

Novel inorganic pre-polymerized composite coagulant reagents: preparation, characterization and applications issues

A.I. Zouboulis

*Professor of Chemical & Environmental Technology
&*

N.D. Tzoupanos and P.A. Moussas, (PhD students)

Department of Chemistry, Division of Chemical Technology,
Aristotle University, Thessaloniki, Greece

Outline

- Coagulation
- Inorganic Polymeric Flocculants (IPFs)
 - Properties of IPFs
 - Preparation of IPFs
- Improved Inorganic Pre-polymerized Flocculants
 - Modified IPFs based on silica addition
 - Modified IPFs based on polyelectrolytes addition
- Future Trends

Introduction

- **Water/Wastewater treatment** can be classified into several categories, according to the nature of the specific treatment process operation being used:
 - physical
 - chemical
 - biological
- **The chemical treatment** consists of using chemical reactions to improve the water quality.
 - The basic chemical treatment methods are considered to be the following:
 - Chlorination/ozonation
 - Adsorption
 - Neutralization/Precipitation
 - Ion exchange
 - **Coagulation/flocculation**

Coagulation process

*Essential Treatment Technique
in Water and Wastewater
Treatment Facilities*

Applied mainly for the removal of:

- | | | |
|--|---|--|
| <ul style="list-style-type: none">- Colloids and suspended particles- Natural Organic Matter | } | Water
treatment |
| <ul style="list-style-type: none">- Metal ions- Phosphates- Toxic metals- Color | | |
| | } | Additionally in
Wastewater
treatment |



Coagulation - Flocculation

■ Coagulation

Particle destabilization through:

1. Compression of the electrical double layer,
2. adsorption and charge neutralization,
3. adsorption and interparticle bridging,
4. enmeshment in precipitate (use of excess coagulant dose, sweep flocculation)

■ Flocculation

Destabilized particles aggregation and sedimentation

1. Micro-flocculation (perikinetic flocculation),
2. Macro-flocculation (orthokinetic flocculation)

Overview of Coagulation Reagents

■ Inorganic Metal Salts

I. Simple Metal Salts (conventional coagulants)

Aluminium: $\text{Al}_2(\text{SO}_4)_3$ (alum), AlCl_3 , NaAlO_2

Iron: FeCl_3 , FeCl_2 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4

↓ *Increase of MW and charge*

II. Pre-polymerized Inorganic Metal Salts

Polyaluminium Chloride (PAC)

Polyferric Sulfate (PFS)

↓ *Further increase of MW*

III. Modified Pre-polymerized Metal Salts (latest developments)

Introduction of several inorganic or organic additives to increase the molecular weight and aggregation ability (e.g. polyaluminium silicate chloride)

Overview of Coagulation Reagents

■ Organic Polymers

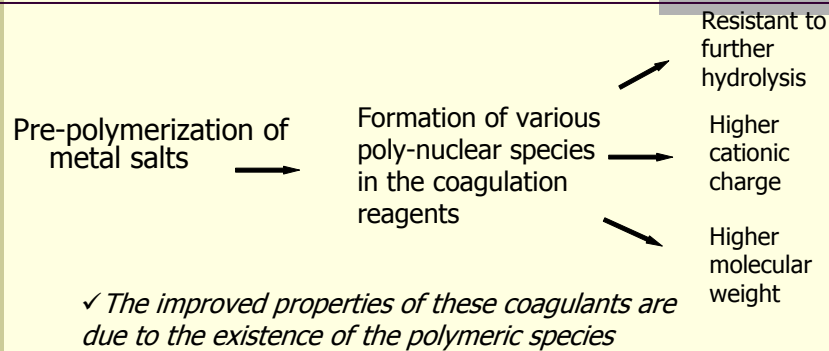
- I. Synthetic (anionic, cationic, nonionic)
based on various monomers, such as acrylamide, acrylic acid, diallyl-dimethyl ammonium chloride (DADMAC), styrene sulphonic acid etc.
 - anionic (e.g. poly-amines)
 - cationic (e.g. poly-DADMAC)
 - non ionic (e.g. poly-acrylamide)
 - II. Natural (biopolymers or bioflocculants)
based on natural polymers, such as starch, cellulose, natural gums and mucilages and their derivatives etc.
(sodium alginate, chitosan, various polysaccharides)
- ✓ ***mainly used as flocculant aids***

Inorganic Polymeric Flocculants (IPFs)

- Widely used during the last two decades
- **Advantages, when compared to the conventional coagulants :**
 - ✓ More resistant to further hydrolysis, leading to production of non-desired precipitates,
 - ✓ Higher cationic charge (coagulation),
 - ✓ Higher molecular weight (flocculation)
- **Effective:**
 - in both low and high concentrations of colloidal species,
 - in a wider range of pH and temperature,
 - in lower dosages of flocculant addition,
 - in maintaining the pH of the water – usually further pH correction is not needed,
 - in DOM (Dissolved Organic Matter) removal

Inorganic Polymeric Flocculants (IPFs)

□ Properties of IPFs



- **Aluminium** dimer ($\text{Al}_2(\text{OH})_2^{4+}$), trimer ($\text{Al}_3(\text{OH})_4^{5+}$), **tridecamer** ($\text{Al}_{13} - \text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{6,7+}$), $\text{Al}_{30} (\text{Al}_{30}\text{O}_8(\text{OH})_{56}\text{H}_2\text{O})_{24}^{18+}$, $\text{Al}_{54} (\text{Al}_{54}(\text{OH})_{144}^{18+})$, etc.
- **Iron** dimer ($\text{Fe}_2(\text{OH})_2^{4+}$), trimer ($\text{Fe}_3(\text{OH})_4^{5+}$), various species: $\text{Fe}_x(\text{OH})_y^{(3x-y)+}$ or $[\text{Fe}_x\text{O}_y(\text{OH})_{x+r}]^{(2x-2y-r)+}$

Improved Inorganic Pre-polymerized Flocculants

- Research is now focused on new synthetic polymeric flocculants with higher efficiency

Organic polymers > IPFs > conventional flocculants

← **efficiency** ←

- **The basic prerequisites for an effective coagulant reagent are:**
 - the charge-neutralisation capacity,
 - the bridge-aggregation ability.
- There are **two ways** for improving the efficiency of the IPFs;
 - by increasing the proportion of the polymeric species in their original composition,
 - by adding other components to produce new, **composite materials/coagulants**

Improved Inorganic Pre-polymerized Flocculants

□ Addition of other components

- The selected modifiers may also act as inhibitors to the precipitation of iron and aluminium

improving the **stability** of the coagulants



- **three types of modifiers:**

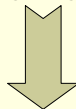
- inorganic anions, such as polysilicates, phosphates,
- organic anions, such as various organic acids,
- organic polyelectrolytes, either cationic, non anionic or anionic

Improved Inorganic Pre-polymerized Flocculants

□ Modified IPFs based on silica addition

- Concerning the second approach of improving the efficiency of IPFs, the additive most frequently used is:

- the **polysilicic acid** (PSiA), which carries a negative charge.
- The main goals of adding such a modifier are:
 - to increase the molecular size,
 - to enhance the aggregating ability of the coagulant.




- Therefore, current research focuses on the development and the detailed study of modified inorganic polymeric flocculants, such as:
 - Polyferric Silicate Sulphate (PFSiS),
 - Polyaluminium Silicate Chloride (PASiC)

Improved Inorganic Pre-polymerized Flocculants

□ Modified IPFs based on silica addition

- However, the incorporation of silica in the structure of polymerized metal solutions results:
 - in the decrease of Al₁₃ content,
 - In the reduction of charge neutralization capability of coagulants.
- Despite these negative effects in the nature and composition of the silica-based coagulants, the increase of colloids/particle size of these coagulants is crucial,


- as it results in the enhancement of the aggregation ability and consequently in more effective coagulation performance.

Comparison of coagulation performance

Comparison of coagulation* performance of Al-based coagulants

Coagulant	Turbidity removal (%)			Absorbance at 254 nm removal (%)			Residual Al concentration (µg/L)		
	pH value of treated sample								
	7	8	9	7	8	9	7	8	9
Alum	85.8	79.0	72.0	69.0	62.1	56.9	400	590	684
PAC-18	92.4	90.5	86.0	78.4	69.8	67.2	243	459	632
PAC_{lab}	93.0	91.8	88.5	82.8	78.0	73.7	177	180	294
PASiC	92.7	92.0	88.2	84.1	79.7	72.4	132	170	232

* Initial turbidity 16 NTU, initial absorbance at 254nm: 0.125, dose of coagulants 2 mg/L

✓ **The major advantages of silica-based Al coagulants are the lower residual Al concentration and the wider pH range effectiveness**

Comparison of coagulation performance

Comparison of coagulation* performance of Fe-based coagulants.

Coagulant	Turbidity removal (%)			Absorbance at 254 nm removal (%)			Residual Fe concentration ($\mu\text{g/L}$)		
	pH value of treated sample								
	5	7	9	5	7	9	5	7	9
FS	80	82	81	37	38	37	540	530	510
PFS	86	84	85	39	42	41	490	510	480
PFSiS	96	97	97	78	66	61	430	400	340

* Initial turbidity 10 NTU, initial absorbance at 254nm 0.120, dose of coagulants 4 mg/L

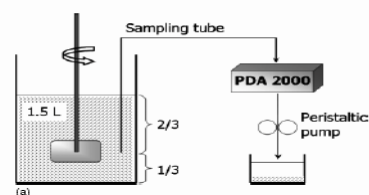
PFSiS:

- ✓ More efficient in removing residual turbidity and UV_{254} ,
- ✓ Lower residual Fe concentration,
- ✓ Effective in a wider pH range

Comparison of coagulation performance

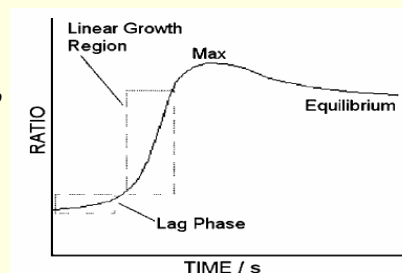
Photometric Dispersion Analyser (PDA)

- Examine the extent of the aggregation and the coagulation dynamics:
 - Determine the appropriate experimental parameters for applying the prepared coagulants in coagulation experiments



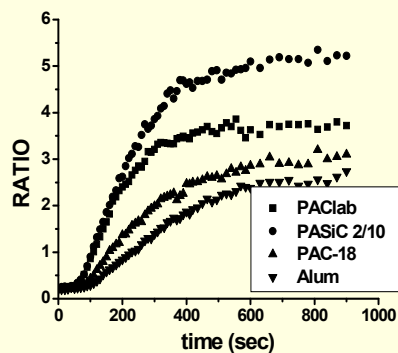
Higher R values imply bigger particles size

a better separation by the application of subsequent sedimentation.

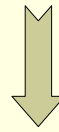


Comparison of coagulation performance

■ Al-based coagulants



The flocs growth during the coagulation of the kaolin-humic acid model suspension has been examined



✓ the addition of silica (PASIc) results in bigger and denser flocs formation.

Improved Inorganic Pre-polymerized Flocculants

□ Modified IPFs based on **polyelectrolytes addition**

Consideration of alternative additives for the further improvement of IPFs properties

Cationic, anionic, non-ionic polyelectrolytes

- **Cationic** → enhancement of charge neutralization capability and aggregating effect
- **Anionic** → stronger enhancement of aggregating effect – mild deterioration of neutralization capability
- **Non-ionic** → improvement of aggregating effect

- Combination of aluminium and iron in one coagulation reagent, and in a second step introducing polysilicates or other agents to produce more complex coagulants.

Improved Inorganic Pre-polymerized Flocculants

□ Modified IPFs based on polyelectrolytes addition

➤ Fe-based composite coagulants

■ Preparation of PFS-PAA

- preparation of the inorganic pre-polymerised Polyferric sulphate, PFS
- predetermined amount of water-based polyacrylamide solution was injected into PFS stock solution

- Polyacrylamide is a non-ionic synthetic polymer, which has been widely used in water treatment applications:

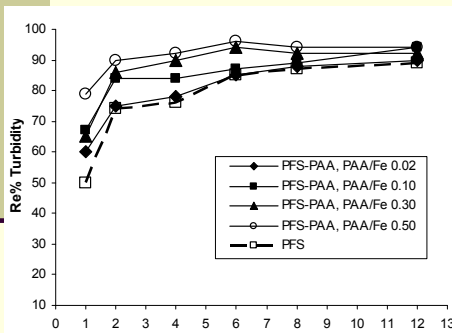
- as coagulant/flocculant aid for water and wastewater clarification and filtration and,
- for thickening of coagulant sludge

Improved Inorganic Pre-polymerized Flocculants

□ Modified IPFs based on polyelectrolytes addition

■ Coagulation experiments – (Fe-based coagulants)

- The test sample was kaolin-humic acid (5 mg/L) model suspension (*Initial turbidity 10 NTU)



- Important parameters affecting the properties of the composite coagulants:

- [OH]/[Fe] molar ratio,
- PAA content, i.e. PAA/Fe ratio

- ✓ PFS-PAA exhibits better performance, than the simple PFS
- ✓ as the PAA/Fe ratio increases, the efficiency is similarly improved

Improved Inorganic Pre-polymerized Flocculants

☐ Modified IPFs based on **polyelectrolytes addition**

➤ **Al-based composite coagulants**

■ **Preparation of PACI-PAA**

- preparation of the inorganic pre-polymerised polyaluminium chloride, PACI,
- predetermined amount of water-based polyacrylamide solution was injected into PACI stock solution.

■ **Most important parameters** affecting the properties of the composite coagulants:

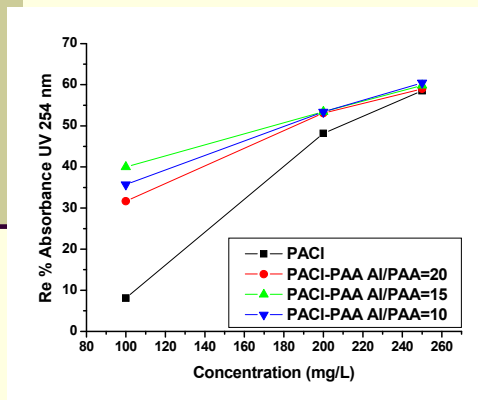
- [OH]/[Al] molar ratio,
- PAA content, i.e. Al/PAA ratio (w/w)

Improved Inorganic Pre-polymerized Flocculants

☐ Modified IPFs based on **polyelectrolytes addition**

■ **Coagulation experiments (Al-based coagulants)**

- Post-treatment of pre-treated **tannery wastewater**



■ Organic matter removal, measured as absorbance UV at 254 nm (initial Abs 3.95)

✓ PACI-PAA exhibits better performance than PACI, especially for lower dosages (i.e. 100 and 200 mg/L)

✓ Most effective Al/PAA ratio should be 10 or 15

Future Trends

- *The tendency in the coagulation field nowadays is the production of modified composite coagulants, which become more and more complicated, regarding their composition. The variety of the possible additives and the different possible mixing ratios between them state clearly that the concept of "mixing" to produce superior chemicals is in an initial stage and more research efforts have be devoted for this purpose.*

***Thank you
for your
attention***