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# JDOC

## Workshop jeune chercheur

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## ***Preface***

*The workshop ‘Jeune Chercheur’ took place at the university Constantine 3, Constantine, Algeria in May 3-5, 2015 and the number of participants mostly from the local universities was around 80 showing the interest to this first yearly event which dealt with the problem of writing a scientific paper, a crucial matter for young PhD and researchers students.*

*The ‘Journal des Doctoriales’ allocated its second volume for the year 2015 as a space for a set of selected papers submitted PhD students, and a priori, affixed as poster contributions concerning their research topics.*

*Six papers were selected for publication in Journal des Doctoriales concerning different aspects and applications of process engineering and as examples one can cite the works on the use of supercritical fluids for extracting essential oils from local natural plants and also for hydrothermal oxidation of organic pollutants, the use of adsorption for the removal of dye compounds from water effluents, the study of membrane processes particularly Ultrafiltration process for water treatment and also the recovery of medicinal compound like V Penicillin, the use of coagulation-flocculation process to improve the reduction of turbidity and dissolved solids in water. The last paper dealt with the modeling of solid-liquid phase equilibria was considered using thermodynamic models like UNIFAC.*

*Finally the dean of the Process Engineering Faculty of Constantine 3 university is very grateful to the Scientific Association for Water Information Systems (SAWIS) guests, namely Aniss MOUMEN, Mohamed BEN-DAOUD and Mohamed EL BOUHADIOUI for having accepted to answer positively to the invitation and to provide a space to publish some of our PhD students.*

*The dean is also very grateful to Prof BOUKERZAZA Hosni Rector of University Constantine 3 for his help and efforts to develop the faculty of process engineering, to his vice-dean of research and post graduate studies, Dr OUTILI Nawel for her initiative, efforts and contacts to concretize this event, as well as Prof SASSI Souad and BENABBAS Chaouki the vice-rectors in charge, respectively, of research and postgraduate studies and international relations, for their support and active participation. The authors and the many referees should be complimented for their contributions and achievements, as so apparent from this volume.*

***Prof Abdeslam-Hassan Meniai***  
*Dean of Process Engineering Faculty*  
*University Constantine 3, Algeria*

## Summary

**Comparative study between aluminum sulfate and ferric chloride in water treatment: turbidity removal. (Benalia Abderrezzaq et Derbal Kerroum ).....4**

**Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from potato peels. (Zaïter Miadanée Benkartoussa, Bellir Karima, Bencheikh Lehocine Mossaab).....10**

**Modeling of hydrothermal oxidation of phenol with air in supercritical water. (Nadjiba Benmakhlouf, Nawel Outili).....14**

**Experimental Study of the microfiltration for the production of the drinking water. (M. Boussemgoune, M. Chikhi, F. Bouzerara).....20**

**Supercritical CO2 Extraction of Essential Oil from Algerian Fennel (Foeniculum vulgare Mill). (I. Haloui, A-H.Menai).....25**

**Modelling of liquid-solid equilibria and determination of a new group interaction parameters for unifac method.(Moudjari Youcef, Louaer Wahida, Menai A-H).....30**

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## Comparative study between aluminum sulfate and ferric chloride in water treatment: turbidity removal

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### **Abstract:**

*The objective of the study is to improve the reduction of turbidity and dissolved solids in water by the coagulation-flocculation process by comparing two coagulants in the presence of polymer. The obtained results show that the uses of aluminum sulphate in combination with ferric chloride gave the maximum turbidity removal.*

*The Jar Test were performed in the laboratory, and several parameters such as pH, coagulant dose, polymer dose, were optimized in order to maximize the turbidity removal.*

**Keywords:** *coagulation, flocculation, turbidity, coagulant dose, organic matter.*

### **1-Introduction:**

Coagulation flocculation is a very effective treatment of clarification whose vital objective is the elimination of the non decantable portion of the suspended matter. This category of substances is represented primarily by colloids, characterized by their great stability.

The purpose of the operation of coagulation-flocculation is the growth of the particles (which are primarily colloidal) by destabilization of the suspended particles then formation of the flocs by absorption and aggregation [1].

The destabilization of the entities in suspension goes through adsorption phenomena [2], explained by the theory of the double layer. It explains how the colloids are treated with clotting.

Coagulation is an operation simple to carry out but the concerned mechanisms are very complex and do not cease occupying a broad place in recent research [3-5]. The comprehension of this phenomenon requires a thorough knowledge of the colloidal state and the chemical structure of the coagulants used like their mode of action.

The experimental study of the coagulation-flocculation aims to determine the choice a reagent and the optimum concentrations required for maximum reduction of the turbidity after simple sedimentation.

In order to satisfy this objective, the experimental gravel bank-test like technique was chosen.

### **2-Materials and methods:**

#### **2-1- Reagents used:**

The metal salts used during the tests in Jar tests are the aluminum sulfate ( $Al_2(SO_4)_3 \cdot 18H_2O$ ), ferric chloride ( $FeCl_3$ );

The metal salt solutions are prepared daily with a concentration of 1g/l.

The flocculants used is the polymer.

The polymer is prepared with concentrations of 0.1g/l.

#### **2-2-other reactive:**

Soda and sulphuric acid used to adjust the pH. The solutions of these reagents are prepared in distilled water.

### 2-3- Experimental Protocol:

The Jar-test was used to determine the optimum values of:

- Coagulants dose
- Polymer dose
- pH and organic mater
- Conductivity, alkalinity and salinity.

Different dose of coagulant were added to raw water in 06 beakers of 1 liter of water volume. The samples are mixed at high speed of 160 rpm, the of pH adjustment were performed by adding a base solution (sodium hydroxide 1 N) or an acid solution (sulfuric acid at 10 g / l), then poured coagulant. The rapid mixing agitation was maintained for 4min, followed by slow phase (30 rpm) for 20 minutes. Finally all parameters such as, turbidity, pH, organic matter, etc. were measured.

The result of turbidity is expressed according to the percentage as:

$$\text{Abatement\%} = \frac{\text{initial value} - \text{value résidualo}}{\text{initial value}}$$

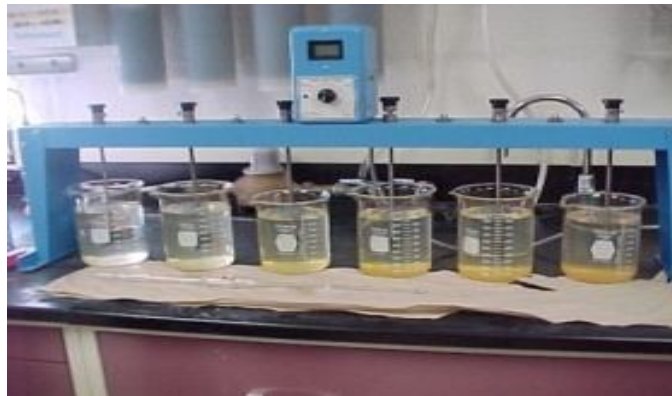


Figure 1: Jar Test

### 3-Results:

#### 3-1-Optimization of pH:

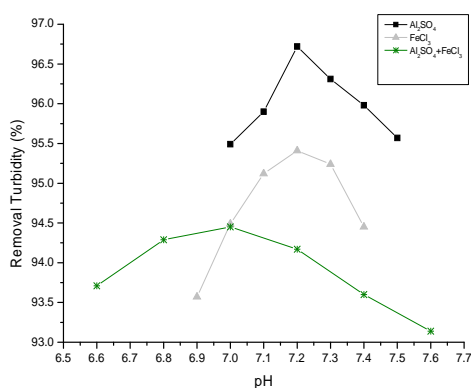


Figure 2: Effects of pH on turbidity removal

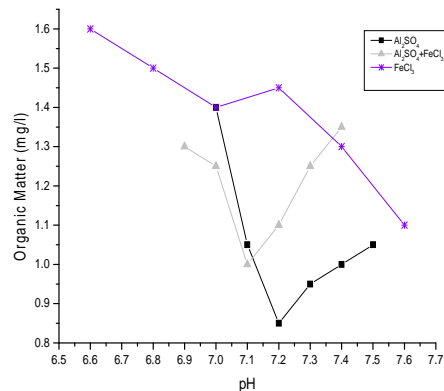


Figure 3: Effects of pH on organic matter

#### 3-2 Optimization of the coagulant dose:

It is noticed well that the addition of coagulant caused the reduction in the value of turbidity with the increase in the concentration of the coagulant.

The particles of the coagulant destabilize colloids negatively charged present in water to be treated, by neutralizing the loads which generate the forces of repulsion enter colloids. The overdose in coagulant causes the destabilization of the colloidal particles and prevents the formation of the intraparticle bridges and there will be thus water very charged in coagulant with a bad clarification.

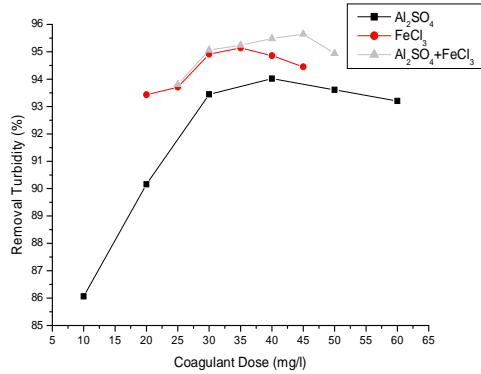


Figure 4: Effects of coagulant dose on removal turbidity

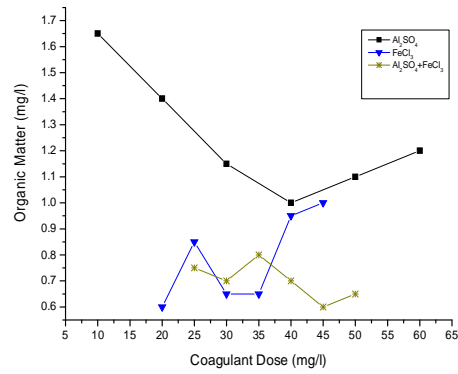


Figure 5: Effects of coagulant dose on organic matter

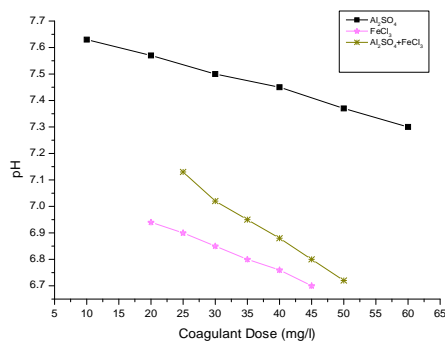


Figure 6: Effects of coagulant dose on pH

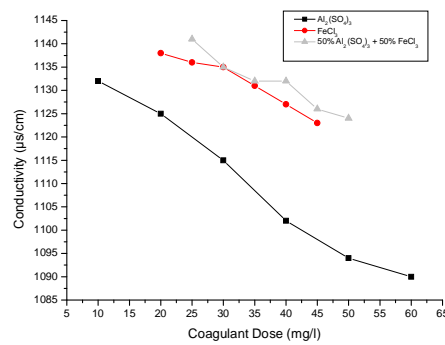


Figure 7: Effects of coagulant dose on conductivity

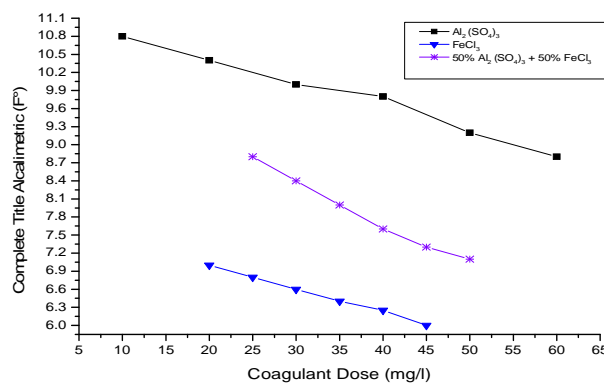


Figure 8: Effects of coagulant dose on Complete Title Alkalimetric

### 3-3 Optimization of the polymer dose:

It is well noticed that the waning of the curves until the optimal dose in the presence of the flocculating agent.

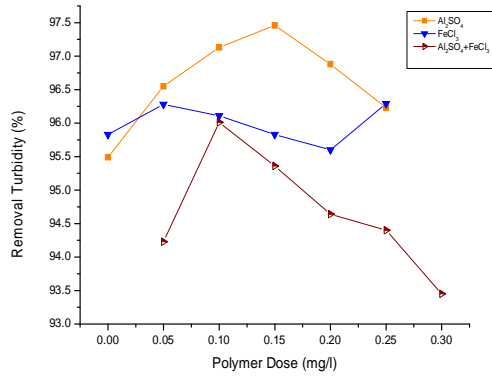


Figure 9: Effects of polymer dose on removal turbidity

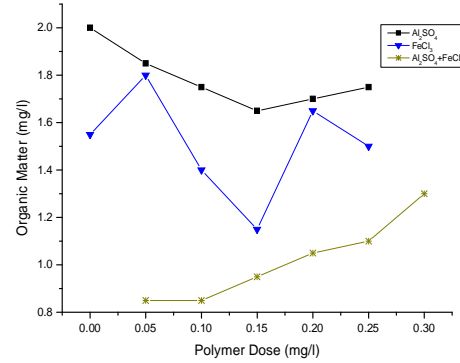


Figure 10: Effects of polymer dose on organic matter

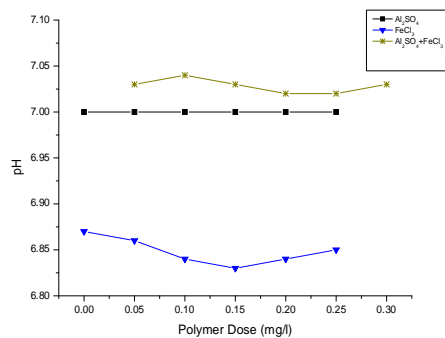


Figure 11: Effects of polymer dose on pH

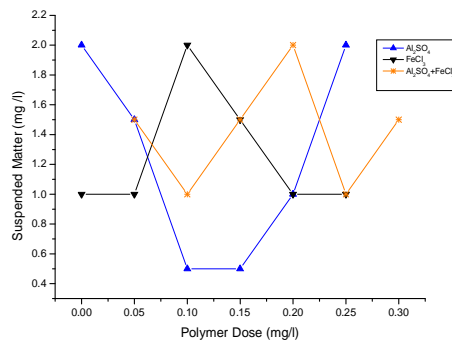


Figure 12: Effects of polymer dose on suspended matter

## 4-Discussions:

### 4-1-Optimization of pH:

The pH 7.2, 7.0, 7.2 represent the optimal values corresponding to the greatest value of reduction of the turbidity (96.72, 94.45, 95.41) of sulfate ( $\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$ ),  $\text{FeCl}_3$ , and mixes it respectively where the curves are decreasing before increasing;

Figure 3 represents the effect of the pH on the elimination of the organic matter where one can see that the optimal pH 7.2,7.0,7.2 gives a content of organic matter 0.85,1.4,1.1 for ( $\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$ ),  $\text{FeCl}_3$ , and mixes it respectively.

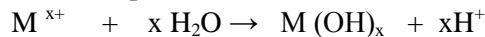
### 4-2 -Optimization of the coagulant dose:

According to the diagram of our experimental results, we got better results for 40, 35 and 45 doses ( $\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$ ),  $\text{FeCl}_3$ , and the mixture respectively, these values represent the optimal dose because are the points corresponding to best the reduction of turbidity 94.02, 95.14, 95.65 respectively where the curves are increasing before this dose then becomes decreasing, The conductivity is reduced with increasing the dose of aluminum sulphate, ferric chloride and mixing, this reduction due to the reaction between the ionic charges in water and the coagulant used;

From the jar test experiments, it was found that the initial pH values for the water withdrawn is greater than 7 for the water to be treated and is basic because of the negative charges of the colloids.

The pH values have progressively reduced by increasing the concentrations of coagulant, coagulant each pH and concentrations of different coagulants, such as the pH value reached 7.30 aluminum sulfate has a concentration 60 mg/l;

Concerning the addition of the coagulant which involves the formation of hydroxide of metal with release of certain acidity (hydrolysis) what explains the reduction in the value of the pH.



The particles of the coagulant bring also positive loads what also contributes to the reduction in the value of the pH and Complete Title Alkalimetric of water;

Figure 5 shows well that the effect of the dose of the coagulant on the content of organic matter, the dose of 40,20,45 gives the low value of organic matter 1.0,0.6,0.6 of  $Al_2(SO_4)_3$ ,  $FeCl_3$ , mixture respectively, the abatement of the organic matter can be explained by simultaneous adsorption on the flocs of hydroxide of metal.

#### 4-3 -Optimization of the polymer dose:

The flocculant used in our study is a polymer as a coagulant aid, which promotes agglomeration and floc formation.

The microfloc-flocs formed by agglomeration of the particles discharged beforehand by the effect of the added mineral coagulant, are reinforced by the macromolecules of the polyelectrolytes or added flocculating agent. In this stage known as flocculation, these microfloc-flocs are incorporated forming flakes which thus hold more suspended particles and consequently become bulkier what facilitates their decantation.

It is noticed well that the waning of the curves until the optimal dose in the presence of the flocculating agent.

The dose of 0.15, 0.05, 0.1 mg/l of polymer gives maximum reduction of turbidity 97.46, 96.28, 96.01%, and organic matter 0.5, 1.0, 1.0 of  $Al_2(SO_4)_3$ ,  $18H_2O$ ,  $FeCl_3$ , mixture of 50%.

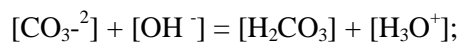
According to the comparison between aluminum sulfate, the ferric chloride and the mixture, one can conclude that aluminum sulfate with polymer is most effective than the others;

The absence of the ionic loads in the formulated of polymer explains the stabilization of pH with the variation of the polymer dose;

The increase in the organic matter by polymer is explained by the organic polymer formulated.

According to the experimental results one can also conclude:

The measurement of title alkalimetric is of only one limited interest, as for the determination of free  $CO_2$  title alkalimetric is cancelled when



In the majority of the cases the pH of turn is close to 8.3, Thus water having a pH lower than 8.3 has a title alkalimetric which is null;

We noticed that the variation of salinity in our experiment independent of variation of pH and the amounts of coagulant and polymer, and a constant value of 0.3%.

#### 5-Conclusion:

- PH, coagulant and polymer dosage are very important parameters;
- Aluminum sulfate combined with ferric chloride give a good result for turbidity removal;
- The polymer contributes also to turbidity removal;
- pH is a very important parameter for an optimal working of used coagulant;
- The overdose in coagulant causes the restabilisation of the colloidal particles and prevents the formation of the interarticular bridges and there will be thus water very charged in coagulant with a bad clarification;



- In coagulation-flocculation, the measurement of salinity is not a true reference mark to obtain information nor to judge the reliability of the process, nevertheless its variation can say to us on the salt reaction of dissolved during the treatment;
- The coagulant by a coagulant containing iron gives a better reduction of the organic matter than of coagulant containing aluminum.

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## Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from potato peels

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### **Abstract:**

*The treatment of colored effluents to eliminate the presence of dyes which have negative effects on the environment and on human health, by means of adsorption was investigated. The choice of this technique is mainly guided by its simplicity and efficiency.*

*This work is concerned with the adsorptive removal of Eriochrome Black T (EBT) from aqueous solution using two types of potato peels: the first one was calcinated whereas the second was treated with HCl.*

*Both sets of the obtained results were compared showing that the retention capacity of potato peels treated with HCl was higher.*

**Keywords:** *potato peels, adsorption, Eriochrome black t ,green of malachite.*

### **1. Introduction**

The rise of dyeing wastewater effluents can be considered as a direct result of dyes production as well as a consequence of their use in many industries. Dyes are usually of synthetic origin with complex aromatic molecular structures, which make them very stable, resistant to fading and difficult to biodegrade. Due to the toxic nature of most dyes to plants and micro-organisms, colored wastewater cannot be discharged without adequate treatment.

Even if they are non-toxic, such wastewaters obstruct light penetration, decrease the photo-synthesis in aquatic plants and raises the COD. Dyes can cause allergic dermatitis, skin irritation, cancer, and mutations. To remove dyes and other contaminants from wastewaters, several physical, chemical, and biological methods have been developed, such as, adsorption, nanofiltration, ion exchange, coagulation-flocculation, precipitation, ozonation, and aerobic or anaerobic treatment. Few of these processes are effective when the concentration of dye in the effluent is small. Some of them produce large quantity of sludge causing disposal problems, thus increasing operational costs. However Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency and stability in comparison to biological methods.

The most common adsorbent used for dye removal is activated carbon, which has a good adsorption capacity for organic molecules. In spite of this, it suffers from a numbers of disadvantages such as its high cost which has prevented its application, at least in developing countries. This has led many workers to search for cheaper substitutes. A number of low cost adsorbents are reported in the literature, like fly ash, peat, sawdust, lignite, rice husk, banana pith [2].

So in this work, the adsorption of Eriochrome Black T (EBT) from aqueous solution using two types of potato peels: the first one was calcinated where as the second was treated with HCl, was considered.

## 2. Material and methods

### 2.1. Adsorbent

#### ▪ Calcination:

The preparation mode of the adsorbent was quite simple, it consisted of washing to remove the impurities, drying at 100°C and keeping in well-capped silica crucibles at 250°C in a furnace for 2h. The product was then powdered and stored in a desiccator until use [2].

#### ▪ Chemical activation:

-Adsorbent used in this study was washed completely and separated into fine particules (to accelerate drying) and dried at room temperature for 5-7 days.

-Biomass (8g) emulsified into 150mL of acidic solution using 1M at 25°C for 30 min to remove impurities, samples were washed with distilled water until the pH rose above 6

-The biomass was dried at 90°C for 24h, the product was powdered.[3]



Fig. 1. Calcinated adsorbent



Fig. 2. Chemical activation

### 2.2. Preparation of EBT solution:

The characteristics of EBT dye are summarized in Table 1 and its chemical structure [2] is shown in Fig. 3

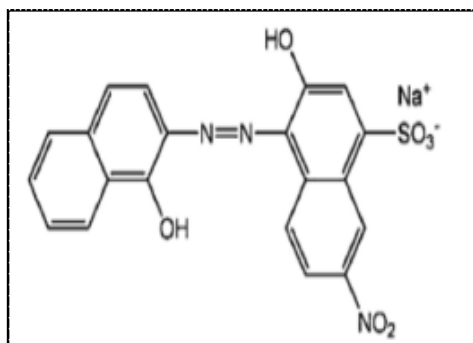


Fig. 3. Molecular structure of EBT dye.

|                                     |   |
|-------------------------------------|---|
| Type of dye                         | Anionic azo dye   |
| Molecular formula                   | C <sub>20</sub> H <sub>12</sub> N <sub>3</sub> NaO <sub>7</sub> S |
| Molecular wt.                       | 461.38 g/mol  |
| Max. wavelength (λ <sub>max</sub> ) | 530 nm  |
| Solubility in water (20 °C)         | 50 g/L  |
| Solubility in ethanol (20 °C)       | 2 g/L   |
| Color                               | Black   |

Table 1: Properties of EBT dye.

The absorbance characteristics were determined using an UV-vis spectrophotometer and a relationship between the absorbance and the concentration was established, which is given in Eq. (1).

$$\text{Concentration} = 95,112 * \text{absorbance} \quad (1)$$

**2.3.Method:**

Adsorption experiments were performed in a batch system using initial concentration (25mg/l) at 650 rpm and 20 °C. pH of solution, adsorbent dose (0.8 g). After adsorption, the treated solution was filtered and final dye concentration was analyzed using an UV–vis. The samples were collected at predetermined time intervals from 5 to 120 min. The adsorption capacity was calculated using this relation:

$$q = \frac{(C_0 - C)}{m} \times V \tag{2}$$

where:

q (mg /g ):the adsorption capacity,

C<sub>0</sub> (mg /l) : the initial concentrations of solution of (EBT),

V (l) : the volume of solution ,

m (g): the weight of the adsorbent [3],

**3. Results and discussion :**

**3.1.comparison between calcined potato peels and activated one:**

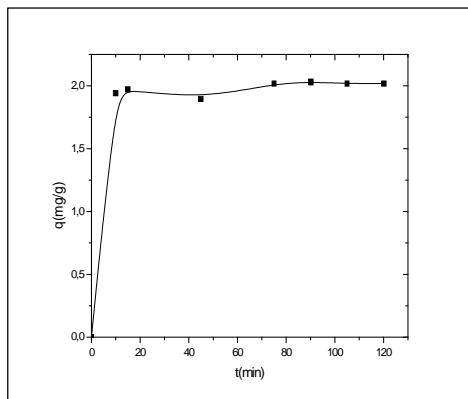


Fig.4.activation, C<sub>0</sub>=25mg/l,r=0.8g/80ml,T=20°C  
pH=6.41(pH of solution) ,v=650tr/min

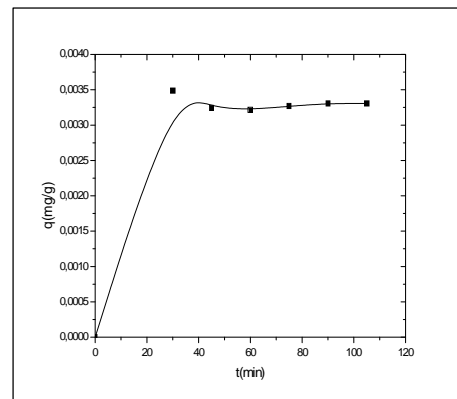


Fig.5.calcination, C<sub>0</sub>=25mg/l,r=0.8g/80ml,T=20°C  
pH=6.41(pH of solution) ,v=650tr/min

The results obtained showed that the adsorption kinetics of calcined potato peels was faster than activated one. However, the amount removed by the activated potato peels may be larger, HCl Eliminated impurities in the pores, increasing their number.

**3.2. Comparison between adsorption of Eriochrome black T and green of malachite:**

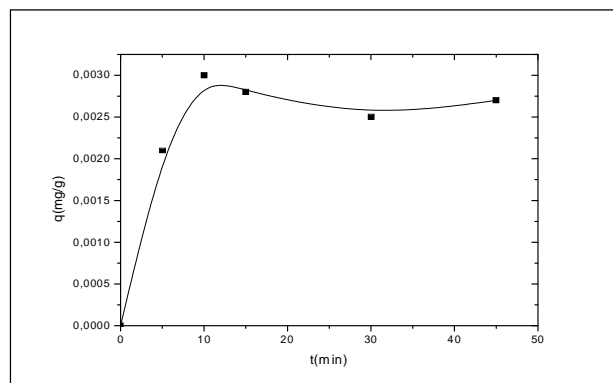


Fig.6. green of malachite,C<sub>0</sub>=25 mg/l,r=0.8g/80ml,T=20°C, pH=6.41 (pH of solution) ,v=650tr/min.

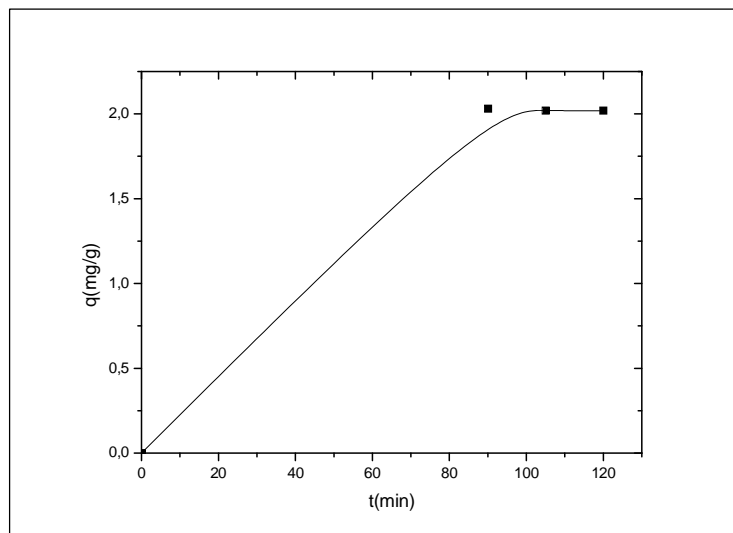


Fig.7. Eriochrome black t , $C_0=25$  mg/l, $r=0.8$ g/80ml, $T=20^\circ\text{C}$ ,  
pH=6.41(pH of solution) , $v=650$ tr/min

The obtained results are compared as shown in Fig 6 and Fig. 7, suggesting that the adsorbed amount of NET was larger than the Green of malachite. This can be explained by the fact that the adsorption is a phenomenon characterized by its selectivity.

#### 4. Conclusion:

This work clearly indicates that the potato peels were excellent adsorbent for the removal of NET from aqueous solutions.

- 0.8 mg of potato peels was found enough to remove 70% of the NET from an aqueous solution of 25 mg /l (80 ml) at pH of solution with a shaking time of 60 min.
- The adsorption of NET on potato peels was better than that of green of malachite [4].

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## Modeling of hydrothermal oxidation of phenol with air in supercritical water

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### **Abstract:**

*Hydrothermal oxidation is an efficient and clean process for the transformation of waste-water containing organic compounds. So-called hydrothermal oxidation, these processes may be considered as subcritical oxidation or supercritical operation depending on pressure and temperature conditions. The main advantage of these processes is the non toxicity of the products.*

*In fact, organic material (C, H, and O) is exclusively converted into carbon dioxide and water. These processes are particularly suitable for the treatment of wastewater too concentrated for biological treatment or too wet for incineration treatment [1].*

*The purpose of this work is to apply a simple mathematical model for a tubular reactor which is often difficult to solve in its general form. The governing equations are momentum, mass and energy balances. According to adequate simplifications, the profiles of temperature and concentration of chemical species are computed along the reactor using finite difference method. IAPWS formulation for supercritical water thermo physical properties was also computed to provide accurate properties in temperature and pressure ranges of study. The developed Mathcad program gave results close to experimental values reported in A. Foucault et al [2] work for temperature and species concentration profiles.*

**Keywords:** *Hydrothermal oxidation, supercritical water, wastewater treatment, modeling environment process.*

### **Résumé**

L'oxydation hydrothermale est un moyen efficace et propre pour le traitement des effluents contenant des composés organiques. Selon les conditions de pression et de température l'oxydation hydrothermale peut être une oxydation supercritique ou sous-critique. L'avantage principal de ces procédés est que les sous-produits finaux sont non toxiques. En effet, la matière organique (C, H et O) est exclusivement convertie en dioxyde de carbone et eau. Ces procédés sont particulièrement adaptés pour le traitement des effluents trop concentrés pour le traitement biologique ou trop dilués pour le traitement par incinération [1].

Le but de ce travail est d'appliquer un modèle mathématique simple pour un réacteur tubulaire d'oxydation hydrothermale à eau supercritique, qui est souvent difficile à résoudre dans sa forme générale. Les équations régissant le comportement de ce réacteur sont issues des lois de la conservation de la masse, du mouvement et de l'énergie donnant lieu à un système d'équations différentielles. En appliquant les simplifications adéquates, les profils de température et de la concentration des espèces chimiques sont calculés le long du réacteur en utilisant la méthode des différences finies. La formulation d'IAPWS (Association internationale pour les propriétés de l'eau et vapeur) a été utilisée pour le calcul des propriétés physiques de l'eau (milieu réactionnel).

Le programme développé sous Mathcad donne des résultats proches des valeurs expérimentales de A.Fourcault et al [2] pour les profils de température et des espèces chimiques le long du réacteur.

## Introduction

When organic content of effluents is more than 1% they are regarded as too concentrated to undergo a biological treatment whereas when it is less than 10%, a treatment by incineration is too expensive because it requires extra-gas. Hydrothermal oxidation in supercritical water is an alternative way to dispose of these effluents [2].

Several pollutants have been studied in previous works and one can cite acetic acid, dodecane, methylene chloride, methanol and phenol which has also been the subject of numerous studies both in subcritical and supercritical conditions with different kinetics obtained according to the operating conditions [3]. So the availability of experimental data and its presence as water pollutant have justified its choice in the present work.

Mathematical modeling concerns concentration and temperature profiles resulting from mass, momentum and energy differential equations resolution. It provides a comprehensive way to understand experimental results, equipment design and scale-up of the process [3 - 4].

In modeling, it is often tried to simplify the model used to facilitate its programming without losing the precision of the results. This is the objective of the present work, especially since the models used to simulate the behavior of supercritical water oxidation reactors are often based on turbulence theories and two-dimensional models, which are complicated to solve without CFD programs.

## 1. Material and methods

The procedure used in this work is the application of a simplified mathematical model to simulate the behavior of the oxidation reactor. The aim is to facilitate its programming in Mathcad and overcome the problem of using a turbulence model. The problem becomes one-dimensional and finite difference numerical method is used for its resolution.

Furthermore, great importance was given to the calculation of physical properties, and one of the most important aspects of this modeling is the accuracy of supercritical water properties which may vary sharply, being quite different from those of normal liquid water or steam. The IAPWS formulations were used [5] in a Mathcad code, that was developed for physical properties estimation at a given temperature and pressure.

To validate the results of the developed programs, comparisons were performed with the data obtained from experimental work for hydrothermal oxidation in supercritical water in a tubular continuous flow reactor, with a single injection of air. The internal diameter was about 12.32 mm and the external diameter was 19.05 mm, with 9 m length and the reactor was not totally adiabatic [2].

### 1.1. Governing equations

For one-dimensional channel flow, the steady-state mass, momentum and energy conservation equations and the equation of conservation of species can be written as follows [6]:

#### Continuity

$$\frac{\partial \rho u}{\partial x} = 0 \quad (1)$$

$\rho$  the density of mixture  $\text{kg/m}^3$  and  $u$  for its velocity in  $\text{m/s}$ .

### Momentum conservation

$$\frac{\partial u^2 \rho}{\partial x} = -\frac{\partial P}{\partial x} + \frac{\partial \tau_{xj}}{\partial x} \quad (2)$$

Where P is the pressure in MPa,  $\tau_{xj}$  is the stress tensor in direction x, linked to a gradient of velocity in the direction j.

$$\tau_{xj} = \mu_{\text{eff}} \cdot \left[ \left( \frac{\partial u_x}{\partial j} + \frac{\partial u_j}{\partial x} \right) - \frac{2}{3} \cdot \frac{\partial u_k}{\partial x_k} \cdot \delta_{xj} \right] \quad (3)$$

For turbulent flow, the effective viscosity  $\mu_{\text{eff}}$  is not equal to dynamic viscosity  $\mu$  as for laminar flow:  $\mu_{\text{eff}} = \mu + \mu_T$  where  $\mu_T$  is the turbulent viscosity [7].

In turbulent mode of operation, the stress tensor should include the Reynolds's stress tensor and an appropriate model to compute it (such: model k- $\epsilon$  and k- $\omega$ ) [8], this complicates the mathematical description of the process and often needs CFD software programs. Thus, for mathematical simplification, and in order to get a one dimensional problem, the divergence of the stress tensor is assumed to be as the local pressure drop over the control volume under consideration [2].

In this study, this computation has been done according to Blasius and McAdams correlations. The resulting balance equation is then:

$$\frac{\partial u^2 \rho}{\partial x} = -\frac{\partial P}{\partial x} + C_k \cdot \rho \cdot u^2 \quad (4)$$

Coefficient  $C_k$  in the momentum conservation equation (6) is given by:

$$C_k = \frac{f}{2 \cdot D_h} \quad (5)$$

Where  $D_h$  is the hydraulic diameter of the channel in meter, and f is the friction factor, which can be determined using the Blasius and McAdams correlations for a smooth tube [9], given by:

$$f = \begin{cases} 0.316 \cdot \text{Re}^{-0.25} & \text{Re} < 30000 \\ 0.184 \cdot \text{Re}^{-0.20} & 30000 < \text{Re} < 10^6 \end{cases} \quad (6)$$

$$\text{Re is the Reynolds number defined as: } \text{Re} = \frac{\rho \cdot u \cdot D_h}{\mu} \quad (7)$$

And  $\mu$  is the dynamic viscosity in (Pas.s).

### Energy conservation

Using the same assumption as above the energy conservation equation is as follows:

$$\frac{\partial u \rho h}{\partial x} = u \cdot (C_k \cdot \rho \cdot u^2) + u \frac{\partial P}{\partial x} - W_{\text{lost}} - r \cdot \Delta_r H(T, P) \quad (8)$$

$\Delta_r H(T, P)$  is the heat of reaction in kJ/kg, and h the enthalpy to weight of the medium.

### Species conservation

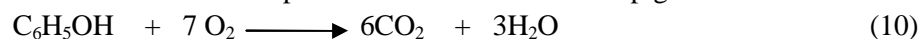
$$\frac{\partial u \cdot \rho \cdot y_j}{\partial x} - M_j \cdot \mathcal{V}_j \cdot r = 0 \quad (9)$$

$\mathcal{V}_j$  : the stoichiometric coefficient of species j (phenol, O<sub>2</sub> and CO<sub>2</sub>).



## 1.2. Model's assumptions

- Reactor is assumed to behave as a plug flow reactor.
- Because of the high water content (more than 70%), the thermodynamic and transport properties of the reacting medium are assumed to be equal to pure water properties and are calculated from the IAPWS formulation developed program (density, viscosity and enthalpy) [5].
- Axial molecular diffusion and thermal conduction are all negligible.
- Injected oxidant is supposed totally and instantaneously dissolved in the fluid phase.
- The chemical oxidation of phenol is described as one step global reaction:



- The reaction rate is assumed to be in the form of a global rate expression:

$$r = k^0 \exp\left(\frac{-E_a}{RT}\right) \cdot C_{\text{C}_6\text{H}_5\text{OH}}^m \cdot C_{\text{O}_2}^n \quad (11)$$

$k^0$  is the pre-exponential factor of Arrhenius law  $(\text{mol.l})^{-1-m-n} \cdot \text{s}^{-1}$ ,  $E_a$ : the activation energy of reaction in kJ/mol,  $m$  and  $n$  the reaction order with respect to waste and oxygen.

- The volumetric power lost by the reactor thermal losses is expressed as:

$$W_{\text{lost}} = \frac{H}{d} \cdot (T - T_{\text{ext}}) \quad (12)$$

$H$  is the overall heat transfer coefficient with the surroundings, estimated experimentally: by A.Fourcault et al [ 2] as  $30 \text{ W.m}^{-2} \cdot \text{K}^{-1}$ ,  $d$  the inner diameter of the reactor in meter, and  $T$ ,  $T_{\text{ext}}$  are respectively the local and the external temperature [1-2].

## 1.3. Operating conditions and parameter values used:

The simulation was performed with an initial temperature of  $450^\circ \text{C}$  and 250 bars, a flow rate of waste is 12.5 l / h, and initial concentration of phenol is 5 g / l. Air also enters the reactor at 250 bars pressure and a temperature of  $200^\circ \text{C}$  and a flow rate of about 3.69 kg/h.

The kinetic parameters used in this model are shown in the following table 1:

**Table 1:** Model's kinetics parameters for oxidation of phenol [2]:

| $K^0$ (mol.l) <sup>1-m-n</sup> .s <sup>-1</sup> | $E_a$ (kJ/mol)   | $m$ | $n$ |
|---|------------------|-----|-----|
| $10^{1.34 \pm 0.77}$                            | $39.2 \pm 10.07$ | 1   | 0   |

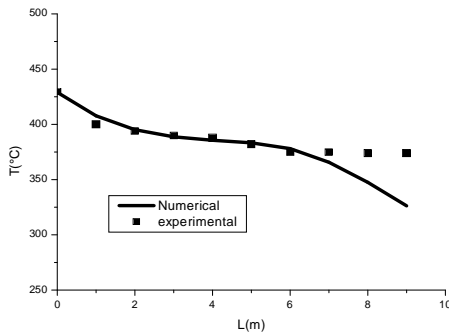
## 1.4. Numerical approach

The governing equations of mass, momentum, energy and species conservation, which form a system of differential equations, were solved numerically. Finite difference method with upwind scheme was used to get a purely algebraic system [10].

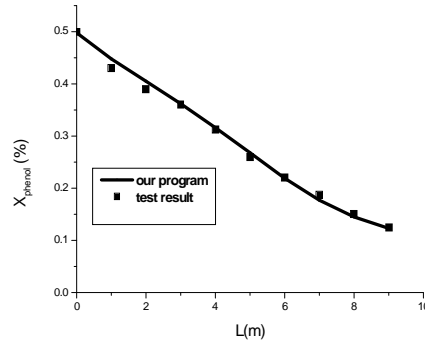
The final system contained the non-linear equations obtained after discretization of the differential system, plus the equations of thermodynamic properties "IAPWS" of pure water: density  $\rho$  (T, P), enthalpy  $h$  (T, P) and viscosity  $\mu$  (T, P). This algebraic model was solved using an appropriate numerical method for system of linear and non linear equations. The intrinsic subprogram *Find* was used in a Mathcad code which was implemented with IAPWS properties calculations.

## 2. Results :

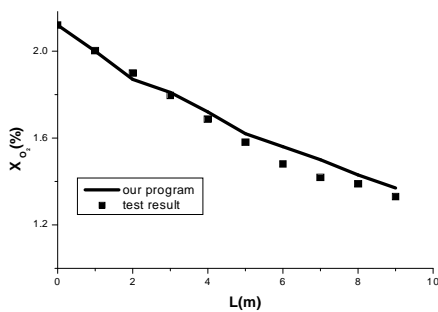
This section shows the results obtained from the Mathcad program execution with the operating data presented above. These results are compared with the experimental data obtained by [2]. Temperature profile and species concentration variation along the reactor are presented in figures: 2.3.4 and 5.



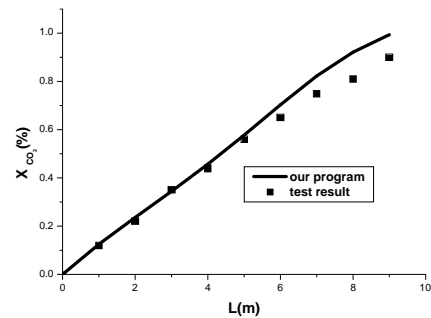
**Figure 2:** Comparison between experiments and numerical predictions for temperature profile



**Figure 3:** Comparison between our numerical predictions and experiments [2] for conversion ratio of phenol



**Figure 4:** Comparison between our numerical predictions and experiments [2] for conversion ratio of Oxygen



**Figure 5:** Comparison between our numerical predictions and experiments [2] for conversion ratio of CO<sub>2</sub>

## 3. Discussion :

The results validate the used model and the accuracy of properties calculations. From figure 3, it is shown that supercritical oxidation allow the disintegration of phenol at 75.3%. Modeling results are close to experimental ones, and mathematical assumption and simplification did not affect the results accuracy, excepted for the temperature profile, which showed a deviation between experimental values at the end of the reactor. This was due to the use of constant global heat transfer coefficient to compute heat losses between the reactor surface and the surrounding. Therefore this encouraged the use of heat transfer correlations to compute a dependence of this coefficient with temperature to be incorporated into the model.

## 4. Conclusion :

This mathematical model for the oxidation of phenol in supercritical water was based on the conservation of chemical species, and energy with the introduction of physical properties variation according to IAWPS formulation. It allowed the prediction of the temperature and species profiles giving a description of the phenomena occurring within the reactor. The results of this model were close to experimental values and numerical results reported in [2].

The disintegration rate of phenol was of the order of 75% and simulation results provided a comprehensive way to understand experimental results, equipment design and scale-up of the process. By varying operation conditions it can be possible to increase the conversion rate.

Other organic pollutants can be studied using the programs developed with appropriate input data.

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## Experimental Study of the microfiltration for the production of the drinking water

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### **Abstract:**

*Our study is related to the introduction of microfiltration into the conventional process of producing drinking water. A microfiltration rig was mounted at the Laboratory of the Engineering of the Processes of the Environment (LIPE) of the university Constantine 3. Raw water from Ain Tine (Mila) was used in all the experiments. The experimental works focused on the determination of permeate flow rate (filtered) for pure and raw water, depending on the transmembrane pressure (TMP). This part also considered the variation of mass transfer resistances and included different physicochemical tests, namely turbidity, matter in suspension (MES) and the dry residues (RS), for both for pure and raw water, filtered water and on the level of recycled water.*

*The results show that membrane of microfiltration can retain the various matters contained in raw water, by major elimination of MES and a better clarification of filtered water*

**Key words:** Membrane, microfiltration, flux, Suspended matter, drinking water.

### **Résumé:**

Notre étude porte sur l'introduction de la microfiltration dans le processus conventionnel de production d'eau potable ; un montage de microfiltration a été réalisé au Laboratoire de l'Ingénierie des Procédés de l'Environnement (LIPE) de l'université Constantine 3 ; l'eau brute utilisée dans toutes nos expériences est celle de Ain Tinn (Mila), Notre travail expérimental est consacré sur la détermination du flux de perméat (filtrât) en fonction de la pression transmembranaire (PTM), et cela pour l'eau pure et l'eau brute cette partie comporte aussi le suivi des résistances de transfert de matière et se concentre englobe sur les différents testes physico-chimiques, à savoir le suivi de la turbidité, la détermination des Matières en suspension (MES) et les résidus secs (RS), et cela pour l'eau brute, eau filtrée et au niveau de l'eau recyclée (concentrât) ; l'ensemble des résultats montre que la membrane de microfiltration peut retenir les différentes matières contenues dans l'eau brute, par une élimination importante des MES et une meilleure clarification de l'eau filtrée.

**Mots clés:** Membrane, microfiltration, flux, matières en suspension, Eau potable.

### **1. Introduction:**

The choice of the microfiltration (MF) is to treat a drinking water, removing organic pollutants, namely organic matter (OM), suspended matter (MES), pathogenic microorganisms, etc. [1- 2]. This has numerous technical advantages such as avoiding the addition of chemicals, its moderate cost [3- 4], etc., whereas, it is significant to note that there is a problem of clogging of the membrane which depend the water quality of the feed and the operating requirements of the process [5- 6].

### **2. Material and methods:**

The tangential microfiltration system was mounted in our laboratory LIPE University of Constantine3.

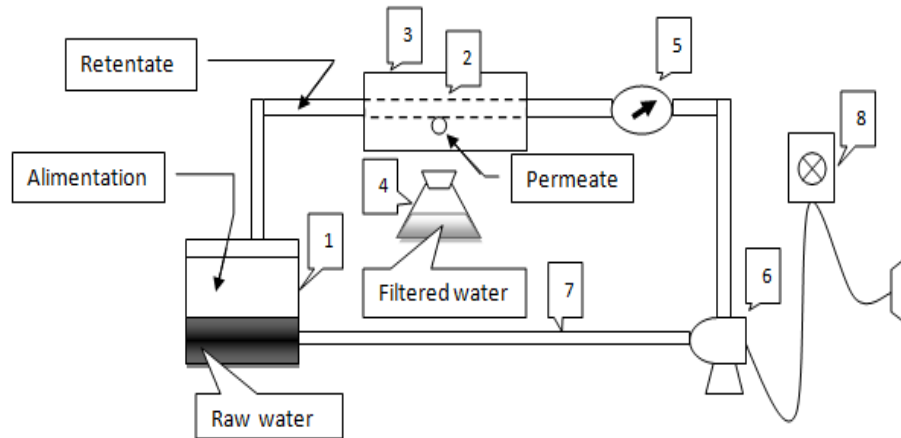


Figure1. Plan of the microfiltration system

The operating principle is as follows: the solution to be filtered (the raw water) was stored in the tank (feed tank (1)). It was pumped by (6) through the tubular micro filters (membrane (2)) held by the module (3). The flow (flow) of the pump could be adjusted by the switch (8) whereas the manometer (5) allowed the reading off the pressure at the entrance of the micro filter. The retentate was sent back into the feed tank (supply) and the permeate (filtered water) was collected in a conical flask (4) for analysis. The filtrate volume was followed according to time, to finally determine the flow of the permeate Knowing the surface area of the membrane.

### 2.1. Permeate flux:

The permeate flux is given by the resistance in series model law:

$$J = \frac{\Delta P}{\mu(R_m + R)} = \frac{\Delta P}{\mu R_T}$$

J: permeate flux;

$\Delta P$ : Transmembrane pressure (PTM);

$R_m$ : membrane resistance;

R: resistance of the deposit;

$R_T$ : total resistance.

## 3. Results:

### 3.1. Flow of permeate and total Resistances:

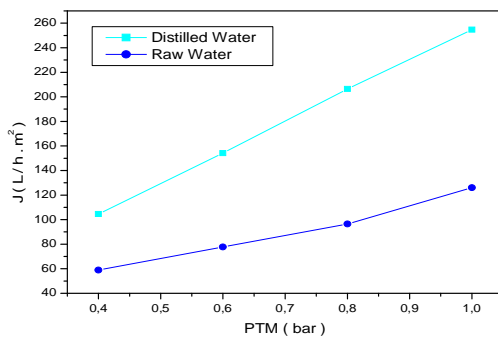


Figure 2. Variation of the flow of permeate transmembrane pressure

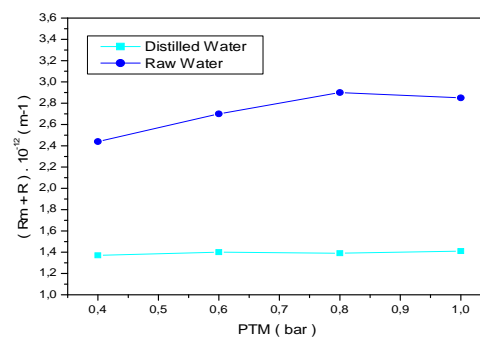


Figure 3. Variation of the Resistances according to the transmembrane pressure

### 3.2. Color of the water

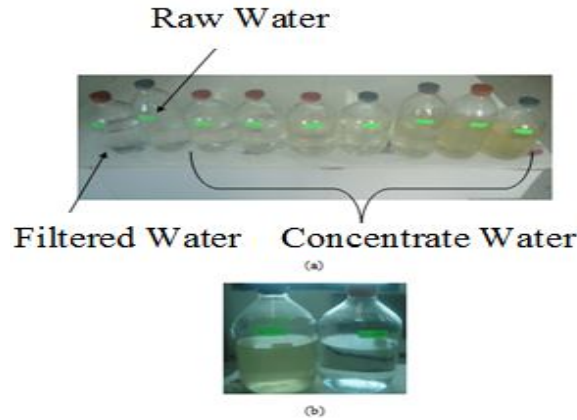


Figure 4. Variation of the color of the filtered water Compared to raw water and the of the concentrate water (recycled)

### 3.3. Suspended matter:

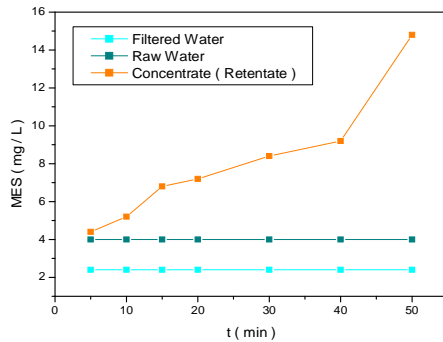


Figure 5. Variation as of suspended matter according to the time of filtration

### 3.4. Dry Residue :

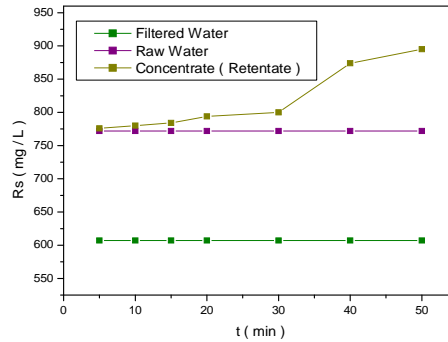


Figure 6. Variation of the dry residue according to the time of filtration

### 3.5. Turbidity:

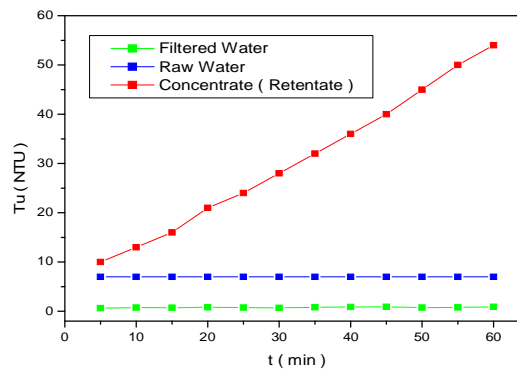


Figure7. Variation of turbidity according to the time of filtration

## 4. Discussion:

### a) Permeate flow:

In this case, the filtration time was set at 10 minutes, and the transmembrane pressure (TMP) was variable. Figure 2 shows that the flow of Permeate increased dramatically according to transmembrane

pressure Darcy's law; The flow in the case of distilled water was higher than that of the raw water. Figure 2 shows a linear distilled water flow rate, with a high slope which means clustering the regularity of the membrane, no deformation or failure of this lathing, and less clogging phenomena during filtration, confirming the maximum flux Darcy's law. In the case of raw water the obtained flow rates were much smaller, indicating a deposit on the surface area of the membrane blocking its pores [1].

### **b) Membrane and total resistances:**

The membrane and total resistances are presented in this part, using the Darcy law knowing the permeate flux values for different transmembrane pressures. The membrane resistance was determined when the distilled water was used, and the total resistance in the case of the raw water was ( $RT = R_m + R$ ) with  $R$  is the resistance of the deposit.

### **d) Color of the water:**

In this case the time of filtration was set up for a period of 50 minutes, it is followed by the color of filtered water this is realized as preliminary experience, the figure 4 ((a) and (b)) shows the variation of the color of filtered water in comparison with the one of the concentrate and raw water.

According to the face (figure4), we notice a very good clarification of the water filtered, translated by very clear (net) change of the color during the microfiltration of the raw water (food) ((supply)). It was noticed as well, as after several tries (essays), an unwanted smell appeared in the raw water and concentrate this unwanted smell disappeared in the filtered water.

### **c) Suspended matter:**

In Figure 5 the lines there for obtained shows that there is one rating of abatement as of suspended matter (MES) for the filtered water in front of raw water, both, show that quantity of the MES constant according to rest time; this result shows that membrane: has a limit of collecting of MES; Reviews on the other hand the concentrate, quantity of suspended matter is increasing through broken line; MES retentate (concentrate) increase during the filtration proves the a retention of suspended matter.

### **e) Dry Residue:**

In Figure 6 there for obtained a one line shows that quantity of the residues is constant dryness in filtered water (It does not vary with the time of filtration) Explains why this has always some quantity of the dry residue After filtration a less wide quantity compared to the second right-hand side which represents the quantity of the residues dryness of feed water (raw water), the last variation of the dry residues of recycled water is that, one note that there is an increase in the dryness residues with time which explains why the membrane lets pass water and pure water prevented a significant amount of the non dissolved matters.

### **f) Turbidity:**

The study of turbidity confirmed the results as of MES and of the dry residues, Figure 7 showed the variation of turbidity according to time, for raw, filtered and recycled water. The time of filtration was fixed at 60 minutes.

In Figure 7 shows obtaining two straight lines parallel with the x-axis, there are filtered water and raw water, it should be noted that for filtered water we obtain a turbidity respecting standards' of drinking

water That we obtains a filtered water turbidity Respecting the standards of drinking waters (Lower Turbidity or equalizes to 1 NTU).

The second line port whose feed water turbidity is between 5 and 10 NTU. A third line there for obtained recycled water (concentrated) but this one Increase with time, this Increase Explains why the pure water from the solution was separated by filtration.

## 5. Conclusion:

Membrane separation processes are more and more developed these last years, particularly those based on microfiltration, ultrafiltration and nanofiltration. These latters have shown their capacities in the production of drinking water.

The present study showed that when microfiltration was used in the treatment of drinking water since significant improvements of water quality were recorded with performance in terms of flow, of permeability, resistors and Suspended matter. Through the obtained results, one can conclude that microfiltration represents a very interesting technology in the field of water treatment destined to consumption

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# Supercritical CO<sub>2</sub> Extraction of Essential Oil from Algerian Fennel (*Foeniculum vulgare Mill*)

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## **Abstract**

*The technology of supercritical CO<sub>2</sub> has real advantages qualitatively and ecologically. In fact, it does not use organic solvents or high temperatures, and does not generate wastes. Its solvent power allows the extraction of many molecules. From an environmental point of view, CO<sub>2</sub> is a non-toxic gas which advantageously replaces many organic solvents subject to regulations getting ever severe. It does not contribute to the greenhouse effect, being used in a closed circuit.*

*The present work presents some findings particularly concerning the use of supercritical fluid in the extraction process of oil fennel at different temperatures and pressures. Fennel oil has been extracted using supercritical CO<sub>2</sub>, investigating the influence of pressure and temperature and representing extraction curves.*

**Keywords:** *Supercritical extraction; Supercritical CO<sub>2</sub>; Fennel seeds, Critical state*

## **Résumé**

La technologie du CO<sub>2</sub> supercritique présente d'incontestables atouts sur les plans qualitatif et écologique. En effet, elle n'utilise pas de solvants organiques, ni de fortes températures, et ne génère pas d'effluents. Son pouvoir solvant à géométrie variable, permet d'extraire de nombreuses molécules.

D'un point de vue environnemental, le CO<sub>2</sub>-SC est non toxique, remplace avantageusement de nombreux solvants organiques soumis à des réglementations de plus en plus sévères. Il ne contribue pas à l'effet de serre, étant utilisé dans un circuit fermé.

Cette étude entre dans ce cadre, elle présente un des travaux réalisés, et concerne en particulier l'utilisation de fluide supercritique dans le processus d'extraction de l'huile de fenugrec à différentes températures et pressions, utilisant du CO<sub>2</sub> supercritique. L'influence de la pression et de la température en tant que variables dépendantes a été étudiée et les courbes d'extraction en représentées.

**Mots-clés:** Extraction supercritique ; CO<sub>2</sub> Supercritique ; Graines de fenouil ; Etat critique.

## **1. Introduction**

Supercritical fluid extraction is a technique where the solvent is a fluid at supercritical conditions. Supercritical fluids are characterized by a low viscosity close to that of gases, a density close to that of liquids and a high diffusivity. Thus, supercritical fluids may behave as solvents with a great solvent power enhancing the solubility of the compounds with adequate changes in the operating conditions of pressure and temperature.

Therefore many industrial fields are interested in the technology of supercritical CO<sub>2</sub> with its numerous applications such as decaffeination, removal of contaminants, purification of protein, extraction of flavors, extraction of essential oils, odor, discoloration, etc. Several other supercritical fluids are considered, particularly water and propane, but the most widely used one remains CO<sub>2</sub> upon which this technology is based due to its adjustable solvent power at the applied conditions of pressure and temperature, its great availability, non toxicity, low cost, etc. Also its supercritical state is reached at a pressure just over 74 bar and a temperature of 31 ° C, making very suitable for thermolabile compounds. CO<sub>2</sub> has also very particular properties like a high diffusivity of the order of that of a gas and a high density similar to that of a liquid, hence a good ability to diffusion, and good transport properties and solvent power, respectively, ensuring good extracting properties [1- 3].

An extraction process with supercritical CO<sub>2</sub> is operated in a closed loop, having pressurizing means (pumps) and heating means (heat exchangers) to bring it above its critical point. The product to be treated is placed in an extractor through which flows a supercritical CO<sub>2</sub> stream. The fluid charged with the extracted compound is then expanded to separate from the extracted compound. The latter is collected in a separator.

Fennel (*Foeniculum vulgare* Mill, family Umbelliferae) is an annual, biennial, or perennial aromatic herb, depending on the variety. It has been known since antiquity in Europe and Asia. The leaves, stalks, and seeds (fruits) of the plant are edible. The dried, aromatic fruits are widely used in culinary preparations for flavoring bread and pastry, in candies, and in alcoholic French liquors, as well as in cosmetic and medicinal preparations [4]

The present study is concerned with the supercritical CO<sub>2</sub> extraction of oil from local fennel seeds as well as the comparison of extraction yields and compositions of the extracts and distilled oil and the evaluation of its organoleptic characteristics obtained according to different methods [2].

## 2. Materials and methods

**Solvents:** Extractions were carried out with carbon dioxide of 99.7% purity supplied by Air Mediterranean sea liquid (France).

**Fennel Seeds:** The fennel seeds used were purchased from a local market in Algeria in the city of Constantine. The moisture content of the raw material was 7.5% (w/w). The seeds were ground to specific particle size before the extractions. A typical particle size distribution was studied.

### Equipment and Extraction.

#### *Analytical SFE Equipment*

The experimental device shown in Figure 1 used at the laboratory scale (SFE20ml) was provided by Separex (champigneulles, France). It allows working with three autoclaves of capacity 5, 10 and 20 cm<sup>3</sup>. In the present work the 5cm<sup>3</sup> was used at a maximum pressure of 400 MPa and a flow rate of 0.5kg / hour.

The extraction autoclave was filled with an homogeneous mixture of fennel powder. The liquid CO<sub>2</sub> was a priori cooled by a cryogenic bath over (0°C), filtered and then pumped into the extractor until the working pressure was reached. Before entering the extraction autoclave, CO<sub>2</sub> was pre-heated to the

desired extraction temperature. Supercritical CO<sub>2</sub> then came into contact with the dried seed. The pressure and the flow rate were maintained constant by using the expansion valve.

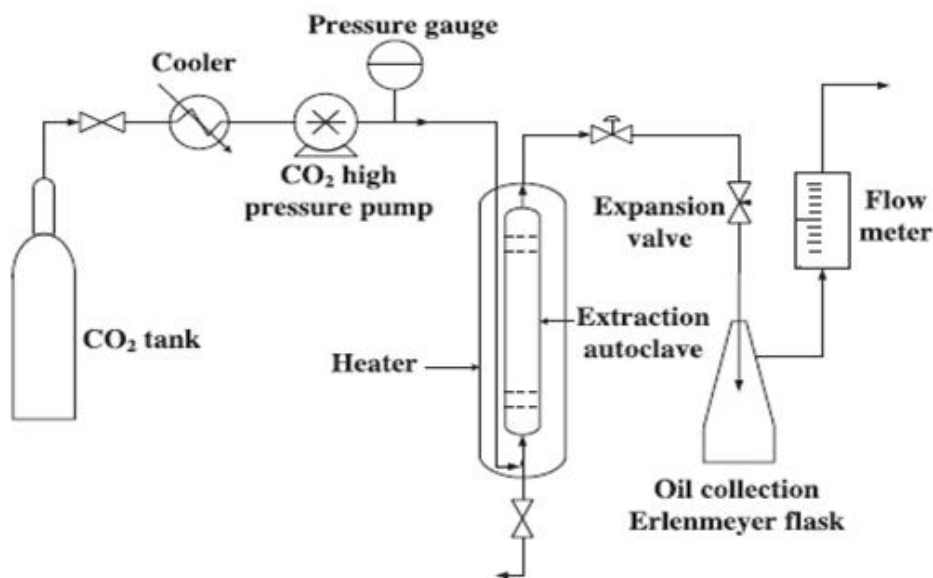


Fig.1. SC-CO<sub>2</sub> extraction apparatus.

### 3. Results and discussion

In order to obtain the best conditions for the SC-CO<sub>2</sub> extraction of fennel seeds, experiments were performed at different pressure–temperature settings of the extractor. The selection of pressure and temperature ranges was based on the fact that a great change in the density and dielectric constant of CO<sub>2</sub> occurred between 100 and 400 bar, and in order to prevent the thermal degradation of some volatile oil compounds, temperatures up to 55°C were applied. The pressure varied from 100 to 400 bar and temperature from 35 to 55°C.

The Extraction yields expressed as grams of extracted oil/grams of seeds are represented in Figure 2. And Table 1 shows the experimental conditions which prevailed in each performed experiment. The effects of pressure and temperature on the supercritical CO<sub>2</sub> extraction yield were studied. The extraction yield was found to vary significantly with temperature and pressure.

Table 1. SFE experimental conditions for fennel seeds extraction

| Run | Pressure (bar) | Temperature (c°) | Time (min) | Flow (g/min) |
|-----|----------------|------------------|------------|--------------|
| 1   | 100            | 35               | 120        | 50           |
| 2   | 100            | 45               | 120        | 50           |
| 3   | 100            | 55               | 120        | 50           |
| 4   | 250            | 35               | 120        | 50           |
| 5   | 250            | 45               | 120        | 50           |
| 6   | 250            | 55               | 120        | 50           |
| 7   | 400            | 35               | 120        | 50           |
| 8   | 400            | 45               | 120        | 50           |
| 9   | 400            | 55               | 120        | 50           |

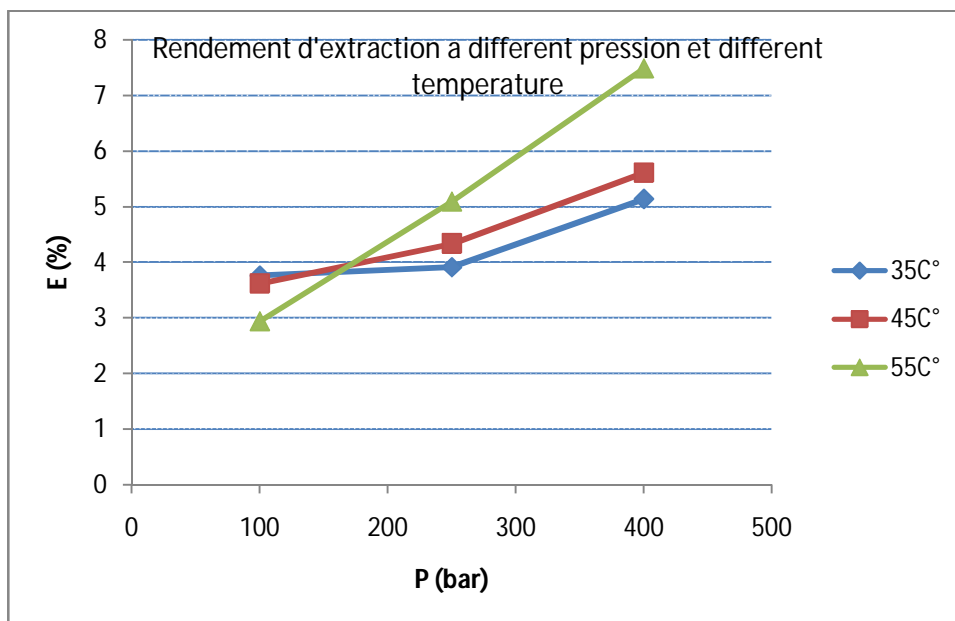


Fig. 2. Effects of the extraction pressure and temperature on the extraction degree of the essential oil

At 100 bar, the total amount of the obtained extract was unusually small but, as pressure increased, the amount of extracted material increased (Fig. 2). It was found that at higher pressures (250 and 400 bar) the solubility of some compounds from vegetable matter changed from negligible to significant. This is explained by the fact that the density and viscosity of supercritical CO<sub>2</sub> changed and, therefore, its extracting power increased. However, the high pressure resulted in greater cost for the extraction operating system.

It should also be noted that the appearance of the extracts changed slightly with the increase of temperature and pressure. The color, which was straw yellow at lower pressure and temperature, became darker, particularly with increasing temperature. Increased temperature at pressure of 250 and 400 bar, had a favorable effect on the extraction efficiency although the change was not significant.

At 100 bar, the effect of temperature on the extraction was negative, the effect of temperature on density was less pronounced and the solute vapor pressure effect dominated, leading to oil solubility and an increase in the yield with temperature. At 400 bar and 55°C the decrease in the diffusivity led to a reduction in the interaction between the supercritical fluid and the solute contained within the matrix and this in turn led to a decrease in the yield of the extraction process. The extraction yields obtained by SFE at 55°C and 400 bar were higher and reached 7.5%.

#### 4. Conclusion

The supercritical CO<sub>2</sub> technology makes use of the supercritical fluid solvent power that can be modulated according to the applied pressure and temperature conditions, allowing selective extractions. The resulting products do not contain solvent residues, an important advantage towards the environment. This is a clean technology without wastes. Furthermore, the use of co-solvents modifies the solvent power of supercritical CO<sub>2</sub> and allows additional opportunities for this extraction process.

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## Modelling of liquid-solid equilibria and determination of a new group interaction parameters for unifac method

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### **Abstract**

The objective of this study is to predict solid-liquid equilibria by means of the UNIFAC model for systems containing certain groups like (AC-Cl) and (CHO) for which the interaction parameters are not available. The model is tested on four systems such as (Hexachlorobenzene – dibutylether), (Hexachlorobenzene – MTBE), (Chloro benzoic acid – diisopropylether) and (Chloro benzoic acid – dibutylether). The agreement between the predicted results and the experimental values was very encouraging. The obtained interaction parameters will be further test on other systems.

**Keywords :** Solid-Liquid equilibria, UNIFAC, group interaction parameters.

### **Résumé**

L'objectif de ce travail est de prédire les équilibres solide-liquide en utilisant le modèle UNIFAC pour des systèmes contenant des groupes tels que (AC-Cl) et (CHO) dont les paramètres d'interaction pour ce modèle ne sont pas disponibles. Le modèle a été testé pour quatre systèmes (Hexachlorobenzène – dibutyléthère), (Hexachlorobenzène – MTBE), (4-Chlorobenzoique acide – diisopropyléthère) et (4-Chlorobenzoique acide - dibutylether). La déviation entre les résultats calculés et les valeurs expérimentales est assez encourageante et les paramètres interaction obtenus seront testés en considérant d'autres systèmes.

**Mot Clé :** équilibre Solide - Liquide, UNIFAC, paramètres d'interaction de groupe.

### **1. Introduction**

Thermodynamic models are increasingly used by the pharmaceutical industry at different stages of the product and process development and optimization processes. At the product development and formulation stage, various solvents are screened for new pharmaceutical molecules. At the later stage of process development and optimization, appropriate selection of a solvent or a mixture of solvents is critical for the crystallization and other processes. Most of the pharmaceutical molecules are significantly more complex than molecules encountered in oil and chemical industry, with multiple functional polar and hydrogen bonding groups. At the same time, experimental physical property data for most of the pharmaceutical molecules of interest are substantially more limited than data for hydrocarbons and other compounds relevant to oil and gas industries. Generally the solubility of pharmaceutical compounds in various solvents is a key parameter. Its measuring is not always easy and may also be an arduous task when several systems are to be tested. Consequently in this work, the modeling of the solubility of Hexachlorobenzene and 4-chlorobenzoic acid reported in the literature [1] and [2] was carried out using the group contribution method UNIFAC (UNIversal Functional group Activity Coefficients) [3]

## 2. Methodology

### 2.1 Thermodynamics of Solid – Liquid equilibrium

Similarly to other phase Equilibria, the required thermodynamic relations for solid –liquid can be derived starting from the isofugacity criterion [4]:

$$f_i^s = f_i^l \quad (1)$$

Where  $s$  refers to solid state and  $l$  to the liquid state. The fugacity of the solute in the liquid phase may be expressed as [5]:

$$f_i^l = x_i^l \gamma_i^l f_i^{\circ l} \quad (2)$$

With  $f_i^{\circ l}$  representing the fugacity of the pure solute in a subcooled liquid state below its melting point. When the solvent does not enter the solid phase, the fugacity of the solid solute remains that of pure solid:

$$f_i^s = f_i^{\circ s} \quad (3)$$

Using Eq. (1), the solubility of the solute  $i$  in the liquid phase can be calculated by:

$$x_i^l \gamma_i^l = \frac{f_i^{\circ s}}{f_i^{\circ l}} \quad (4)$$

An expression for the ratio of the standard fugacities can be obtained via a thermodynamic cycle and after some justified simplifications (Gmehling and al, 1992), as follows:

$$\ln \frac{f_i^{\circ s}}{f_i^{\circ l}} = \frac{\Delta H_m}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right) \quad (5)$$

With the subscript  $m$  denoting the melting point.

Substituting Eqn. 4 into 5 gives:

$$\ln(x_i^l \gamma_i^l) = \frac{\Delta H_m}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right) \quad (6)$$

And hence the solubility  $x_i^l$  of a solute in a solvent or solvent mixture which is expressed as:

$$x_i^l = \frac{\exp\left[\frac{\Delta H_m}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)\right]}{\gamma_i^l} \quad (7)$$

For the determination of the solubility, knowing the melting point  $T_m$  and the heat of fusion  $\Delta H_m$  the only required parameter is the activity coefficient of component  $i$ . While the pure component data can directly be read from the Dortmund Data Bank (DDBST) [5], which presents one of the most reliable data banks for pure component and mixture properties. The activity coefficient  $\gamma_i$  can be calculated by means of thermodynamic models.

### 2.2 Modeling section

UNIFAC is based on the group contribution concept, which assumes that a mixture does not consist of molecules but of functional groups. This reliable and fast technique is described in detail by Fredenslund et al (1977) [3]. According to this model the activity coefficient is expressed as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (8)$$

The first term  $\ln \gamma_i^C$  concerns the combinatorial part and takes into account the differences in sizes and shapes of the molecules. It can be calculated using van der Waals volumes  $R_k$  and surface areas  $Q_k$  of the functional groups. The second term  $\ln \gamma_i^R$  is the residual part which takes into account the intermolecular forces. The determination of these two contributions requires the knowledge of volume ( $R_k$ ) and surface area ( $Q_k$ ) group parameters as well as binary interaction parameters ( $a_{mn}$ ) which may or may not be available in the corresponding tables reported in the literature base [6].

### 2.3 Estimated interaction parameters procedure

The binary group interaction parameters involving ACCL group with ether groups, required for the UNIFAC model were retrieved in the present work using the Nelder-Mead method [14] for the minimization of the following objective function ( $F_{obj}$ ) defined as the sum of the squared deviations between the experimental and calculated mole fractions:

$$F_{obj} = \sum_{i=1}^N (x_{i(exp)} - x_{i(cal)})^2 \quad (9)$$

with N denoting the number of data points.

### 3. Results and discussion:

Table 1 shows the solubility data results obtained by means of UNIFAC equation and the experimental data reported by Acree Jr (2013) for the considered systems presented in this work, which are assessed by calculating the average absolute relative deviation (AARD) defined as follows:

$$AARD = \frac{1}{n} \sum_{i=1}^n \left| \frac{x_{i(exp)} - x_{i(cal)}}{x_{i(exp)}} \right| \quad (10)$$

Where  $n$  is the number of experimental points;  $x_{i(cal)}$  is the solubility calculated using UNIFAC equation;  $x_{i(exp)}$  is the experimental solubility reported in literature. This comparison is also shown by Figures 1 where clearly the predicted results using UNIFAC model are in very good agreement with the experimental values.

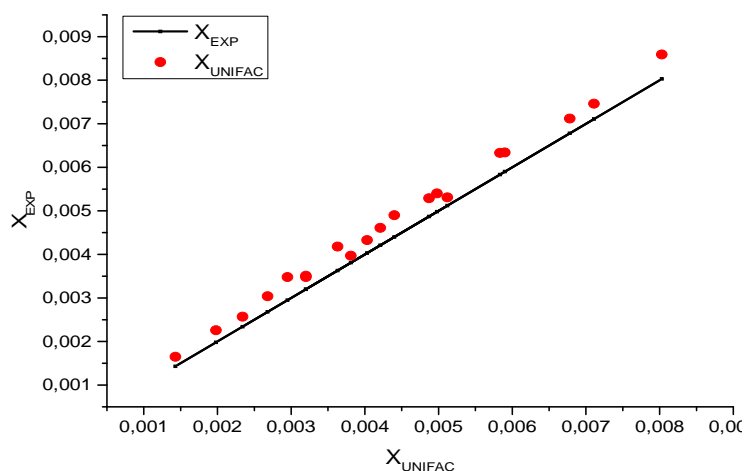


Figure 1: Assessment of UNIFAC model.

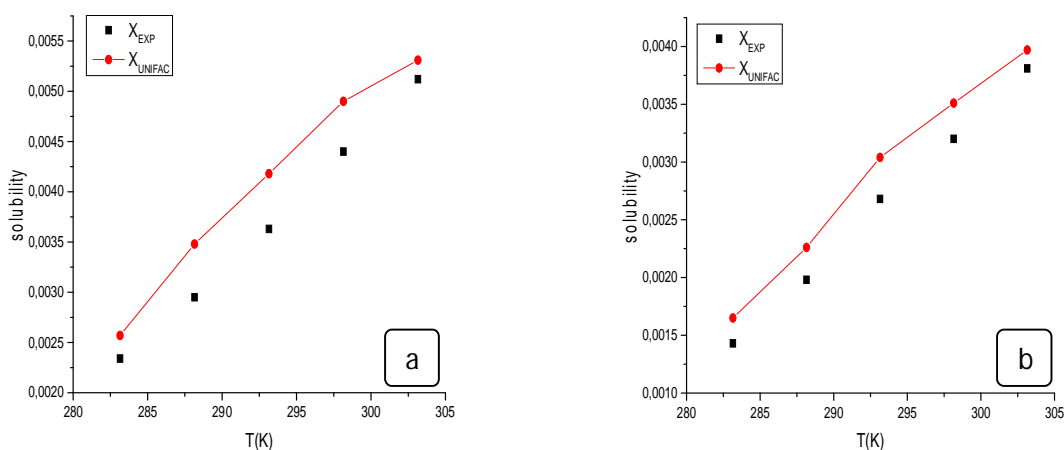


**Table 1:** Comparison of experimental and calculated solubilities.

| SOLUTE               | SOLVENT         | T(K)   | X <sub>EXP</sub> | X <sub>UNIFAC</sub> | AARD (%) |
|----------------------|-----------------|--------|------------------|---------------------|----------|
| Hexachlorobenzene    | Dibutylether    | 283.15 | 0.00234          | 0.00257             | 9.8290   |
|                      |                 | 288.15 | 0.00295          | 0.00348             | 17.9661  |
|                      |                 | 293.15 | 0.00363          | 0.00418             | 15.1515  |
|                      |                 | 298.15 | 0.0044           | 0.0049              | 11.3636  |
|                      |                 | 303.15 | 0.00512          | 0.00531             | 3.7109   |
| Hexachlorobenzene    | MTBE            | 283.15 | 0.00143          | 0.00165             | 15.3846  |
|                      |                 | 288.15 | 0.00198          | 0.00226             | 14.1414  |
|                      |                 | 293.15 | 0.00268          | 0.00304             | 13.4328  |
|                      |                 | 298.15 | 0.0032           | 0.00351             | 9.6875   |
|                      |                 | 303.15 | 0.00381          | 0.00397             | 4.1994   |
| 4-chlorobenzoic acid | disopropylether | 283.15 | 0.00421          | 0.00461             | 9.5011   |
|                      |                 | 288.15 | 0.00498          | 0.0054              | 8.4337   |
|                      |                 | 293.15 | 0.0059           | 0.00634             | 7.4576   |
|                      |                 | 298.15 | 0.00678          | 0.00712             | 5.0147   |
|                      |                 | 303.15 | 0.00803          | 0.00859             | 6.9738   |
| 4-chlorobenzoic acid | Dibutylether    | 283.15 | 0.0032           | 0.00348             | 8.75     |
|                      |                 | 288.15 | 0.00403          | 0.00433             | 7.4441   |
|                      |                 | 293.15 | 0.00487          | 0.00529             | 8.6242   |
|                      |                 | 298.15 | 0.005833         | 0.00633             | 8.5204   |
|                      |                 | 303.15 | 0.00711          | 0.00746             | 4.9226   |

The estimated interaction parameters of (ACCl /CH<sub>2</sub>O) and 1 (CH<sub>2</sub>O / ACCl) were 2273.81 and 3031.74, respectively and their use led to solubility results in a quite good agreement with the data reported in the literature

For a better representation of solid-liquid phase equilibrium, the corresponding diagrams are shown for chosen systems. Figures 2(a & b) and 3(a & b) show the comparisons of the obtained results by means of UNIFAC model with the experimental values. UNIFAC results were in a very good agreement with the experimental values.



**Figure 2:** Solid-liquid equilibrium for Hexachlorobenzene in a)Dibutylether and b) MTBE

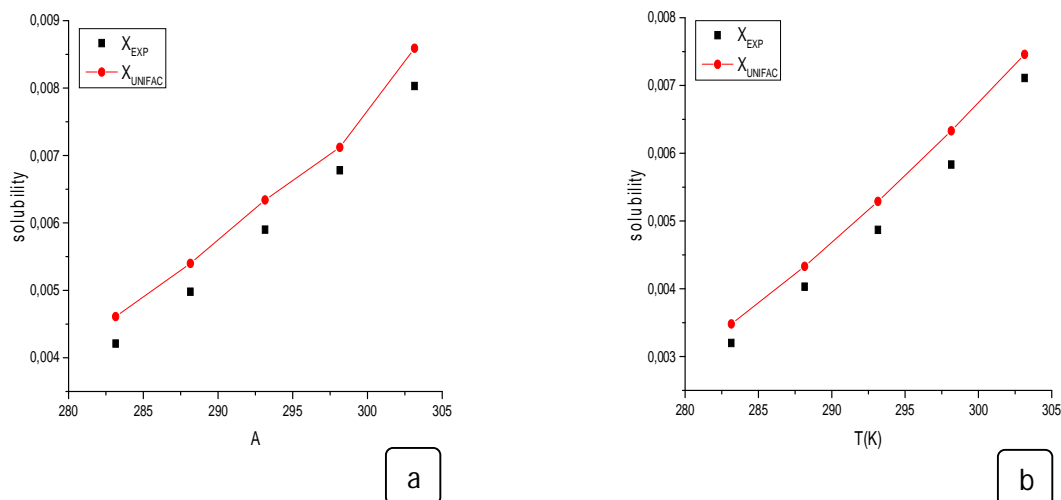


Figure 3: Solid-liquid equilibrium for 4-Chlorobenzoic acid in a) Diisopropylether and b) Dibutylether

#### 4. Conclusion :

The present study has clearly demonstrated the importance of modeling solid-liquid phase equilibria, particularly for sensitive industrial fields like pharmaceuticals. However, the influence of the molecular structure decomposition into groups, on the accuracy of activity models like the UNIFAC has also been showed. Globally the models using molecular interaction parameters led to more accurate results compared to models using group interaction parameters like the UNIFAC. This is perhaps due to the fact that any group contribution approach is assumed approximately to be additive.

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