COMBINING LIME SOFTENING WITH COAGULATION/FLOCCULATION TO MINIMIZE THE ENVIRONMENTAL IMPACT OF REVERSE OSMOSIS REJECTS

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7th ANQUE's INTERNATIONAL CONGRESS

"INTEGRAL WATER CYCLE: PRESENT AND FUTURE“

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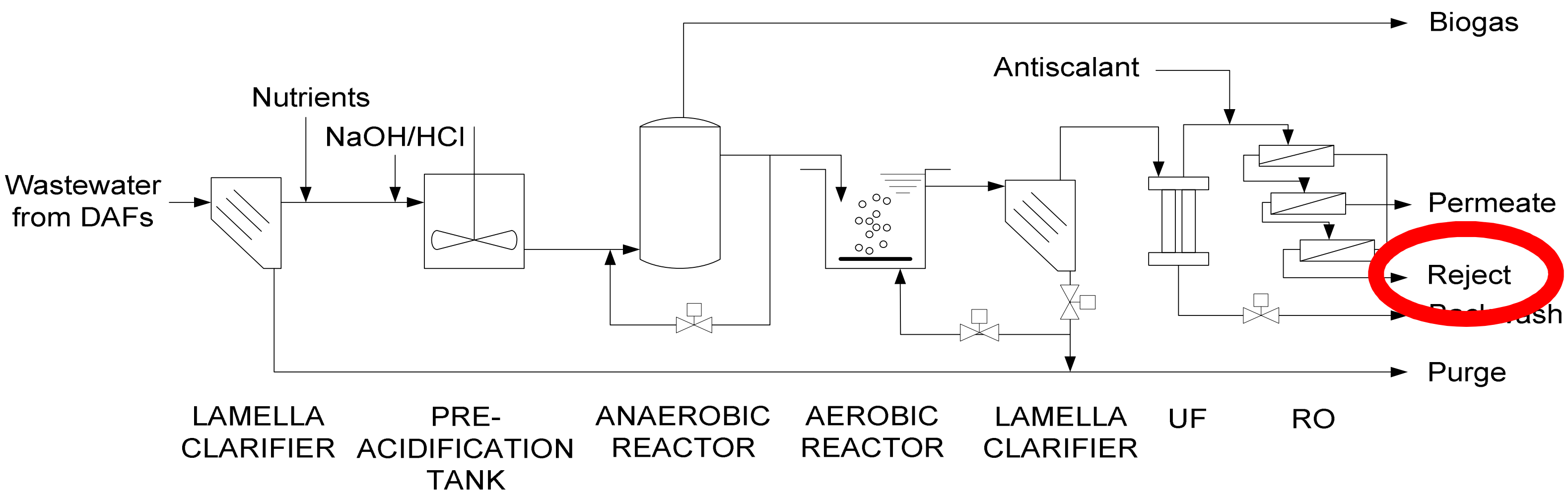
1. BACKGROUND

Reduce fresh water consumption in a paper mill producing 100% recycled paper by recycling its own effluent.

PILOT PLANT



How to manage the reject stream?

- **Send it to a Municipal Wastewater Treatment Plant (mWWTP) with the effluent → Potential limitation!**
- **Recirculate it to the mill effluent treatment.**

1. BACKGROUND:
Characterization of RO rejects

PARAMETER	UNITS	VALUE
Conductivity	mS/cm	9.10
pH	-	8.02
COD	mg/L	2365
Alkalinity	mg $CaCO_3$/L	3224
Hardness	mg $CaCO_3$/L	1100

- **Law 10/1993 (Madrid Region, Spain) for industrial effluents to mWWTP → - Conductivity < 7.5 mS/cm**
  - COD < 1750 mg/L

- **The COD is highly non-biodegradable → Not affected by biological processes**

COAGULATION + SOFTENING + FLOCCULATION

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2. MATERIALS AND METHODS:
Chemicals

1. Coagulation

Coagulant	Basicity (%)
PACl1	42 ± 2
PACl2	43 ± 5
PACl3	70 ± 5
PACl4	85 ± 10
PACl5	85 ± 10

- $FeCl_3$
- Polyaluminium chlorides (PACls)
- Polyaluminium nitrate sulphate salt (PNSS)

2. Softening

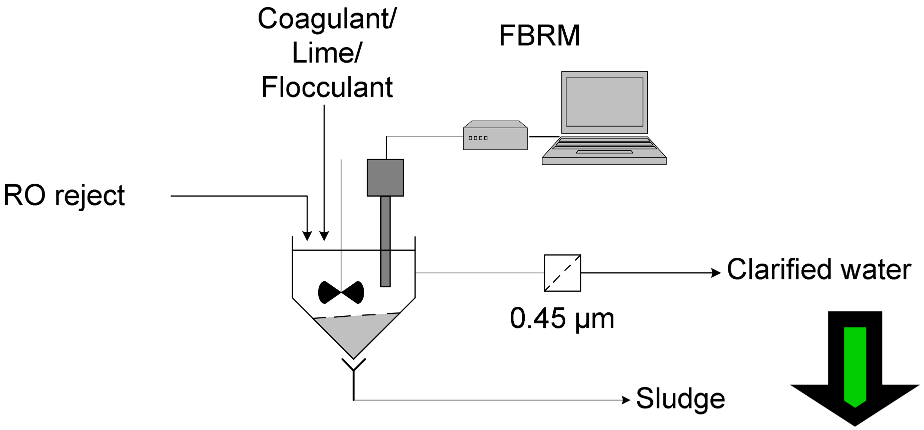
- $Ca(OH)_2$
- 2 min after coagulant addition

3. Flocculation

- Anionic polyacrylamide (aPAM): Medium MW, 15%-charged
- Cationic polyacrylamide (cPAM): Medium MW, 60%-charged
- 2 min after lime addition

2. MATERIALS AND METHODS:
Equipment/Analyses

Sample → 150 mL
Stirring → 200 rpm



- **Conductivity**
- **COD**
- **Absorbances**

- **254 nm:** Unsaturated compounds
- **284 nm:** Aromatics, such as phenols
- **310 nm:** Restrained conjugated rings
- **350 nm:** Aromatics rings with certain level of resonance
- **500 nm:** Colored substances with high level of resonance

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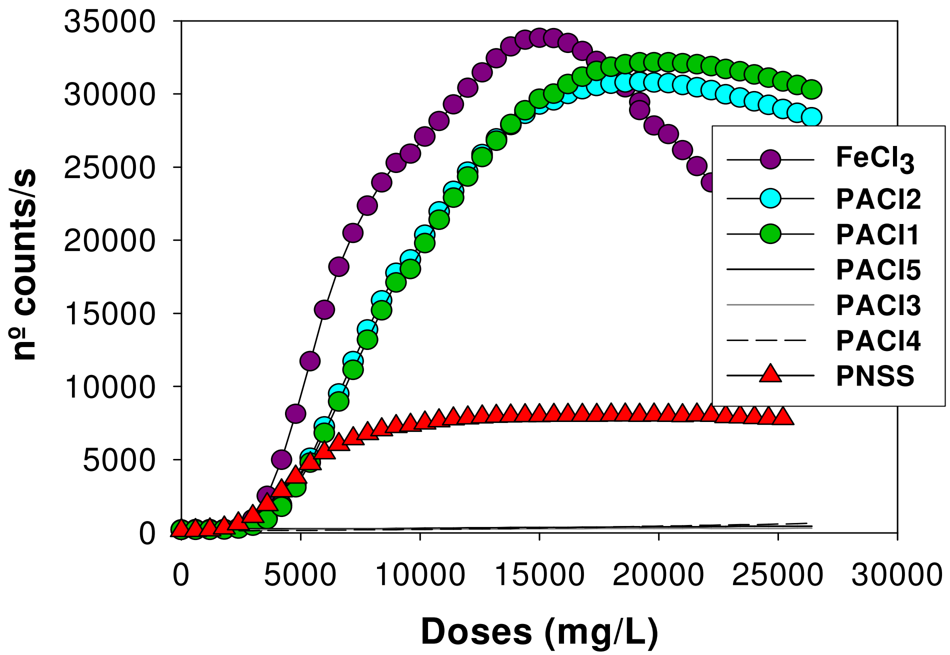
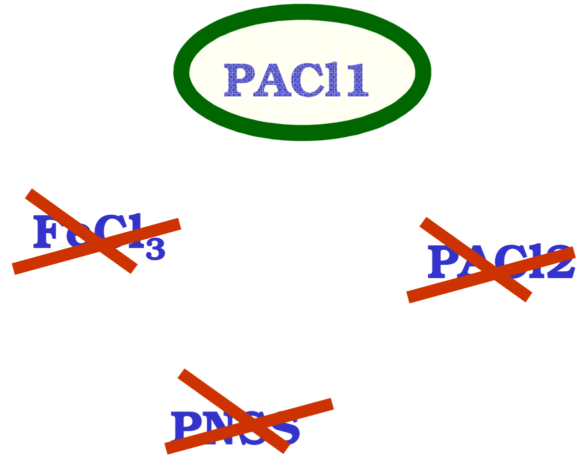
1. Selection of the best coagulant/doses by FBRM:

- 600 mg/L of coagulant were added each 10 seconds to the water.





DCM destabilisation is detected by the FBRM, increasing the nº of counts.

3. RESULTS:
3.1 Coagulation

2. Coagulation mechanisms:

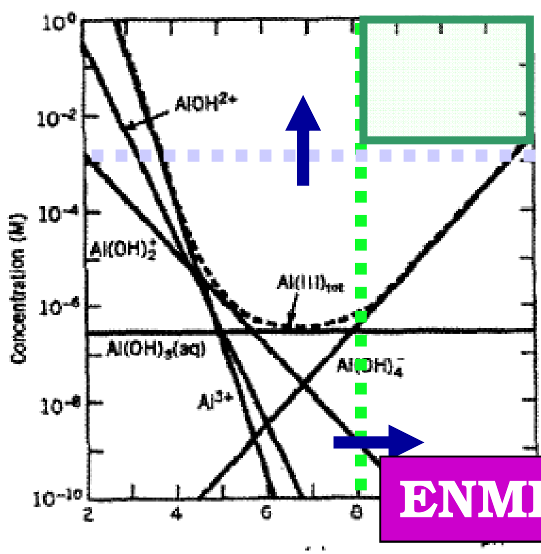
PACls hidrolysis → (Al^{3+}, $Al(OH)^{2+}$), dimers ($Al_2(OH)_2(H_2O)_8{}^{4+}$), polymers ($Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$) and amorphous precipitate ($Al(OH)_{3(am)}$).

$FeCl_3$ hydrolysis → $Fe(OH)_{3(s)}$ coexist with Fe^{3+}, $Fe(OH)_2{}^{+}$, $Fe(OH)^{2+}$.

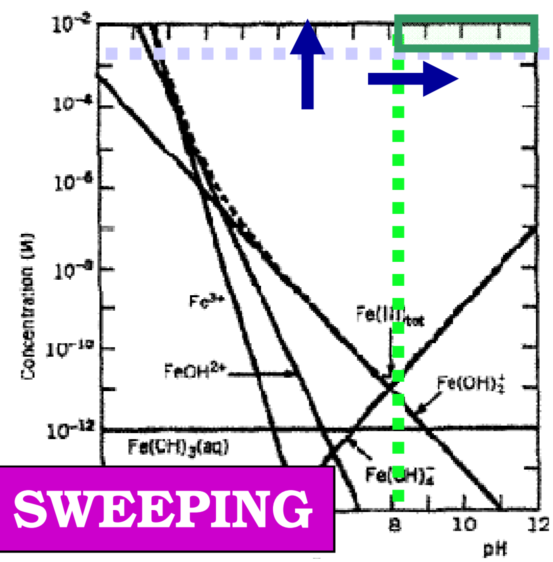
Depending on the coagulant species in the solution:

1) Charge neutralization.
2) Enmeshment of colloids in precipitated $Al(OH)_3$ or $Fe(OH)_3$ solids.

Species distribution = f (pH, [coagulant])



Doses mg/L	Al, (M)
2500	1.2×10^{-3}
5000	2.4×10^{-3}
10000	4.8×10^{-3}
18500	8.8×10^{-3}

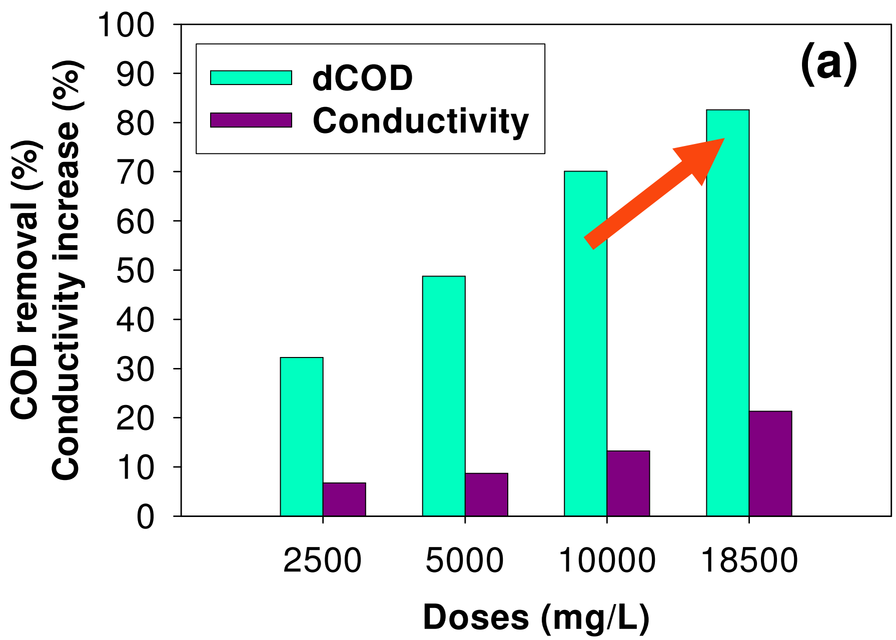


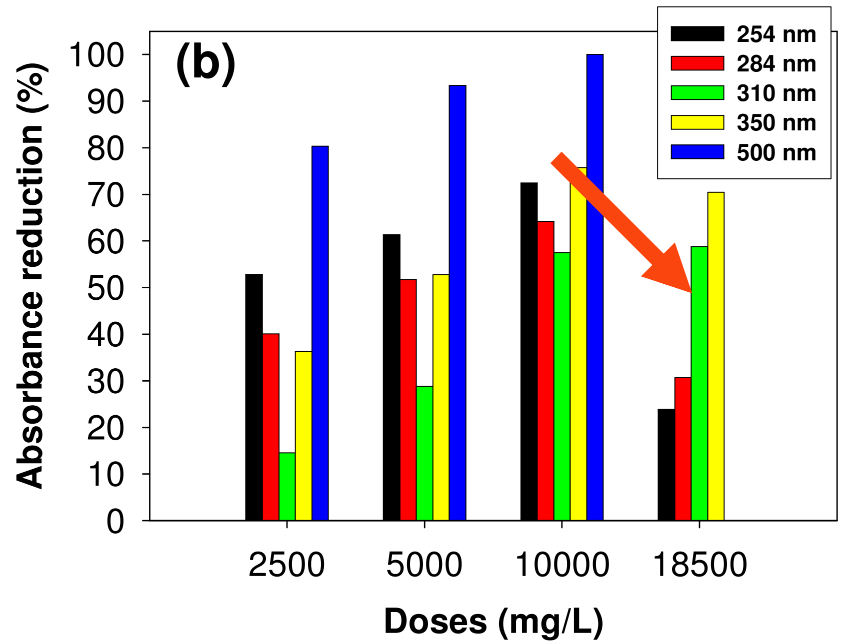
Doses mg/L	Fe, (M)
2500	$6.0\text{-}7.2 \times 10^{-3}$
5000	$1.2\text{-}1.4 \times 10^{-2}$
10000	$2.4\text{-}2.9 \times 10^{-2}$
18500	$4.4\text{-}5.4 \times 10^{-2}$

ENMESHMENT OR SWEEPING

3. RESULTS:

3.1 Coagulation





- > 10000 mg/L resulted
- **↑ biodegradable compounds (*Figure a*)**
- **↓ recalcitrant compounds (*Figure b*)**

- Although more dCOD is removed, conductivity increased (5-20%).

3. RESULTS:

3.2 Cogulation/Softening/Flocculation

Water softening with lime, $Ca(OH)_2$:

- Soluble salts are transformed into insoluble.
- At pH ≥ 9.5 maximum precipitation of $CaCO_3$ is produced (carbonate hardness):

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow \downarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow \downarrow 2CaCO_3 + \downarrow Mg(OH)_2 + 2H_2O$$

- At pH ≥ 10.5 maximum precipitation of $Mg(OH)_2$ is produced (non-carbonate hardeness):

$$MgCl_2 + Ca(OH)_2 \rightarrow \downarrow Mg(OH)_2 + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \rightarrow \downarrow Mg(OH)_2 + CaSO_4$$

Flocculation with anionic/cationic polymers:

- It is known that organic polymers can aid the coagulation process, achieving the same % of removal but reducing the amount of coagulant needed.

3. RESULTS:

3.3 Experimental design

Faced centered-central composite experimental design was run:

- **3 independent variables:** X_{coag}, X_{pH}, X_{floc}.
- **Response variables:** COD, Conductivity, A_{254}, A_{284}, A_{310}, A_{350}, A_{500}.

Number of experiments → $n = 2^{k-p} + 2 \cdot k + n_c$

15 experiments

- k = nº variables = 3
- p = 0
- n_c = 1 central point
- $2 \cdot k$ = 6 axial points

(-1, 0, 1)

- X_{coag}: 2000, 2500, 3000 mg/L
- X_{pH}: WL, 9.5, 10.5
- X_{floc}: 3, 5, 7 mg/L (*Bibliography*)

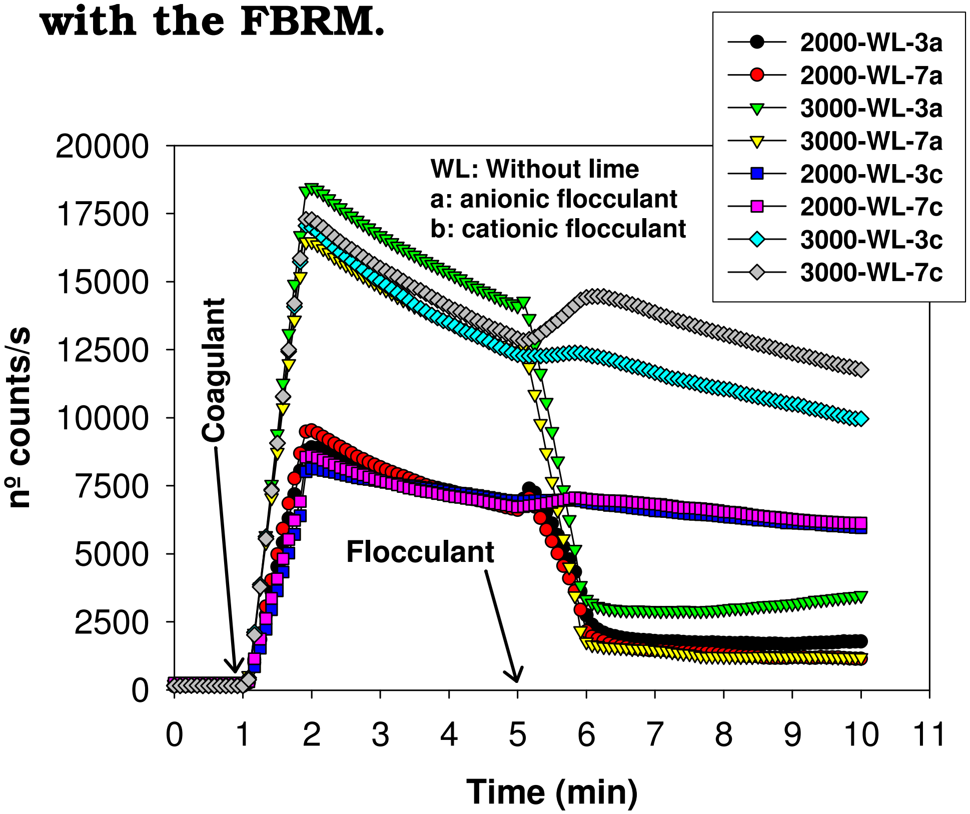
As 2 flocculants wanted to be tested, 2 experimental designs with 15 experiments each one, were done.

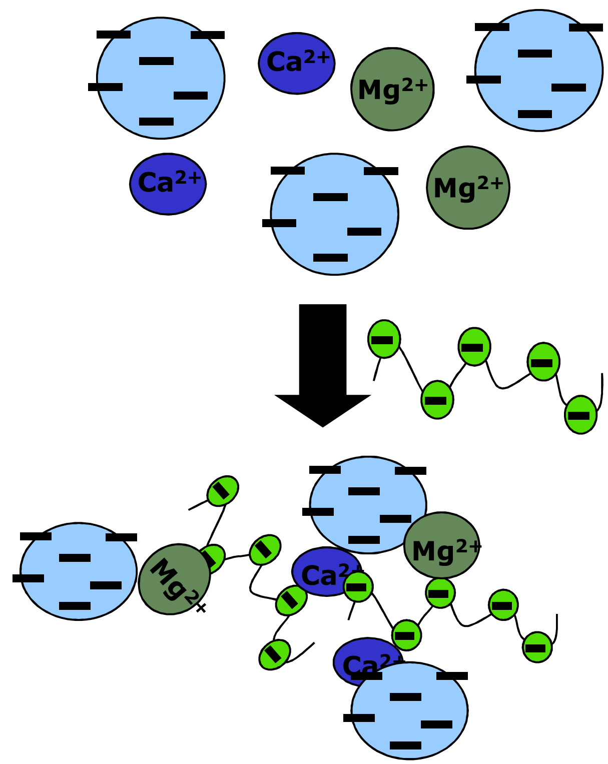
Adjusted to a polynomial model of second order

3. RESULTS:

3.3 Experimental design

- **The experiments from the experimental design without lime were monitored with the FBRM.**





1. **aPAM aggregates the particles formed by PACl1.**

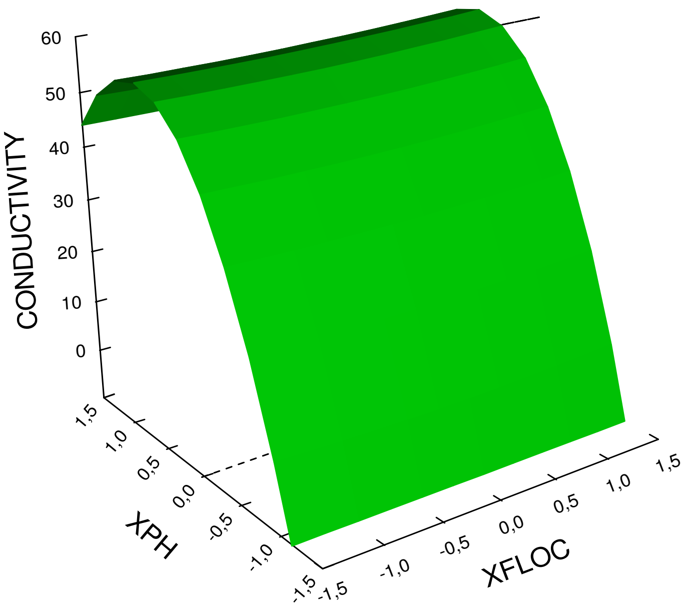
2. **cPAM did not affect solution → Ca^{2+} and Mg^{2+} avoid interactions.**

3. RESULTS:

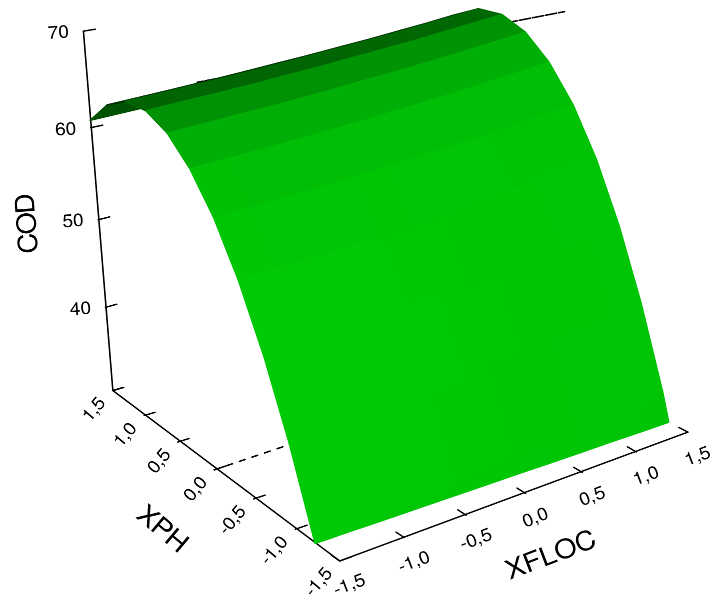
3.3 Experimental design

- **Main conclusion → Conductivity, COD and Absorbances ≠ f([flocculant])**

aPAM



aPAM



- **When lime is added Ca^{2+} and Mg^{2+} are removed from the water.**
- **aPAM resulted NOT EFFECTIVE because those "bridges" have disappeared.**
- **cPAM resulted again NOT EFFECTIVE because as pH increases (> 8.0), it hydrolyses, losing its cationic groups.**

3. RESULTS:

3.3 Experimental design

Coagulant (mg/L)	Lime	Flocculant (mg/L)	COD removal (%)	Conductivity reduction (%)
2500	NO	NO	30	0
	NO	5 (aPAM)	40	0
	9.5	3 (aPAM)	60	45
	9.5	5 (aPAM)	60	45
	10.5	5 (aPAM)	60	55

+10%
+30%
=
=
+45%
+10%

Coagulant (mg/L)	Lime	Flocculant (mg/L)	COD removal (%)	Conductivity reduction (%)
2500	NO	NO	30	0
	NO	5 (cPAM)	20	0
	9.5	3 (cPAM)	50	45
	9.5	5 (cPAM)	50	45
	10.5	5 (cPAM)	50	55

-10%
+20%
=
=
+45%
+10%

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4. CONCLUSIONS

1. $FeCl_3$ and low basicity PACl's (PACl1 & PACl2) → the best coagulants to destabilize DCM.
2. PACl1 removed rCOD →coloured compounds with a high level of resonance.
3. Drawback → conductivity increases as more coagulant is added.
4. aPAM → the best option to aid PACl1 when NO LIME was added.
   COD removal was improved a 10% when 2.5 g/L of PACl1 was combined with 5 mg/L of aPAM.
5. Conductivity reduction → only dependent on pH.
6. [Flocculants] (at the studied doses) did not produce any effect on COD, conductivity and absorbances.
7. With 2.5 mg/L of PACl1, at pH=9.5 and independently of [flocculant]:
   - COD removal was improved in a 30% in the presence of aPAM.
   - cPAM only improved COD removal in a 20%.

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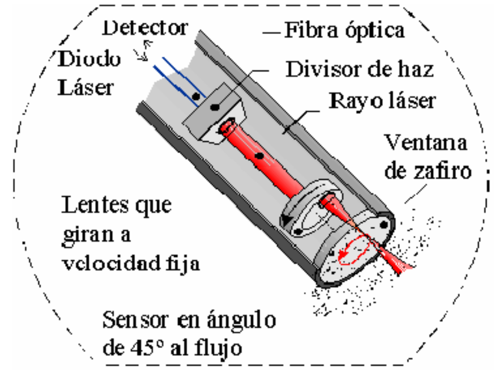
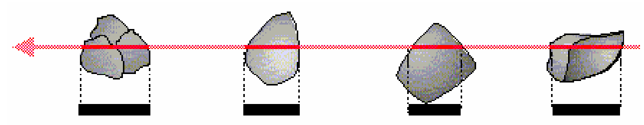
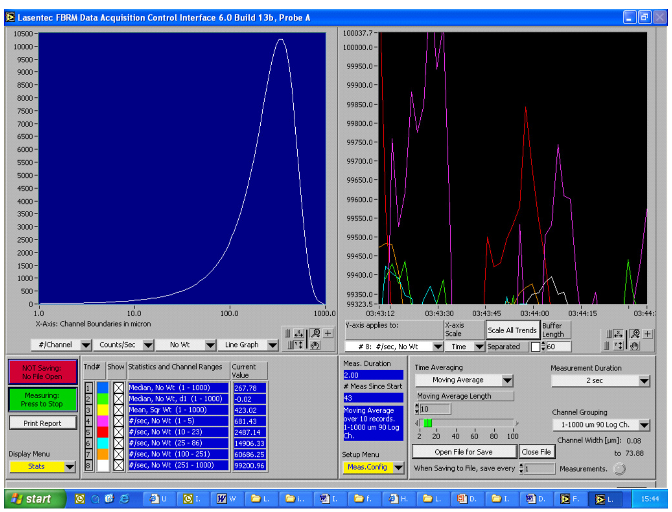
2. MATERIALS AND METHODS:

2.2 Equipments: FBRM







PLC information

Scanning by a highly focused laser beam at a fixed speed (2000 rpm) the particles in suspension.

3. RESULTS

3.1 Experimental design

- **The experimental data were adjusted to a polynomial model of second order.**

PACl1 + Lime + aPAM

Equations	R^2	Error (%)
$\%Conductivity = -19.43 \cdot X_{pH}^2 + 2.09 \cdot X_{Coag} \cdot X_{pH} + 3.27 \cdot X_{Coag} + 27.61 \cdot X_{pH} + 47.04$	0.997	2.5
$\%dCOD = 13.60 \cdot X_{pH} + 53.96$	0.884	6.3
$\%A_{254} = 4.89 \cdot X_{Coag} \cdot X_{pH} + 46.00$	0.740	3.5
$\%A_{284} = 4.50 \cdot X_{Coag} + 3.96 \cdot X_{Coag} \cdot X_{pH} + 38.47$	0.889	2.7
$\%A_{310} = -11.77 \cdot X_{Coag}^2 - 16.02 \cdot X_{pH}^2 - 8.06 \cdot X_{Coag} + 11.21 \cdot X_{pH} + 70.71$	0.891	9.8
$\%A_{350} = -9.18 \cdot X_{Coag}^2 - 6.63 \cdot X_{pH}^2 + 3.40 \cdot X_{Coag} \cdot X_{pH} + 9.32 \cdot X_{pH} + 70.53$	0.943	4.4
$\%A_{500} = 5.42 \cdot X_{Coag} \cdot X_{pH} + 3.84 \cdot X_{Coag} + 82.29$	0.857	3.4

Error < 10%

R^2=0.857-0.997

PACl1 + Lime + cPAM

Equations	R^2	Error (%)
$onductivity = -15.30 \cdot X_{pH}^2 + 2.2 \cdot X_{Coag} + 27.76 \cdot X_{pH} + 43.06$	0.996	2.4
$COD = 6.60 \cdot X_{Coag} + 14.63 \cdot X_{pH} + 47.85$	0.919	6.3
$_{254} = 10.55 \cdot X_{pH}^2 + 56.66$	0.677	5.8
$_{284} = -7.52 \cdot X_{Coag}^2 + 9.78 \cdot X_{Coag} + 42.68$	0.947	3.3
$_{310} = 9.78 \cdot X_{Coag} + 37.67$	0.866	4.9
$_{350} = -7.58 \cdot X_{Coag}^2 - 6.68 \cdot X_{pH}^2 + 9.41 \cdot X_{Coag} + 6.47 \cdot X_{pH} + 70.17$	0.962	3.8
$_{500} = 5.29 \cdot X_{Coag}^2 + 6.47 \cdot X_{Coag} - 1.21 \cdot X_{Coag} \cdot X_{pH} + 87.86$	0.973	1.6