distribution. Then, sodium sulphite was added to remove dissolved oxygen. An agitation is recommended in order to activate the deoxygenating reaction; the stirring velocity must be relatively low to avoid the vortex which can reoxygenate water.

The characteristics of clean tap water and the summary of the experimental conditions are given in Tables 1 and 2 respectively.

Results and Discussion

In order to calculate the volumetric mass transfer coefficients from ASCE model using Eq. (5), a series of reoxygenation tests at different current density were performed.

Figure 2 shows a fast evolution of the oxygen concentration, then stabilization due to the saturation of the liquid solution with dissolved oxygen. The contaminated solutions have the same aspect but with different slope.

Impact of impurities concentration on $K_{L,a}$

In Figs 3-5 the volumetric mass transfer coefficient ($K_{L,a}$) has been plotted as a function of impurities concentrations at different current densities. As shown in Fig. 3 the volumetric mass transfer coefficients decreases with surfactant (BDHACl) concentration but it increases with current density. The decrease in $K_{L,a}$ is attributed to the fact that part of generated oxygen is used in the oxidation of surfactant.

As shown in Fig. 4 the volumetric mass transfer coefficients $K_{L,a}$ decreases with diatomaceous earth (DE) concentration but it increases with current density.

As shown in Fig. 5 the volumetric mass transfer coefficients $K_{L,a}$ decreases with the soybean oil concentrations until a concentration of 8 g/m$^3$, from which $K_{L,a}$ undergoes a slight increase. This last phenomenon can be explained by the fact that the increase in the number of the oil molecules in water enhances their coalescence. Thus, a reduction of the surface screen and an improvement in the oxygen transfer in water takes place.

Figure 6 presents the variation of the volumetric mass transfer coefficient with current density for different liquid phases. This figure indicates that $K_{L,a}$ increases with the current density when J reaches some intense values superior to 220 A/m$^2$ $K_{L,a}$ remain roughly constant for each liquid phase. This variation of $K_{L,a}$ can be explained as follows: When the current density increases, the number of oxygen bubbles increases, too. This suggests an amelioration in the exchange surface due to the interfacial area. The increase of the number of bubbles generates an intense agitation which decreases the transfer resistance in the liquid phase and increases the liquid-side mass transfer coefficient$^{24}$.

| Table 1—Characteristics of clean tap water in the ambient conditions |
|----------------|-------------------|
| pH             | 7                 |
| Salinity       | 1000 g/m$^3$     |
| Oxygen equilibrium concentration | 8 g/m$^3$       |
| Chloride (Cl$^-$) | 326 g/m$^3$   |
| Calcium (Ca$^{2+}$) | 112 g/m$^3$ |

| Table 2—Summary of the experimental conditions |
|----------------|-------------------|
| Water temperature | 289-297 K        |
| Volume of aerated liquid | 2 L             |
| Surface of electrodes | 38.84 $10^{-4}$ m$^2$ |
| Current density | 60-260 A/m$^2$ |
| Soybean oil concentration | 0-10 g/m$^3$     |
| Surfactant concentration | 0-9 g/m$^3$     |
| Diatomaceous earth concentration | 0-1500 g/m$^3$ |

Fig. 2—Experimental oxygen concentration in clean tap water at different time for different current densities

Fig. 3—Experimental mass transfer coefficient at different surfactant (BDHACl) concentrations
The stabilization of $K_{L}$a for the intense densities can be explained by the coalescence of the bubbles that decreases the surface of transfer and also by the stabilization of the liquid-side mass transfer coefficient $K_{L}$ that tend towards a limiting value $^{25}$.  

Figure 7 (A) shows that $K_{L}$a decreases with each impurities concentration, as the surfactant BDHACl, the diatomaceous earth DE and the soybean oil SO, but with different decreasing rates. In the surfactant case, a uniform layer of surfactant is adsorbed at the surface of the oxygen bubble, in spite of the increase of the interfacial area, as a result $K_{L}$ decreases following the increasing of mass transfer resistance $^{26}$.  

The soybean oil molecules may orient themselves on the interfacial surface of the gas bubbles and create a barrier to diffusion of oxygen, the liquid-side mass transfer coefficient will decrease significantly $^{18}$.  

The presence of the diatomaceous earth in the liquid phase disadvantages the hydrodynamic behavior of the gas bubbles and contributes to the reduction of the gas holdup, therefore the reduction of the transfer coefficient $K_{L}$a $^{18}$.  

Figure 7 (A) also shows that the volumetric mass transfer coefficient $K_{L}$a for soybean oil solution is significantly lower than those obtained with surfactant solutions until $C_{imp}=6 \text{ g/m}^3$ from which $K_{L}$a of surfactant solutions continues to decrease whereas it stabilizes in the soybean oil case. The effect of diatomaceous earth occupies an intermediate position between the soybean oil and the surfactant in the $K_{L}$a reduction.  

As shown in Fig. 7 (B), all the alpha factors decrease exponentially with increasing impurities concentration which well confirms the direct relation between $\alpha$ and $K_{L}$a.  

Figure 7 (C) shows that the capacity of oxygenation decreases as a function of each impurity concentration since it is in direct relation with $K_{L}$a.  

**Modeling of data**  
In order to explain the results of present studies the mathematical models that permit to express the volumetric mass transfer coefficient according to the current density and the impurity concentration were selected. For this objective, an appropriate mathematical program DataFit (version 8.1.69) that permitted to find these models was used and the following models were obtained.  

* Impact of current density on $K_{L}$a  

$$K_{L}a = 0.281 J^{0.53}; R^2=0.93$$  

… (9)  

* Impact of surfactant concentration and current density on $K_{L}$a  

$$K_{L}a = 0.0756 \ J^{0.82} \ C_{BDHACl}^{-0.125}; R^2=0.96$$  

… (10)  

* Impact of diatomaceous earth concentration and current density on $K_{L}$a  

$$K_{L}a = 0.968 \ J^{0.59} \ C_{DE}^{-0.26}; R^2=0.93$$  

… (11)  

* Impact of soybean oil concentration and current density on $K_{L}$a  

$$K_{L}a = 0.114 \ J^{0.68} \ C_{SO}^{-0.0053}; R^2=0.95$$  

… (12)
These models indicate that the volumetric mass transfer coefficient increases with the current density. This is valuable for current density inferior to 220 A/m². These models also indicate that the $K_{L,a}$ decreases with the small concentrations of impurities.

Figure 8 shows the experimental mass transfer coefficient as a function of the calculated values in the presence of impurities. The difference between the calculated values and the experimental values is therefore considered acceptable since the average of regression coefficient is about $R^2 = 0.95$ for all models.

**Conclusion**

In the present work, the effect of the impurities on the volumetric mass transfer coefficient for different current densities in an electroflotation cell functioning in batch mode has been studied.

The presence of a surfactant, soybean oil and diatomaceous earth as pollutants in wastewater reduce the volumetric mass transfer coefficient as well as the alpha factor that relates volumetric mass transfer coefficient $K_{L,a}$ of wastewater to that of the clean water. The developed models allow the determination of volumetric mass transfer coefficient $K_{L,a}$ as a function of the current density and concentration of impurity.

**Nomenclature**

-\(a: \) volumetric interfacial area \([m^2/m^3]\)
-\(A: \) interfacial area \([m^2]\)
-\(C: \) dissolved oxygen concentration in liquid phase \([g/m^3]\)
-\(C^*: \) equilibrium oxygen concentration in liquid phase \([g/m^3]\)
-\(CO: \) capacity of oxygenation \([g/m^3\cdot h]\)
-\(C_{imp}: \) impurity concentration \([g/m^3]\)
-\(C_{BDHACl}: \) surfactant (BDHACl) impurity concentration \([g/m^3]\)
-\(C_{DE}: \) diatomaceous earth impurity concentration \([g/m^3]\)
-\(C_{SO}: \) soybean oil impurity concentration \([g/m^3]\)
-\(J: \) current density \([A/m^2]\)
-\(K_L: \) liquid-side mass transfer coefficient \([m/h]\)
-\(K_{L,a}: \) volumetric mass transfer coefficient \([h^{-1}]\)
-\(T: \) temperature \([°C]\)
-\(t: \) time \([min]\)
-\(V: \) volume of liquid phase \([m^3]\)

**Greek symbols**

-\(\alpha: \) alpha factor \([\text{dimensionless}]\)
-\(\theta: \) theta factor \([\text{dimensionless}]\)
-\(R^2: \) regression coefficient \([\text{dimensionless}]\)

**References**