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OPTIMUM PHOSPHORUS AND ORGANIC MATTER REMOVAL BY COMBINING DIFFERENT TYPES OF COAGULANTS

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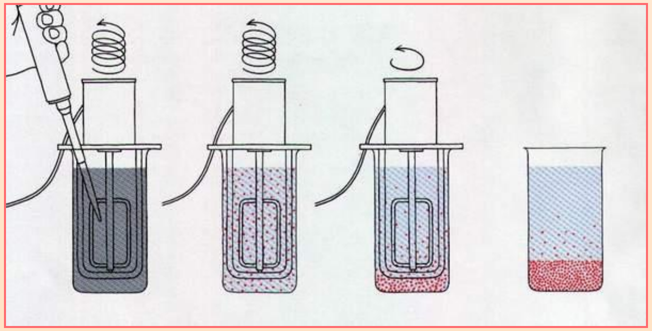


CHEMICAL WASTEWATER TREATMENT

- primary aim is often P-precipitation
- addition of Fe/Al salts to transform soluble ortho-phosphate to weakly soluble precipitate

$$Me^{3+} + PO_4^{3-} \rightarrow FePO_4$$

- theoretically 1:1 (Me to P ratio in precipitate)
- applied reagents take part in many other (competing) reactions
- precipitate is more likely a mixture of metal (Fe or Al), phosphate and hydroxide (composition depends on environmental conditions)

$\Rightarrow$ Me/P > 1 in the reality

CHEMICAL WASTEWATER TREATMENT

- Hydroxide formation (simplified)

$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+$
$[Fe(H_2O)_5OH]^{2+} + H_2O \rightarrow [Fe(H_2O)_4(OH)_2]^{+} + H_3O^+$
$[Fe(H_2O)_4(OH)_2]^{+} + H_2O \rightarrow Fe(OH)_3 \cdot 3H_2O + H_3O^+$

- intermediate hydroxide compounds (average positive charge)
- coagulation/flocculation – removal of suspended solids
  ⇒ 50–85 % organic matter removal (COD, BOD)

  \+ adsorption, chemical bond of PO_4^{3-}, complex forming, etc.

relative importance of these processes is still under discussion

CHEMICAL PRE–TREATMENT

removal of organic matter in primary settling tank

⇒ biological stage receives a lower organic load (present mainly in dissolved form)

⇒ efficiency of biological treatment improves

⇒ nitrification can be more efficient

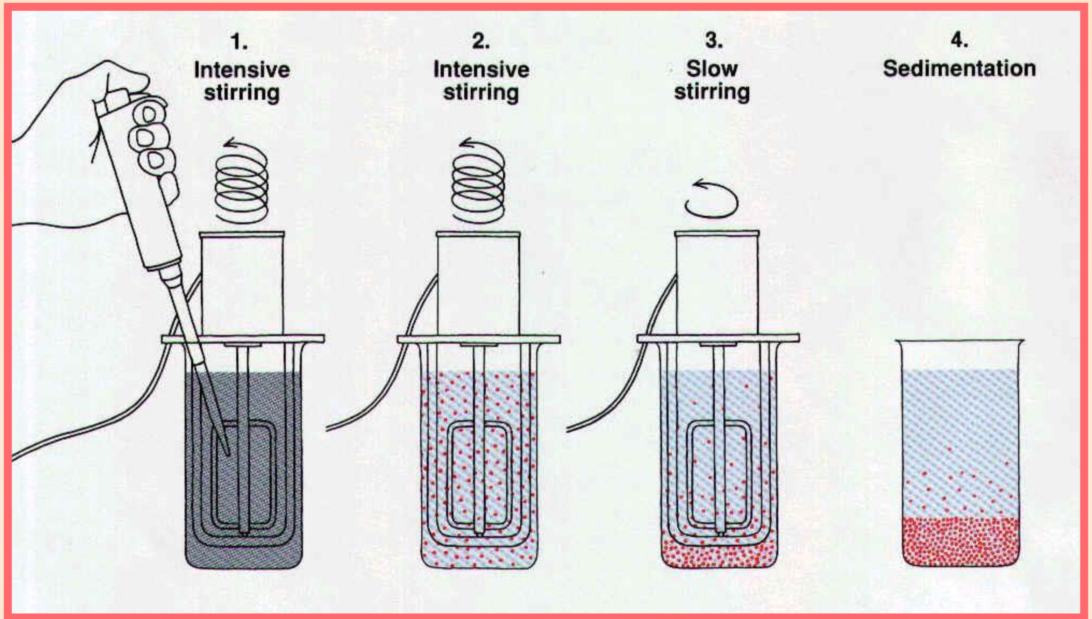
- ➢ pH decrease (due to hydrolysis reactions)
- ➢ efficient organic removal often requires high doses ⇒ small residual PO_4–P concentration

⇒ bacterial deterioration

OBJECTIVES

- Examining the importance of different processes taking place in chemical ww. treatment (precipitation, coagulation–flocculation, adsorption, etc.)
- Assessing the possible effects of pre–precipitation on biological treatment processes
- Investigating the combined feeding of simple (trivalent) metal salts and pre–polymerised metal salts
- Setting an optimal removal of ortho–P and organic matter at the same time

COAGULATION-FLOCCULATION LABORATORY JAR TESTS



1-litre glass cylinders with Kemira's flocculator device

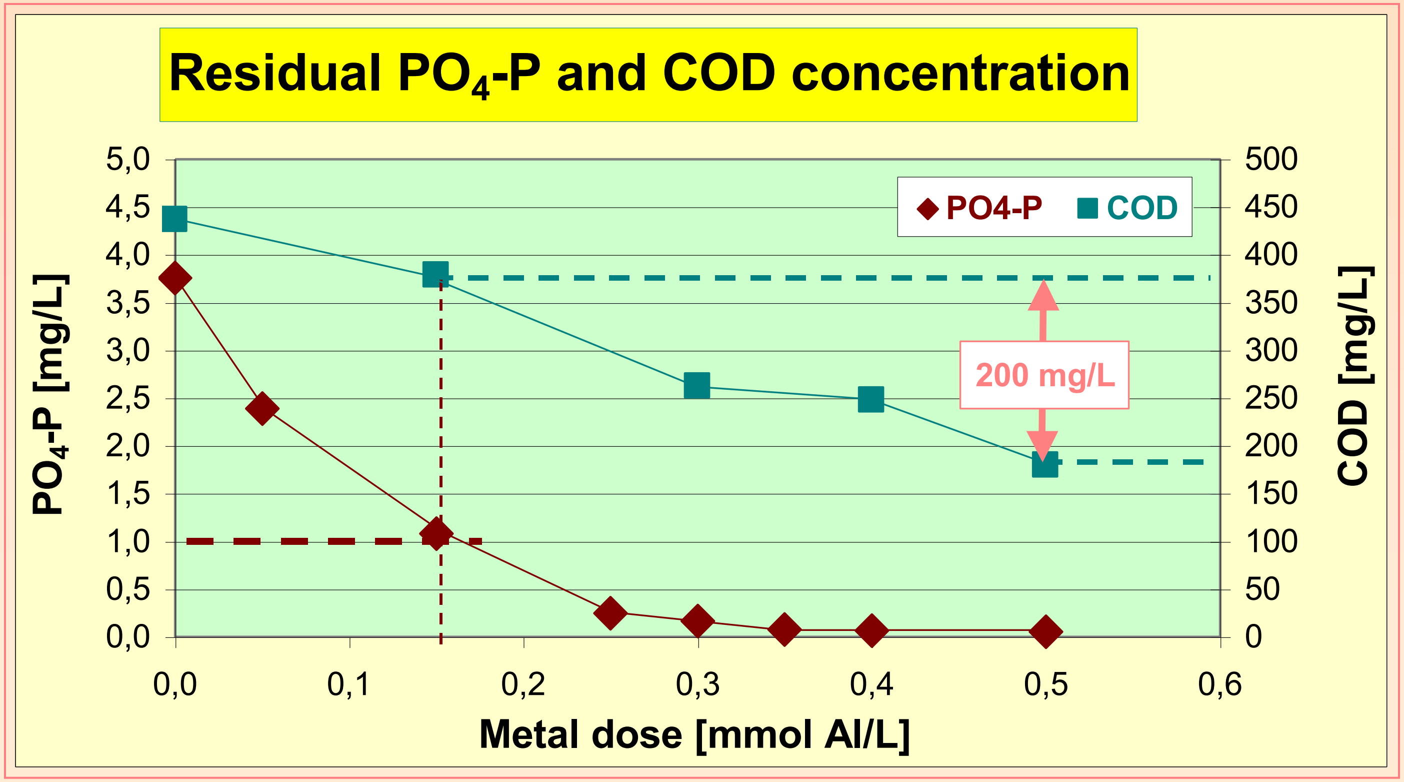
LABORATORY TESTS

Applied coagulants:

- Prefloc (iron(III)-sulphate)
- BOPAC (poly-aluminium-chloride)
- $FeCl_3 \cdot 6H_2O$
- $Al_2(SO_4)_3 \cdot 18H_2O$

Analysed parameters:

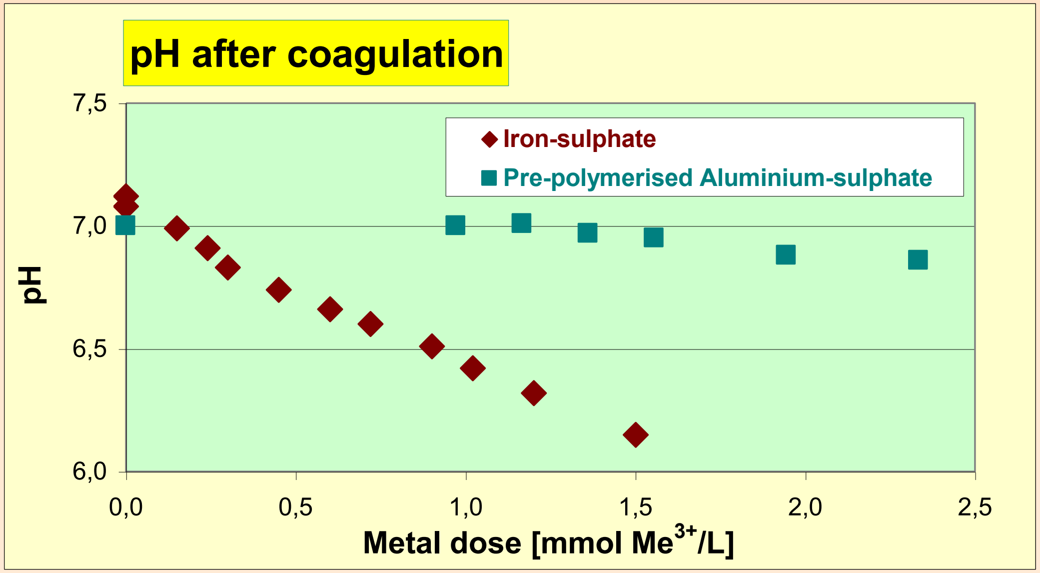
- pH
- alkalinity
- chemical oxygen demand (COD_{cr})
- biochemical oxygen demand (BOD_5)
- dissolved COD_{Cr} and BOD_5 (0.45 μm membrane filter)
- total phosphorus (TP)
- ortho-phosphate (PO_4-P)
- total suspended solids (TSS)

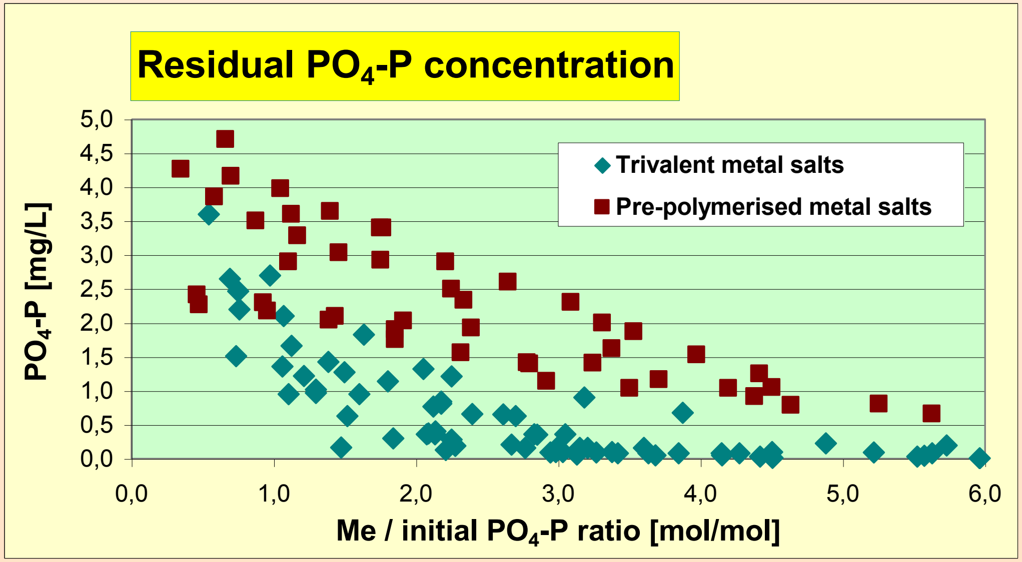


- Non-polymerised metal salts effectively precipitate ortho-P (at small doses)
- pre-precipitation ⇒ it is aimed to leave certain amount of soluble P for bacterial growth
- 1 mg/L PO$_4$-P shall be enough – can be reached by <0.2 mmol Me^{3+}/L
- Maximum organic removal occurs at higher doses
- At high doses pH can get to low levels (esp. in low alkalinity ww)

Pre-polymerised metal salts

- have smaller effect on pH
- do not precipitate P as efficiently as trivalent salts





Metal-hydroxides are efficient in coagulation-flocculation ⇒ the different salts cause similar organic removal

Appropriate combination of trivalent and pre-polymerised metal salts can result in optimal organic matter and phosphate removal at an acceptable resulting pH

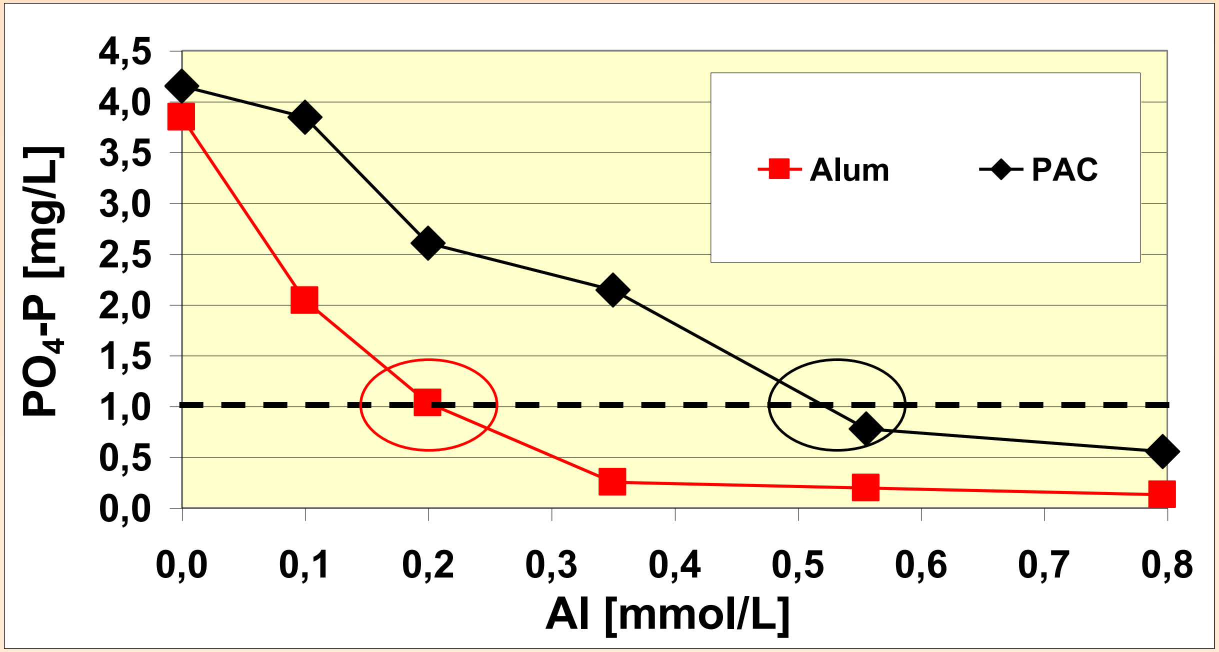
Aim: to reach maximum organic removal while PO_4-P concentration is 1 mg/L at the same coagulant dose

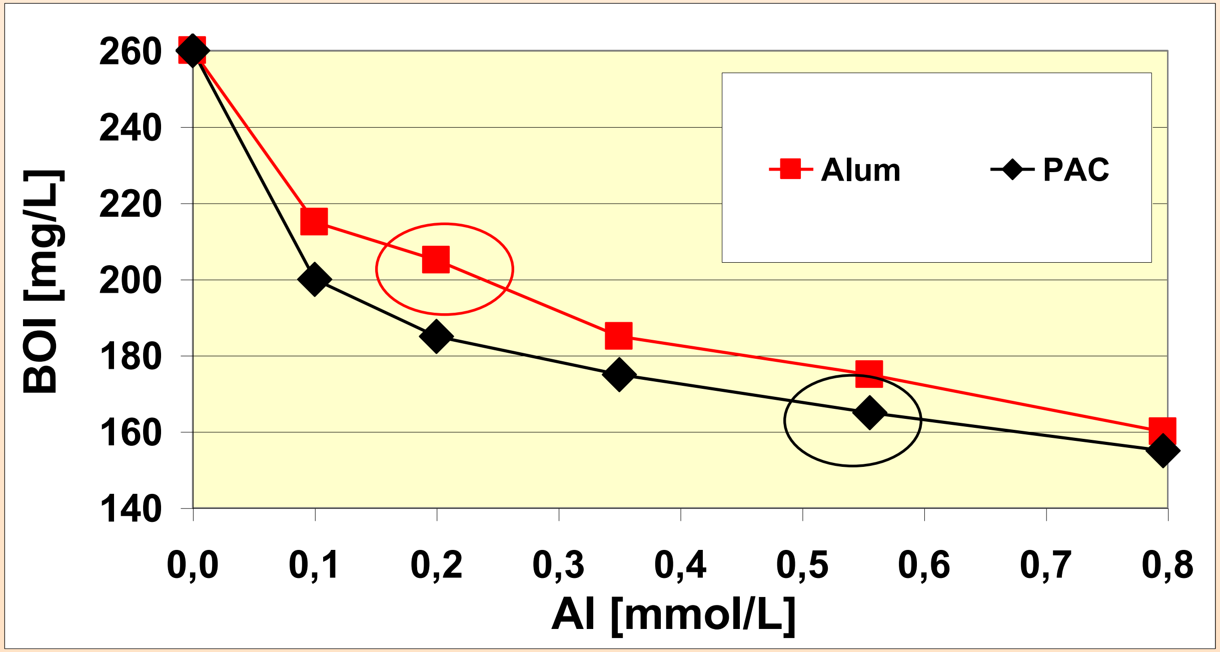
Simple (trivalent) metal salts:

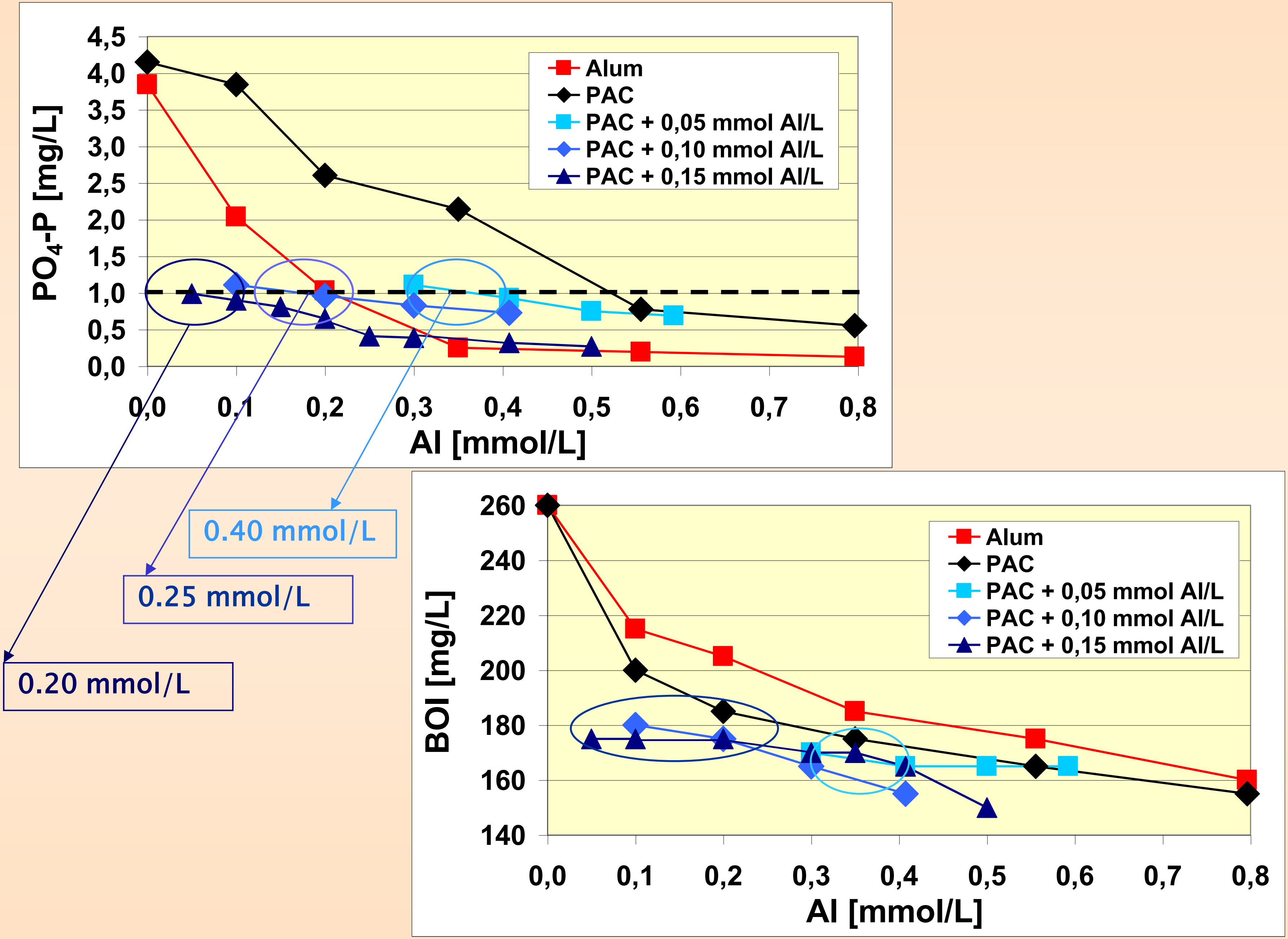
to approach the required precipitation of P (1.0-2.5 mg/L PO_4-P) + start the coagulation of SS

Pre-polymerised Al-salt:

to complete the precipitation and enhance coagulation of organic matter


Alum
PAC
PO$_4$-P [mg/L]
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
Al [mmol/L]


Alum
PAC
BOI [mg/L]
260
240
220
200
180
160
140
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
Al [mmol/L]

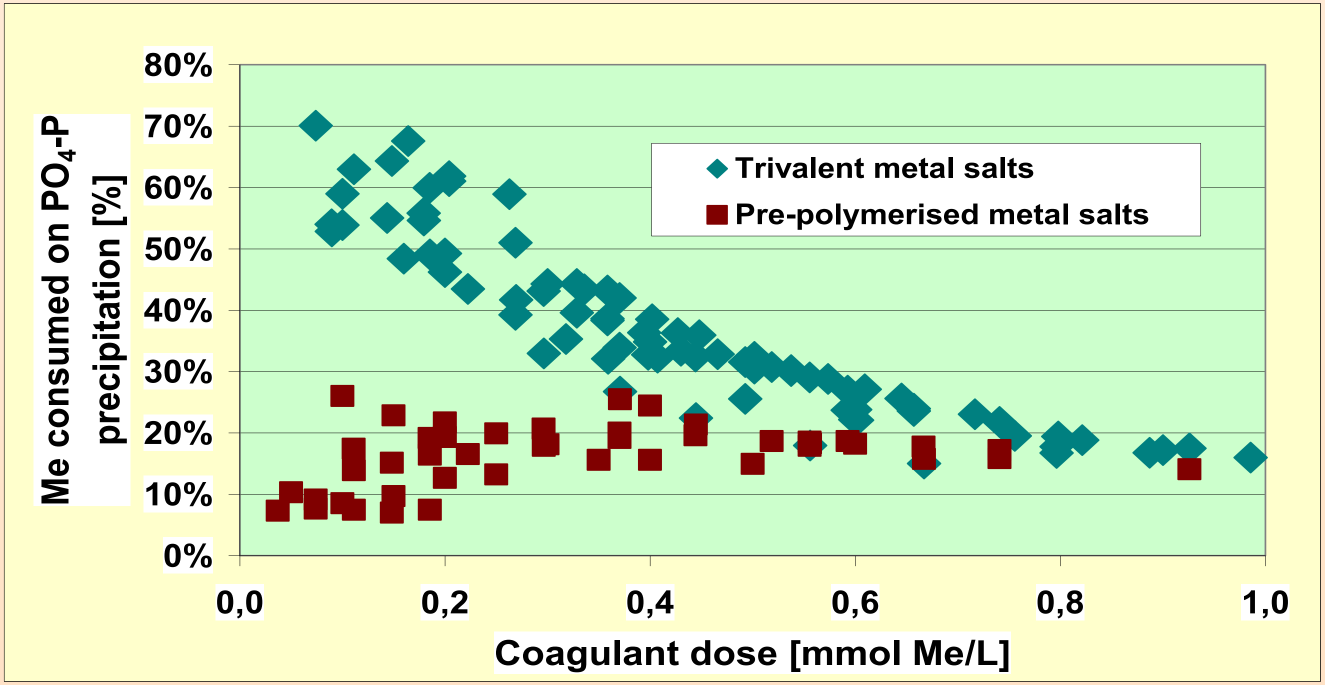


0.40 mmol/L

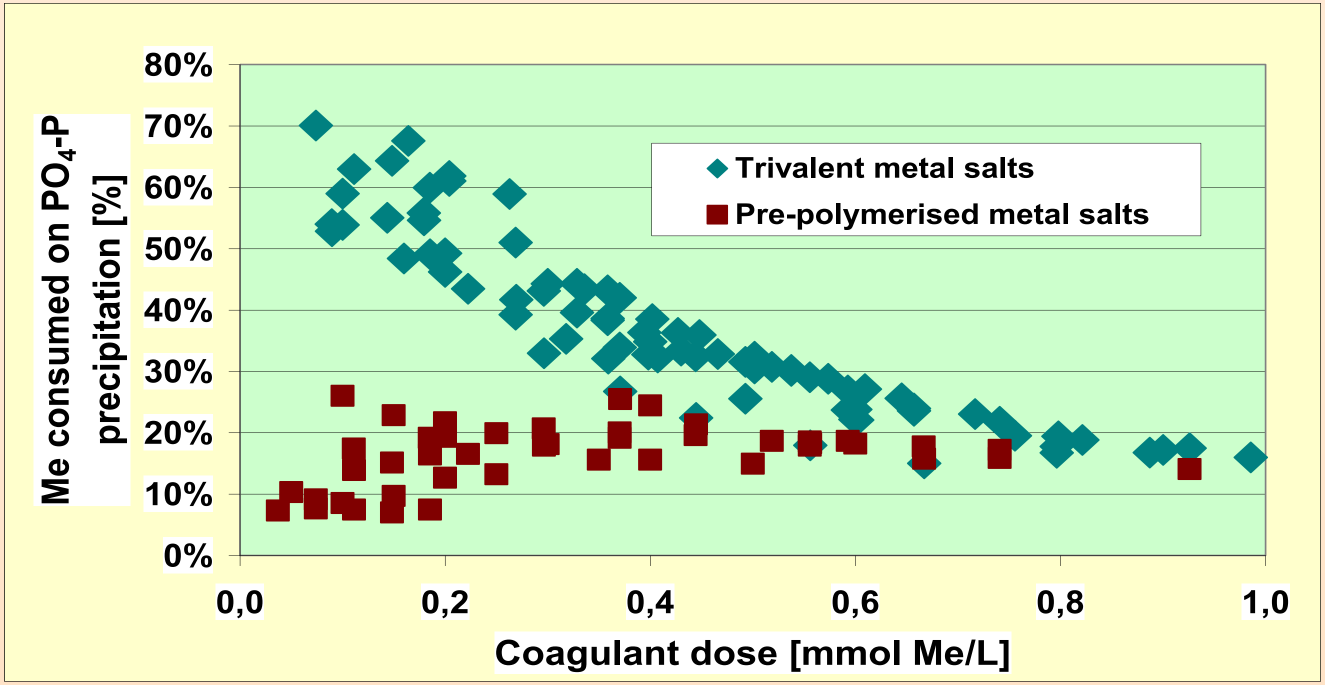
0.25 mmol/L

0.20 mmol/L

- It is assumed that P precipitation can have a priority compared to the hydroxide formation, coagulation and other reactions (depending on environmental conditions) – trivalent salts
- 60–90% of the applied coagulant is used in the precipitation reaction at doses <0.2 mmol Me3+/L (depending on raw water pH, PO4–P concentration, organic content)
- With increasing coagulant dose smaller portion of the added metal ions is consumed on phosphate precipitation ⇒ hydrolysis reactions – that promote the removal of suspended solids – start predominating



- Pre-polymerised salts:
  - Only 8-25% is consumed on P removal
  - Formation of chemical bond with the intermediate hydrolysis products and adsorption on metal-hydroxides can have a more pronounced role in phosphate removal

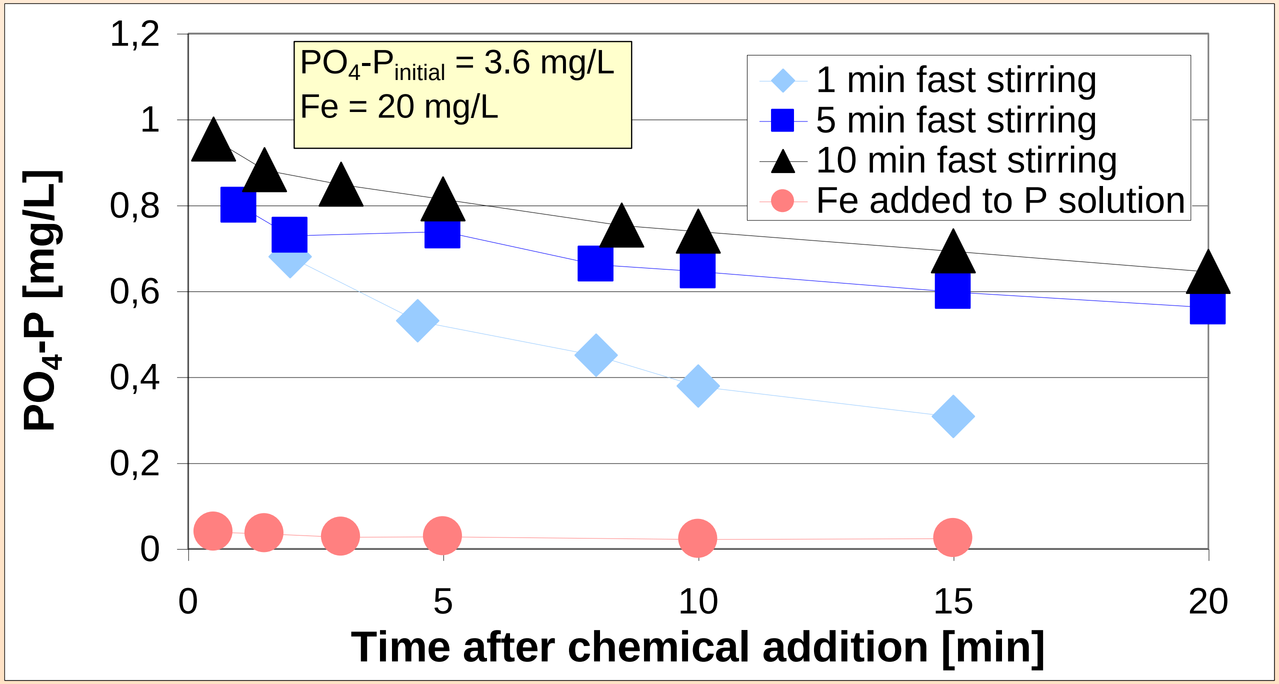


- P removal is much more efficient when metal-hydroxides are formed in the presence of phosphate (direct metal-phosphate precipitation and co-precipitation of metal-hydroxide-phosphates)
- Pre-formed metal-hydroxides: two processes
  1. Very fast (<0.5 min)

     responsible for the majority of P removal

     chemical binding of phosphate ions on the positively charged metal-hydroxides (pseudo-precipitation)
  2. Slow – continuing even after 1 day

     Adsorption



CONCLUSIONS

- Predefined optimal removal rate of ortho-phosphate and organic matter and appropriate resulting pH can be reached by the combined feeding of simple and pre-polymerised metal salts
- In trivalent metal salt addition direct precipitation and co-precipitation are the dominant mechanisms
- Pseudo-precipitation (chemical binding of phosphate ions on the positively charged metal-hydroxides) and adsorption prevail in the case of pre-polymerised metal salts