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Investigation of Coagulation/Flocculation Process for the Removal of Specific Micro-Pollutants

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Abstract **-** The potential of coagulation/flocculation process for the removal of the selected pharmaceuticals SIbuprofen, Diclofenac, Carbamazepine, Valsartan, and Ethinylestradiol was investigated. For this purpose, several composite coagulants were prepared in the laboratory from the combination of polymerized aluminium (PACl) and an inorganic additive (polysilicates, pSi) and an organic positively charged additive (p-DADMAC). By applying two synthesis methods (co-polymerization and composite polymerization) and different basicities or [OH]/[Al] ratios, several products were produced. The prepared coagulants (of PASiC, PACSi and PACL-pDADMAC type) were characterised by means of basic properties such as pH, turbidity, conductivity. Moreover, the impact of the synthesis process with the different additives and conditions on the Al species distribution was studied. The treatment efficiency was studied by using model tap water after adding 1 mg/L of each compound. Several jar-tests were conducted, and the final concentrations of IBU, CBZ, IBF, DCF and VLS were determined by HPLC-UV/DAD. It was revealed that the composite polymerization results in more efficient coagulants than the Co-polymerization method. PACSi was the best one, achieving up to 90 % removal of Ethinylestradiol 90 %, 80% both Ibuprofen and Diclofenac, while 60% Valsartan, and only 10% Carbamazepine. The basicity has a strong impact on the efficiency, with the [OH]/[Al] = 1 achieving the best results, whereas the increase of the [OH]/[Al] to 1.5 and 2 reduced the performance significantly. pH and dose were adjusted to achieve the best removal efficiency and it was 6 and 10 ppm respectively.

Keywords**:** Coagulation and Flocculation – Micro-pollutant – Poly silicate – Poly aluminum – HPLC

1. Introduction

1.1. Coagulation/Flocculation process efficiency

The presence of hazardous substances such as pharmaceuticals, pesticides, endocrine disrupting compounds, etc. in low concentrations in water (micropollutants) is still of great concern [1]. Conventional water or wastewater treatment is not efficient regarding the removal of micropollutants and therefore advanced techniques are applied, such as filtration, advanced oxidation processes (AOPs), adsorption with modified adsorptive materials. Despite their effectiveness, the wider application of those techniques is restricted by the complexity, higher operational costs and uncertainty in several cases regarding the formed by-products. Coagulation/flocculation (C/F) is a widely used treatment technique in water and wastewater treatment, which could pose a potential alternative due to its simplicity and cost effectiveness. C/F has been applied for the removal of micropollutants, with poor to moderate results in most cases. Considering the pharmaceuticals studied in this work, the following removal efficiencies were reported: carbamazepine (CBZ) 6-15 %, ibuprofen (IBF) 4-19 %, diclofenac (DCF) 2-10 %, whereas valsartan (VLS) and, ethinylestradiol (EE2) were not mentioned [2] – [8].

An efficient way to improve C/F performance is the development of coagulants with improved properties, by introducing suitable additives in the structure of the prepolymerized coagulants. Those additives can be introduced either before (co-polymerization) or after the polymerisation (composite polymerization) and should have preferably high molecular weight to improve the flocculation properties of the coagulants. The combined products can be characterised as composite coagulants and have been developed during the last 20 years, showing great potential compared to the simple pre-polymerized coagulants. However, their performance in the treatment of micropollutants has not been studied in detail yet [9],[10].

In this study, aluminium-based composite coagulants were produced by the use of two additives, silica in the form of polysilicates and the positively charged polyelectrolyte p-DADMAC, a commonly used polymer in wastewater treatment with a high MW up to 2–3 10^6 Da [12] and high toleration against pH variation [11]. Several different coagulants were prepared by the two polymerization methods and varying basicity or [OH]/[Al] ratio. The basicity is an important parameter, indicating the polymerization degree of the coagulants and controlling the formation of the polymerised species such as dimers (...), trimers (...), Al_{13}, etc. The coagulants were characterised by means of basic properties and Al species distribution and were tested for the removal of CBZ, IBF, DCF and VLS in tap water. The study was conducted in Egypt, where DCF and IBF were detected in concentrations 15-20 ppm along Rosetta Nile river branch [14]. Persistent organic pollutants represent about 95 % of the industrial sector effluents in Egypt [15]. More recently, there is a study as monitoring for pesticides water pollution at three sampling points along Nile river in Egypt (the pesticides are founded in 0.9-4 ppm) [16].

2. Materials and methods
2.1. Preparation of coagulants
2.1.1. Pre-polymerized inorganic coagulants
To prepare polyaluminium chloride (PACl), following solutions were used:

Primary Al solution a 0.5M AlCl3.6H20 (SIGMA-ALDRICH) was used.

0.5M NaOH solution (SIGMA-ALDRICH) for the polymerization.

Process: The calculated amount of NaOH solution to achieve [OH]/[Al] ratios of 1, 1.5 and 2 were added dropwise with a rate of 0.12 mL/min in the Al solution under stirring with a peristaltic pump. The prepared coagulants were stored in the dark for at least 48 hours before characterization and application.

2.1.2. Composite coagulants
There are two of polymerization methods: Co-polymerization and composite polymerization. In Co-polymerization method, initially, the calculated amount of the additive to achieve the desired Al/Additive ratio was introduced to the Al solution dropwise (ratio 0.3 mL/min), and afterwards the polymerization followed by adding the NaOH solution. In composite polymerization the desired ratio of the additive solution is added to an already polymerized PACl. The ratio “Al / Additive” used was: 10 parts of Al to 1 part of Additive in all preparations (w/w).

PACl-pDADMAC
For this group of composite coagulants, a 10% w/v pDADMAC solution on from MERCK-MILLIPORE was used. Composite polymerization is used to get this type of coagulant. Addition rate was 0.2 mL/min - 0.3 mL/min for the polyDADMAC into the already fresh pre-hydrolyzed PACl under magnetic stirring 800 - 1000 rpm.

Poly aluminum silicate
Silica in sodium silicate solution needs activation to interact with Al species in PACl polymer. Sodium is used as a counter ion for silicate solution due to its ability to surround silica species preventing it from polymerization [17]. Al, in contrast, seems to be able to break silica species [18]. The effect of Al on dissolved Si species was recorded in the research of Lyudmila [19] which is showed that Al ions can interact with dissolved silicate species such as Q_2, Q_3 types forcing re-arrangement of species. For preparation of polysilicates, and combine it with based Al coagulants; following steps were taken according to Tzoupanos and Zouboulis [20]:

- A 0.5 M silica solution was prepared from raw solution (30% Na2SiO3), pH of new solution around 12.
- 1 N HCl solution was prepared in order to do the polymerization process of silica.
- The silica solution is placed in a plastic beaker and HCl 1 M is carefully added under constant mixing and pH control. From an initial pH 12, the drop in pH starts. It was observed that dropping velocity must be increased to avoid gelatinization of the Silica solution, as the rate of gelatinization is high between pH 9-7. Adding acid from pH 6 until reach 4, in contrast, should be very slow as the pH is dropping quickly (suddenly) within this range. At pH 4, HCl addition stops. Ideally at pH 4 no more acid should be added, therefore the solution is kept under gentle mixing for 90 minutes. Then, few drops of HCl were added until ph = 2 (zero point of charge), and kept it under stirring for 60 minutes.

- Polysilicate solution is ready to combine (maximum storage is 5 days) with freshly prepared PACl to get PACSi (composite method). Or to combine with Al first then add NaOH to get PASiC (Co-polymerization method)
- Al/Silica = 10 molar ratio in all preparations.

2.2. Characterization methods

2.2.1. Ferron method

It is a spectrophotometric analysis for the classification of Al species distribution into three categories: monomer Al, polymeric species (including Al13) and large, colloidal polymeric species which do not react with Ferron reagent (Table 1). Fixed time point on the curve of the absorbance variation with time determined in the LPP by Ferron-timed spectrometry, which is used to quantify the Al species in the Polyaluminum solution. Characterization with a 370nm wavelength was taken depending on Changui's study [21].

Table 1: Al species depend on Ferron analysis [27].

	Ala	Alb	Alc
Definition	Primarily monomeric specie	Polynuclear Al species	Colloidal, solid phase or polymeric Al
Importance	Show a strong ability to react with some unsatisfied coordinate bonds of organic matter to facilitate removal of particles and dissolved organic carbon (DOC).	Have superior quality and possess structures that are fairly stable to further hydrolysis and solution chemistry, resulting in higher coagulation efficiency	It is non-reactive fraction of Al with Ferron within the time of experiment.
Duration of Rx with Ferron reagent	0-1 min	1-120 min	>120 min

Solutions Description:

A. 0.2 % Ferron: 0.525 g of Ferron + 0.0255 g of o-Phenantroline (also known as: Ferroin) in 250 mL of water under boiling.

B. Sodium Acetate 35% w/v: 35 g of CH_3COONa in 100 mL of water.

C. Hydroxylamine 10% w/v + 8 mL HCl v/v (this amount may vary depending on the final pH adjustment to the ABC mix solution) to make a 100 mL total solution.

Once the solutions A, B, and C are prepared, these three solutions must be mixed in a 500 ml volumetric flask, in the same sequential order A - B - C. The final pH of the solution must be between 5.2 and 5.4, otherwise adjustment has to be done with HCl 1M.

2.2.2. UV absorbance

It was measured during the Ferron method characterization with a 370nm wavelength. The equipment used for this purpose was a SPECORD® 200 PLUS from AnalytikJena. A solution with a known Al amount is prepared: 0.01% Al^{+3} w/v (0.01 gr. Al/ 100 ml). It is required 0.0894 gr. of $AlCl_3 \cdot 6H_2O$ in a 100 ml solution. Ultrapure water is used with an average conductivity of 0.051 µS/cm. Before completing the solution to 100 mL, HCl 1 M is used to drop the solution's pH below 2, at this pH level Al is found only in a monomeric form and Al polymerization reactions are prevented. Once the CSS is ready it is sealed and stored in a dark place. With the calibration standard solution ready, a calibration curve at 6 different known concentration points had to be performed by measuring Absorbance 370 nm.

2.2.3. PH, conductivity, turbidity

Conducted by pH benchtop meter inoLab® pH 7310 from WTW, inoLab® Cond 7310 from WTW, 2100N Turbidimeter from HACH.

2.3. Evaluation of treatment performance

2.3.1. Jar test

By AQUALYTIC jar tester, using 500ml of the tap water samples. A stock solution of five micropollutants was added to the water samples. The jar test consisted of rapid stirring at 160 rpm for 2 min, reduced stirring at 45 rpm for 10 min, and then settling for 40 min [22]. After the coagulation process, the supernatant samples were filtered using a 0.45 filter and analyzed byhigh performance liquid chromatography (HPLC). The removal trends of MPs were examined.

2.3.2. HPLC UV/DAD

An Agilent 1260 Infinity HPLC with UV/DAD detector was used to observe the efficiency of C/F process on the selected pharmaceuticals removal. Conditions of the device and run are set as follows: Colum (Poroshell 120 EC-C18 2.7um 50*3mm), flow (1mL/min), pressure (max. 400 bar), temperature (30 C), duration (depend on method), detector type (variable wavelength), eluent mixture (ACN: H2O), gradient (90 : 10), flow rate (1ml/1min), operating pressure (up to 600 bar), software (OpenLAB CDS ChemStation Edition)

3. Results and discussion

3.1. Characterization of LPP

There are three types of coagulants present in Fig. 1. The first type is poly aluminium chloride without any additives (PACl with [OH]/[Al]= 2, i.e. PACl 2). The second type is PACl in combination with pDADMAC by composite polymerization method to form PACl-pDADMAC 2/10 ([OH]/[Al]= 2 and Al/pDADMAC = 10 w:w). The third type is PACl in combination with activated polysilicate solution by two polymerization methods; co-polymerization and composite polymerization to produce PASiC and PACSi respectively.

Three coagulants are produced from PASiC type by change [OH]/[Al] ratio while [Al]/[Si] = 10 is fixed. The same approach for PACSi. In conclusion, PASiC 1/10, PASiC 1.5/10, PASiC 2/10, PACSi 1/10, PACSi 1.5/10, and PACSi 2/10 are the LPP related to the third type.

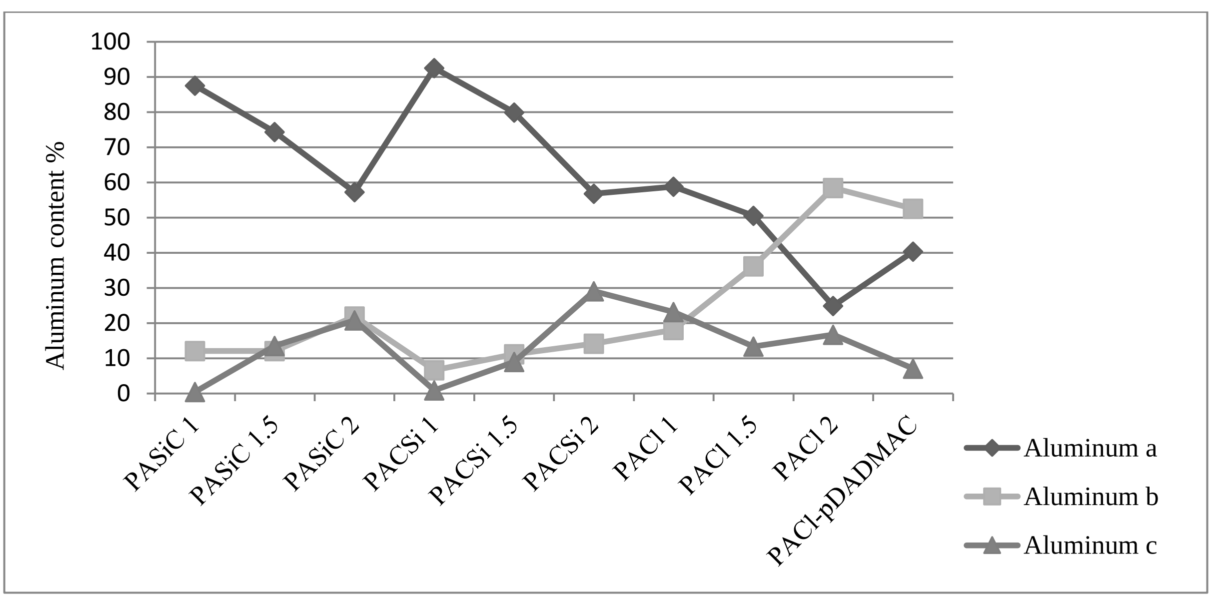

Fig. 1: Aluminum species distributions depend on Ferron analysis.

Three coagulants are produced from PASiC type by change [OH]/[Al] ratio while [Al]/[Si] = 10 is fixed. The same approach for PACSi. In conclusion, PASiC 1/10, PASiC 1.5/10, PASiC 2/10, PACSi 1/10, PACSi 1.5/10, and PACSi 2/10 are the LPP related to the third type.

3.2. Treatment of model water (MOW)

Tap water supplied by the Reverse Osmosis desalination plant of El-Gouna is used as media of jar test experiments.

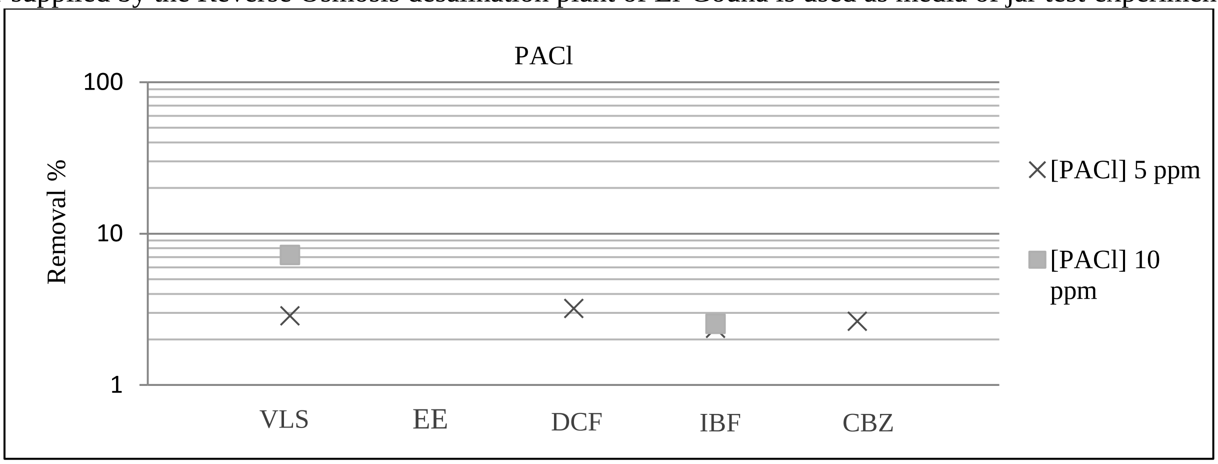

Fig. 2: Percentage removal of selected MPs with 1ppm concentration in tap water using 10ppm Al of PACl2 coagulant.

The maximum removal of TOC and UV254 is obtained by using PACl and Alum [23]. These products are still not able to remove MPs as shown in Fig. 2. Evidently, it is known that Polyaluminum chloride alone doesn't have the ability to remove MPs, even with changing B value, however, many jar tests were conducted to exclude PACl practically and looking for new options.

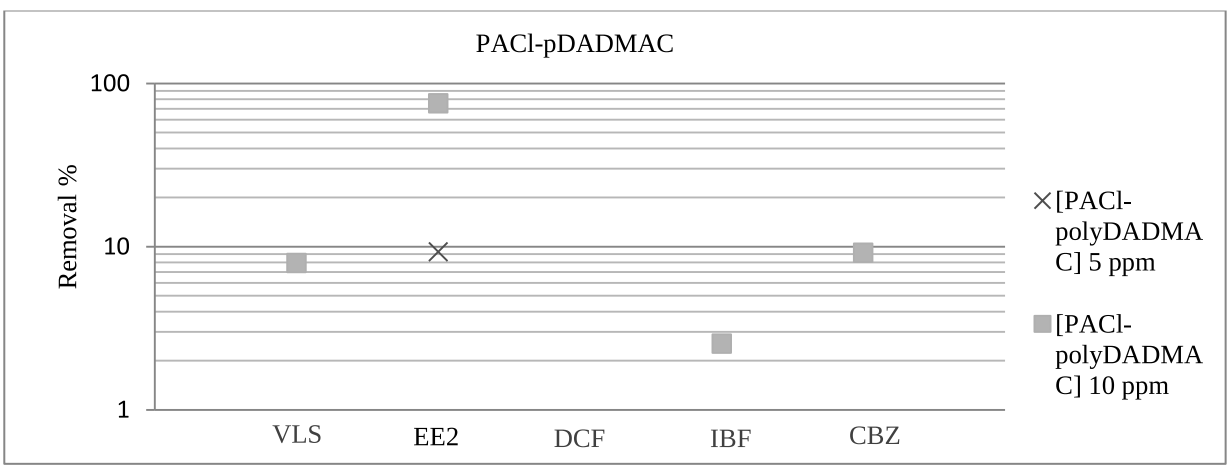

Fig. 3: Percentage removal of selected MPs with 1ppm concentration in tap water using 10ppm Al of PACl-pDADMAC coagulant.

Al_b is predominant (52%) in PACl-pDADMAC as shown in Fig.1. The majority of Al species in PACl are positively charged [22]. Therefore, an electrostatic interaction between these species and positively charged pDADMAC cannot take place. One possible interaction that could lead to new species formation is with the only negatively charged Al species, i.e. $Al(OH)_4$. Consequently, most of Al anion consumed for Al_{13} formation [9]. The positive charge of DADMAC is reactive mainly with negative species of Al which are the main precursors of Al_b which is not efficient for MPs removal as mentioned before. By using 10 ppm PACl-pDADMAC 2/10, VLS and CBZ were removed by almost 10% while EE2 removal reached almost 80% (Fig. 3). The strong hydrophobic character of EE2 and especially the steroid ring is a main difference compared to the other studied compounds. Park [24] studied the effects of Al flocs on activated sludge characteristics, and removal of 17-a-ethinylestradiol in wastewater systems. They concluded that higher Al-fed activated sludge give better settling, dewatering, and effluent quality with better EE2 removal. Furthermore, a significant correlation existed between effluent proteins and EE2 for all size fractions; it may be because those hydrophobic proteinaceous colloids (which are represented by Al-PACl-pDADMAC complex) provide binding sites for EE2 and washout together into the effluent. Another explanation is revealed by Jiang et al. [25], suggesting that EE2 was adsorbed through hydrogen bonding, proved by Fourier transform infrared and X-ray photoelectron spectroscopies.

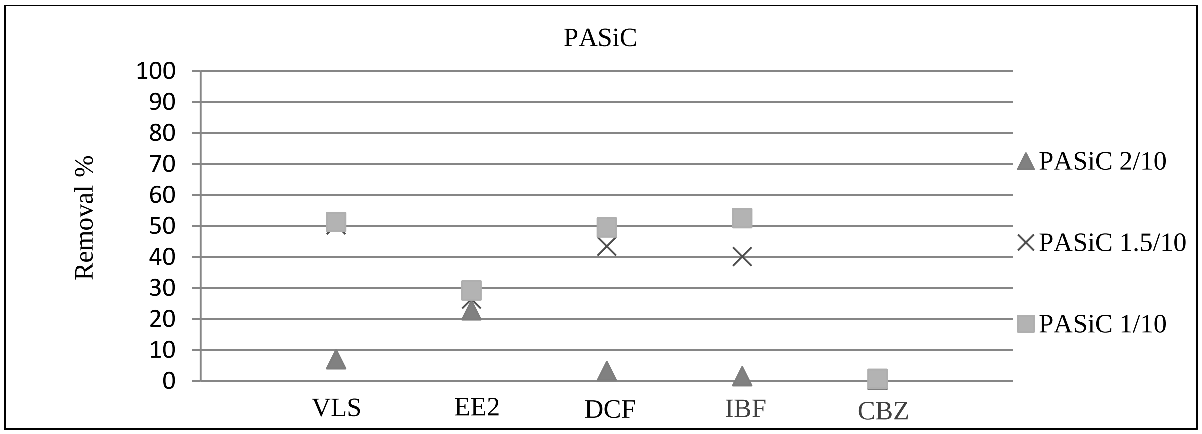

Fig. 4: Percentage removal of selected MPs with 1ppm concentration in tap water using 10ppm Al of different B value PASiC coagulants.

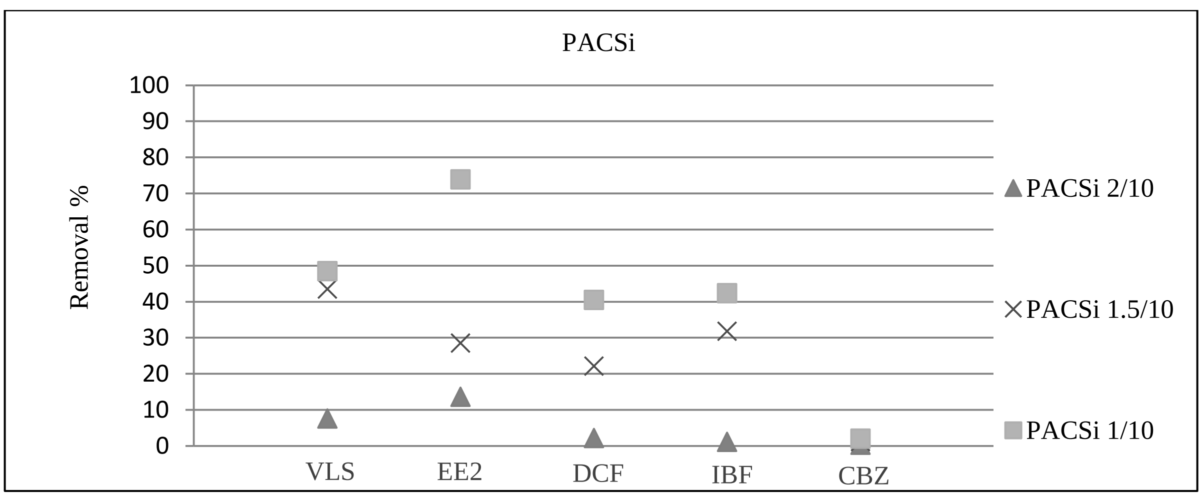

Fig. 5: Percentage removal of selected MPs with 1ppm concentration in tap water using 10ppm Al of different B value PACSi coagulants.

It is obvious that changing B value is influencing the efficiency of both; PASiC and PACSi coagulants (Fig. 5, 6). When B value equals 1, the highest efficiency was obtained. By increasing the B value to 1.5, the efficiency decreases, whereas the B value of 2 decreases further the removal rate. It seems that there is a relation between Al species distribution in silica-based coagulant (second type) and the removal efficiency. Results (Fig. 5, 6) exhibit that the efficiency of removing MPs increases with increasing Ala content (Fig .1). This can be explained as Ala (in PASiC and PACSi 1/10 with Ala%

reached 87.5 and 92.6 respectively) is suggested to have a strong ability to react with some unsatisfied coordinate bonds of organic matter to facilitate particle and DOC removal, while Alb and Alc are mainly related to turbidity removal [26]. The highest partial negative charge for silica can be obtained at pH 8-10 [27]. Activated silica, is composed of an ionized micelle formed by polysilicic acid-sodium polysilicate, this becomes negatively charged colloidal micelle [28]. As pH of MW is 7.9, Al will bind ideally with silica producing polyaluminum silicate coagulants with a molecular weight higher than conventional PACl. This binding between activated silica and Al yields a kind of aggregation of Al which will facilitate its coagulation mechanism. It is popular that silica has special adsorption properties. Crittenden [27] mentioned the three types of commercially available adsorbents merit consideration in water treatment: (1) zeolites (aluminosilicates with varying Al to Si ratios) tend to have very small pores, which will exclude some synthetic organic compounds, (2) synthetic polymeric adsorbents, and (3) activated carbon. So it's valuable to use this feature of silica in the coagulation process. Amirtharajah and Mills [29] demonstrate the relation between the concentration of Al and pH, therefore, the mechanism of Al could be revealed. Al is added with 10 ppm concentration which is equal to -3.4 on Y-axis and on X-axis, pH is 8, therefore, optimum sweep flocculation mechanism will take place. This mechanism will give the best result, especially if in the presence of compounds like silica in combination with Al. Precisely, Al floc will catch MPs and silica will fix these MPs on its surface by adsorption.

3.3. Treatment of simulated water (SW)

Initial Characterization of SW:

pH	Conductivity	Turbidity	UV absorbance
8.9	1.1 mS/cm	14.3 NTU	0.198

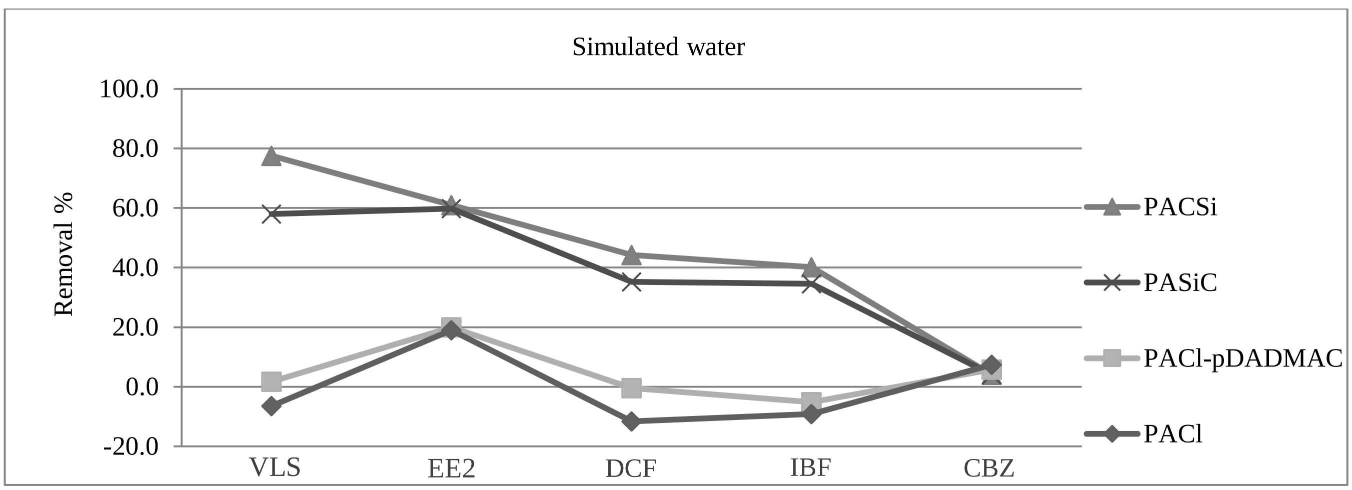

Fig. 6: Treatment of simulated water PASiC 1/10, PACSi 1/10, PACl-pDADMAC 2/10 and PACl 1. [Al]=10 ppm

Characterization of treated SW:

pH	Conductivity	Turbidity	UV absorbance
9.1	0.98 mS/cm	1.7 NTU	0.05

At a higher particle concentration by adding 5ppm humic acid and 10 ppm Kaolin, the concentration of particles still too low for effective flocculation. Some flocculation and settling occur, in which adsorption and charge neutralization take place [29]. Moreover, decrease the coagulant dose in SW may also yield a better result as particles could be removed by sweep floc mechanism [29]. Reduction of removal of selected compounds (except VLS) can simply be explained by a possible reduction of active sites of coagulant as these sites occupied by the added humic acid and kaolin particles.

4. Conclusions

Promising results were obtained regarding the removal of selected pharmaceuticals by improved, composite Removal level reached 90% for Ethenylestradiol and 60% for VLS, while DCF and IBF removal was reduced to 80%. was poorly removed (only 10%).

A low [OH]/[Al] ratio should be preferred regarding the removal of micropollutants. Particularly, PACSi 1/10 is the most efficient coagulant compared to the other Al-based composite coagulants (PACl-pDADMAC, PASiC). All composite coagulants performed better than PACl.

Efficiency is enhanced for all coagulants when anionic polyelectrolyte was added as flocculant aid.

It is suggested that the main removal mechanism is sweep flocculation.

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