Tertiary treatment of a secondary effluents by Coagulation adsorption ultrafiltration

Comparative Study between two coagulants used:
The Ferric Chloride and the Calcium Chloride

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Abstract

In view of deficiency of the water resources in Algeria, the wastewater treatment and reuse permits, on the one hand to protect the environment and, on the other hand, to bring fertilizers to the cultures, while reducing or eliminating employment of chemical fertilizers. In order to limit the pollution to the hydrosphere and to find non conventional hydrous resources, we were interested in the treatment by coupling coagulation – adsorption with the ultrafiltration of the secondary effluents of the wastewater treatment plant at Staouéli with the average characteristics in the chemical oxygen demand (COD) 46mg/l and turbidity, 16 NTU. (Algeria). The comparative study was made by using two coagulants: the ferric chloride FeCl₃, 6H₂O and the calcium chloride CaCl₂, 2H₂O. In a first stage, gravel bank tests were made giving the best efficiency on chemical oxygen demand. The coagulation test showed a COD value equal to 12 mg/l at pH = 6.5 for CaCl₂, concentration equal to 50 mg/l. The best COD final value equal to 10 mg/l can be obtained with FeCl₃ concentration 20 mg/l at pH 6. In the second step, the coupling coagulation ultrafiltration was made by using a tubular mineral membrane of ultrafiltration M2 (15Kg/mol) in tangential mode with a transmembrane pressure ∆P = 1bar and a cross flow velocity U = 3 m/s. The results showed residual values of COD equal to 5 mg/l in the presence of CaCl₂ and 3.6 mg/l in the FeCl₃ presence. The process corresponds to interesting permeate flux, an increase of 30 % for FeCl₃ and 18 % for CaCl₂ are observed. This is allotted to the particles agglomeration and consequently to the larger flocs formation inside the feed tank; the possible deposit on the membrane would be thus more permeable. In a third step, the coupling coagulation adsorption to ultra filtration was made. The adsorbent selected is powder activated carbon (PAC). Indeed, the addition of concentration 20 mg/l of FeCl₃ and 40 mg/l of PAC made it possible to increase 34 % of the permeate flux for FeCl₃ with and residual COD equal to 3 mg/l. In the same way, the addition of 50 mg/l in CaCl₂ and 40 mg/l of PAC permits to increase 23 % in the permeate flux with a final COD value equal to 4mg/l. The use of calcium hydroxide as a coagulant can advantageously replaces ferric chloride. Its relatively low cost, availability and ecological innocuity make it preferable compared to other coagulants usually used. Keywords: Wastewater; Coagulation; Adsorption, Ultrafiltration; Reuse

Introduction

The last decade gave place to a degradation which does not cease threatening the man and his environment and particularly water. The objective of the secondary
wastewater treatment is obtaining a water which could be used within the framework of measurements necessary to a good management of water (recycling, reuse).

Former studies were undertaken and proved the efficiency of the treatment by coupling coagulation- microfiltration, or by coupling coagulation ultrafiltration. Thus, Al Malack and Anderson [1] which used aluminium sulphate like coagulant to amounts from 20 to 120 mg/l with pH=7 coupled with microfiltration for the domestic wastewater treatment, led to an improvement of the permeate flux values. Caroll et al. [2] showed that the coagulation treatment improves the removal of natural organic matter and reduces membrane fouling, while small molecular weight, non ionic, hydrophilic NOM that are poorly removed by coagulating are responsible for fouling after coagulation process.

Shon et al. [3] showed that the ultrafiltration membrane was used with this pre-treatment: flocculation followed by adsorption leading to a total organic carbon removal of 90 % in order to treat biologically treated sewage effluent.

Sharp et al. [4] studied that the dynamic membrane’s mode of operation achieved higher state flux values than ultrafiltration alone and than conventional coagulation pre-treatment ahead of ultrafiltration, while in line coagulation displayed the worst flux decline. Kim et al. [5] were suggested that organic matter in the molecular weight ranges 300-2000 and 20000-40000 Da were mainly responsible for the fouling. Choi et al. [6] have evaluated in line coagulation to improve performance during ultrafiltration. In line coagulation means use of coagulants without removal of coagulated solids prior to ultrafiltration. It has been reported that effective conventional coagulation conditions produced larger particles and this reduced fouling during membrane filtration by reducing adsorption in membrane pores.
- To this end, we implemented treatments of coupling coagulation ultrafiltration and coagulation adsorption ultrafiltration on a secondary effluent.
- The coagulants used are calcium chloride, ferric chloride; and the adsorbent, of the powder activated carbon (PAC).

**Experimental conditions**

1. Experimental set-up

   It consists of a feed tank (1) where each coagulant is added at the beginning of the test, a heat exchanger (2), a centrifugal pump (3), a flow meter (4), control valves (5), manometers(6), and a tubular ultrafiltration module (7).

![Experimental set-up](image-url)
The membrane used is inorganic membrane (CARBOSEP M2) with respectively 15Kg/mol. The operating conditions are: transmembrane pressure $\Delta P = 1$ bar, cross flow velocity $U = 3$ m/s, temperature 298 K, Duration of the filtration tests: 180 minutes.

2. Characteristics of the raw water
The secondary effluent of the wastewater treatment plant of Staoueli (Algeria) has the following average characteristics:
Temperature = 23 °C; pH = 7.5; Turbidity = 16 NTU; SS = 35 mg/l; BOD$_5$ = 30 mg/l; COD = 46 mg/l; Conductivity = 1150 µS/cm.

3. Experimental procedures
This study was made in three steps:
- Step 1: gravel bank tests – test normalizes AFNOR (coagulation) in order to determine the optimum conditions of pH and concentration in each coagulant giving the best efficiency on the COD.
- Step 2: the test of coupling coagulation - ultrafiltration in tangential mode.
- Step 3: the test of coagulation - adsorption – ultrafiltration, we simultaneously added powdered activated carbon and coagulant in the feed tank in order to identify the most effective treatment meeting the required irrigation standards.

4. Reagents used
The coagulant used: CaCl$_2$ 2H$_2$O, Its masse molar is 147.02 g/mol and FeCl$_3$ 6H$_2$O with a molecular mass of 270.3 g/mol.
The powdered activated carbon PAC (anticromos) obtained from Ceca Italiana whose characteristics are given in the table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>The BET surface area, m$^2$/g</td>
<td>600-800</td>
</tr>
<tr>
<td>The iodine number, g/g 10$^3$</td>
<td>760</td>
</tr>
<tr>
<td>Humidity, %</td>
<td>15.6</td>
</tr>
<tr>
<td>Density, g/ m$^3$ 10$^{-3}$</td>
<td>0.41</td>
</tr>
<tr>
<td>Granulometry, refusal on a sieve of an opening of 20. 10$^{-6}$ m</td>
<td>85 %</td>
</tr>
</tbody>
</table>

Results and discussion

1. Determination of the coagulation optimal conditions
1.1. COD reduction
The figures 2, 3 show the variation of COD, as function of each coagulant concentrations at different pH values.
Figure 2 : Test of coagulation- setting in the jar test : Residual chemical oxygen demand as function of coagulant concentrations FeCl₃ (a) ; CaCl₂ (b) at different pH values.

Shape of the curves giving the evolution of the COD according to the concentration in coagulant revealed three distinct zones: a decreasing zone with reduction in the parameter as proportional to the increasing coagulant concentration, which corresponds to a destabilization of the colloidal particles; a zone representing the interval of the optimal amounts in coagulant and thus a neutralization of the electric charges of the particles; an increasing zone; which corresponds to a restabilisation of the colloidal particles. The figure 2a shows that the best values of the residual COD is 12 mg/l corresponding to the optimum conditions for coagulation with a concentration in CaCl₂ equal to 50 mg/l at pH = 6.5. The best COD final value equal to 10mg/l can be obtained with FeCl₃ concentration 20 mg/l at pH 6.

2. Coupling coagulation – ultrafiltration
2.1. Variation of the permeate flux according to time

The variation of the permeate flux according to the concentration in FeCl₃ (a) and CaCl₂ (b) is represented on fig. 3. These values are more significant after coagulation. This is allotted to the agglomeration of the particles and consequently to the formation of bulkier flocs inside the vat of food; the deposit made up with the membrane wall would be thus more permeable. An increase of 30 % for FeCl₃ corresponds to interesting permeate flux for FeCl₃ concentration equal to 20 mg/l at pH 6. An increase of 18 % of the permeate flux is observed at concentration of 50 mg/L in CaCl₂ at pH = 6.5.
3. Performances Coagulation-Adsorption-Ultrafiltration (FeCl₃/PAC/UF)

3.1. Evolution of permeate flux with time (Membrane M2)

Fig. 3 shows the variation of the permeate flux according to the time for the different processes. It gives place to a significant improvement of the permeate flux. Indeed, the addition of concentration 20 mg/l of FeCl₃ and 40 mg/l of PAC made it possible to increase 34% of the permeate flux for FeCl₃. In the same way, the addition of 50 mg/l in CaCl₂ and 40 mg/l of PAC permits to increase 23% in the permeate flux. These values emphasise that the adsorbent addition (PAC) indeed contributed to the increase in this permeate flux.

3.2. COD Reduction

The quality of the permeate was very good with a residual COD equal to 3 mg/l for FeCl₃ and the variation with time was quite similar for both coagulants (FeCl₃ and CaCl₂) with a final COD value equal to 4 mg/l for CaCl₂.
3.3. Comparative study between two coagulants

In order to better justify the use of CaCl\textsubscript{2} 2H\textsubscript{2}O as a coagulant, and to judge its efficiency in the wastewater treatment worn for a reuse, in irrigation, we compared the most satisfactory results obtained after treatment by coagulation – adsorption – ultrafiltration coupling with those obtained by a former study, in the presence of ferric chloride (FeCl\textsubscript{3} 6H\textsubscript{2}O) which already proved reliable like coagulant under the same operating conditions. We will compare also these results with the irrigation and potability standards (table 2).

Table 2: Comparison of the obtained results after coagulation: by CaCl\textsubscript{2} 2H\textsubscript{2}O; FeCl\textsubscript{3} 6H\textsubscript{2}O, with the norms of irrigation and potability

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Values</th>
<th>Coagulation by CaCl\textsubscript{2}</th>
<th>Coagulation by FeCl\textsubscript{3}</th>
<th>Irrigation Norms</th>
<th>Potability Norms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity, NTU</td>
<td>16.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>COD, mg d'O\textsubscript{2}/l</td>
<td>46.0</td>
<td>5.0</td>
<td>3.6</td>
<td>150.0</td>
<td>2.0</td>
</tr>
<tr>
<td>BOD\textsubscript{5}, mg d'O\textsubscript{2}/l</td>
<td>15.0</td>
<td>4.0</td>
<td>3.0</td>
<td>10.0</td>
<td>3.0</td>
</tr>
<tr>
<td>PO\textsubscript{4}\textsuperscript{3-}, mg/l</td>
<td>6.0</td>
<td>1.3</td>
<td>1.2</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}, mg/l</td>
<td>3.2</td>
<td>2.8</td>
<td>2.8</td>
<td>*</td>
<td>50.0</td>
</tr>
<tr>
<td>NO\textsubscript{2}\textsuperscript{-}, mg/l</td>
<td>0.15</td>
<td>0.107</td>
<td>0.100</td>
<td>*</td>
<td>0.100</td>
</tr>
<tr>
<td>Fe, mg/l</td>
<td>0.23</td>
<td>0.205</td>
<td>0.250</td>
<td>0.500</td>
<td>0.300</td>
</tr>
<tr>
<td>Mn, mg/l</td>
<td>0.11</td>
<td>0.10</td>
<td>0.07</td>
<td>0.20</td>
<td>0.50</td>
</tr>
</tbody>
</table>

* N\textsubscript{total} = 40.0 mg/l

The results obtained by using calcium chloride are of the same order of magnitude as those obtained with ferric chloride. In addition, these results are in conformity with the standards of irrigation. The calcium chloride thus proves to be a good coagulant and would be more adequate for a re-use in irrigation.
Conclusion

The addition of FeCl$_3$ or CaCl$_2$ and PAC with ultrafiltration improves the permeate flux and the quality of the permeate. The use of Calcium chloride as coagulant can advantageously replace that of FeCl$_3$ with the variability of raw waters (turbidity of water during the rain time). Its relatively weak cost, its availability and its ecological inocivity, make it possible to privilege it compared to the other coagulants usually used.

References


 ومعالجة المياه القذرة الثانوية باستعمال تخلير - امتزاز فوقي تصيفية لدراسة التقارن بين تخترين: الكلوريد الحديد بالكلوريد الكلسيوم

عبد الصمد جمال و.ن.زال

جامعة هواري بومدين للعلوم والتكنولوجيا - باب الزور - الجزائر

إن الهدف من الدراسة الآتية هو معايلة المياه القذرة الثانوية بطريقة الازدوج تخلير - امتزاز مع تقسيم غشائية - فوق تصيفية معايلة في محطة تصيفية سطحية الجبال. خصصت المياه أين أجريت عليها التجاري هي الطلب الكيميائي الأكسجين (COD=46 مع/ل) قياساً للنVBoxLayout في المرحلة الأولى تم تجارب معالجة المياه عن طريق تقنية واحدة ألا وهي التخلير وذلك باستعمال محتار و كانت النتائج بالنسبة للمرحل الأولى وهو الكلوريد الكلسيوم>CaC2 محصلة على الطلب الكيميائي الأكسجين12 مع/ل في وسط pH=6.5. تركز تماستل إلى 50 مع/ل بالنسبة المجرح الثاني وهو الكلوريد الحديد تركيز 20 مع/ل في pH=6.10 مع/ل إلى خفض الطبي الكيميائي الأكسجين من 46 إلى 10 مع/ل.

في المرحلة الثانية تم دراسة توصية أبدًا تقنياً لازدوج تخلير - فوق تصيفية وكذا باستعمال غشاء U=3m/س وضغط P=1bar سطحي (15gK/molM2) في وضغط P=1bar. وقد أصلحت نتائج المعالجة من خلال ازدوج تطير تقني في خفض الطبي الكيميائي الأكسجين حتى 5 مع/ل (الكلوريد الكلسيوم) إلى 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، استخدم ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد). في المرحلة الثالثة، تم استخدام ثلاث تقنيات في آن واحد، تخلير - امتزاز فوق تصيفية مضمنة 3 مع/ل(الكلوريد الحديد).