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Optimising powdered activated carbon dosing strategy in aspect of NOM removal and the floc strength

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ABSTRACT

Most previous studies have focused on the adsorption efficiency of powdered activated carbon (PAC). However, very few studies have investigated the floc properties produced in the coagulation–adsorption process. In the presented studies, the authors analyzed the effect of the PAC and the coagulant dosing strategy on adsorption–coagulation efficiency in the aspect of the removal of organic compounds and residual turbidity. The effect of the type of coagulant, that is, aluminum sulfate (alum) and high-basicity polyaluminum chloride (PACl), was also tested. The main purpose of the research aimed at investigating the impact of dosing strategies on floc strength. It was found that the removal efficiency of natural organic matter noted as absorbance UV254 was very high and did not depend on the PAC dosing strategy. PAC dosing before coagulant (strategy 1) resulted in a decrease of absorbance UV254 in filtered samples from 21.05 m^{-1} in raw water to 2.95 and 2.0 m^{-1} for PACl and alum, respectively. Simultaneous reagent dosing strategy (strategy 2) and coagulant followed PAC dosing (strategy 3) resulted in similar effects. However, the dosing sequence of PAC and coagulant was decisive for residual turbidity and the strength of flocs produced in coagulation–adsorption processes. Both strategies, that is, 2 and 3 were ineffective. In strategy 2 the final turbidity was 14.36 NTU for PACl, 15.24 NTU for alum and in strategy 3 turbidity was noted at 12.78 NTU for PACl and 18.53 NTU for alum. It was demonstrated that the most resistant to breakage were flocs produced in a sequence of PAC dosing before PACl. It was mainly confirmed by the least color increase in floc breakage tests. After the sedimentation stage, the color was noted at 107 CU for PACl and 155 CU form alum. The results also demonstrated that independently of the PAC dosing sequence, PACl flocs were less prone to rupture than alum flocs.

Keywords: Powdered activated carbon; Dosage strategy; Coagulation–adsorption; Floc strength

1. Introduction

Natural organic matter (NOM) is a group of compounds with a high content of negatively charged functional groups: carboxyl ($COOH^-$) and hydroxyl (OH^-). Due to the electronegativity of these groups, NOM has a strong anionic character, which makes them susceptible to attracting cationic ions such as metal salts, that is, susceptible to removal during coagulation. It is worth noting, however, that even the most effective process does not ensure complete removal of NOM.

NOM removal during coagulation can be improved by a number of additional processes. One of them is adsorption [1–7]. To improve the removal of organic compounds, the addition of powdered activated carbon (PAC) in advanced conventional water treatment processes is commonly used in full-scale water treatment plants. The combination of adsorption and flocculation processes can effectively

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improve the removal of low molecular weight dissolved organic matter that cannot be effectively removed by coagulation–flocculation alone. On the other hand, the addition of PAC may affect the effluent turbidity and floc formation process in the coagulation–flocculation process. Generally, flocs are the basic aggregates of particles, colloids and organics and are usually highly porous, irregularly shaped, and loosely connected. The addition of PAC will affect the floc characteristics, which will also impact on the separation of the PAC.

PAC used in the water purification system makes it possible to react quickly to changes in the quality of raw water. It is the main reason for using PAC in cases when the increase in the concentration of pollutants occurs periodically. The cost of PAC is high because post-coagulation sludge with incorporated PAC particles is usually discharged and not reused. However, precipitated sludge may be recycled to a flocculation tank to enhance organics removal while maximizing the use of PAC adsorption sites before being wasted, for example, in the ACTIFLO CARB process.

The effectiveness of PAC in removing NOM depends on many factors primarily on the properties and a dose of PAC and the nature of organic molecules in water. Research results also indicate that both the PAC and a coagulant dosing sequence and a time interval between the dosing of individual reagents are important. The efficiency of adsorption of impurities of varying sizes is primarily dependent on the porosity and specific surface area of activated carbon. Adsorption most effectively occurs in pores with dimensions similar to the size of the adsorbed molecules. The results of the study conducted by many researchers have shown that when the pores of carbon are sufficiently large in relation to micro-impurities but too small in relation to NOM particles present in water, then the phenomenon of their blocking dominates. In the case where the pores of carbon are large enough in relation to both types of impurities, the effectiveness of the adsorption process is determined by the mechanism of direct competitiveness for active places on the surface of activated carbon [8–10].

Some researchers indicate that there is an optimal ratio of pore size to adsorbate particle size. Kasaoka et al. [11] suggested that absorption was the most effective when the diameter of the micropores was 1.7 times the particle diameter of the second-largest adsorbate. Therefore, the PAC with a high content of micropores will not be suitable for the adsorption of larger molecules such as NOM. The use of PAC adsorption as an independent process is usually not a cost-effective method of NOM removal due to the long time needed to achieve the maximum adsorption resulting from diffusion into the pores and the cost of PAC itself. The time required to reach a steady-state is 2–24 h [12]. This shows that only the adsorption–coagulation strategy is suitable for removing of NOM in water treatment systems.

Younker and Walsh [13] investigated the impact of adding PAC with ferric chloride ($FeCl_3$) coagulant in terms of dissolved organic compounds removal and changes to the flocs characteristics and their ability to be separated in dissolved air flotation (DAF) or sedimentation processes. The results proved that adsorbent addition reduced the coagulated floc size but did not affect floc strength or regrowth potential after breakage. It also demonstrated that sedimentation was more effective than DAF for clarification of $FeCl_3$-PAC floc aggregates.

Huang et al. [14] tested the effects of PAC dosing strategy on the coagulation–flocculation in humic acid (HA) water treatment. They studied two dosing strategies: PAC and aluminum sulfate (alum) simultaneously or PAC dosing 2 h before aluminum sulfate. The results showed that dissolved organic carbon (DOC) removal efficiency, floc size, and growth rate were relatively smaller when PAC was added 2 h before alum. However, the pre-adsorption of HA onto PAC led to the formation of stronger and more compact flocs than by simultaneous PAC and aluminum sulfate dosing strategy.

The research carried out by Altmann et al. [15] on PAC application as an advanced wastewater treatment step for the removal of organic micropollutants indicated that the dosing sequence of coagulant and PAC was not critical for efficient adsorption of organic micropollutants onto PAC. It was also indicated that the relationships between adsorptive organic micropollutants removal and a corresponding reduction of UV absorption at 254 nm may be a surrogate correlation for the development of a real-time system to predict organic micropollutants removal efficiency and PAC dosing control.

Adsorption–coagulation efficiency is especially important in membrane technologies. Bu et al. [16] stated that coagulation followed by adsorption decreased the transmembrane pressure. It was concluded that the addition of adsorbent after coagulation is a potentially important approach for alleviating ultra-filtration membrane fouling and hence more effective treatment performance.

Adding agents enhancing the treatment process significantly affects the properties of flocs. In conventional coagulation–adsorption with sludge recovery, floc strength is very important for the purification efficiency.

The paper presents the results of laboratory tests focused on investigating the impact of the PAC and the hydrolyzing or high-basicity coagulant dosing strategies on the quality of treated water and post-coagulation flocs recovery after breakage.

2. Materials and methods

2.1. Adsorbent and coagulants

The adsorbent was powdered activated carbon CWZ 22 (Gryfskand). Its characteristics are presented in Table 1.

Two types of coagulants: high-basicity polyaluminum chloride (PACl) and alum (ALS), characterized in Table 2, were tested.

2.2. Raw water

A water sample was prepared by mixing the peat extract with tap water. A stock solution of humic substances was obtained by extraction of peat soil with 0.1 N sodium hydroxide. After 1 week, the clarified solution was collected. Test samples were prepared by diluting a stated volume of aqueous humic extract in a tank providing the volume of water necessary to carry out all the tests.

Table 1
PAC characteristics

Brunauer–Emmett–Teller surface area (m^2/g)	960
Iodine number (mg/g)	1,032
Methylene number (cm^3)	29
Granulation < 0.06 mm (%)	93.1
pH_{IEP}	10.8

Table 2
Coagulants characteristics

	PACl	Aluminium sulphate (ALS)
Density (g/cm^3)	1.29	1.59
pH	4.2	3.4
Al^{3+} (%)	12.0	9.2
Cl^- (%)	6.5	0
Basicity (OH/Al) (%)	85	0

The quality of raw water used in laboratory tests was as follows:

- pH: 7.5,
- color (spectrophotometrically): 110 CU,
- turbidity: 4.18 NTU,
- absorbance UV254: 23.35 m^{-1} (non-filtered samples),
- absorbance UV254: 21.05 m^{-1} (filtered samples - membrane filters 0.45 μm),
- total organic carbon (TOC): 4.6 mg C/dm^3,
- DOC: 4.4 mg C/dm^3.

Color was measured at 455 nm with a Hach DR5000 spectrophotometer. Using this spectrophotometer, measurements of absorbance UV254 were carried out in non-filtered samples and filtered through a 0.45 μm membrane filter. A Pastel UV spectrophotometer was used to measure TOC and DOC. The research was conducted at the water treatment plant, so portable equipment was necessary. However, to make TOC and DOC results reliable some water samples were analyzed both by Pastel UV and in an independent laboratory (QBD1200 Hach analyzer) to make sure that values measured by both methods were comparative. Before each analysis, the measuring cuvette was first rinsed with distilled water, then with a small sample volume, and finally filled with the sample and analyzed. Each sample was analyzed in triplicate. The average value of all results was presented as a final result. Turbidity was measured by a Hach 2100 Q turbidimeter.

The value of the SUVA index for raw water was 4.8 m^3/g m. This indicates that mainly humic acids with high hydrophobicity and high molecular weight were present in the water.

2.3. Laboratory test procedure

On the base of the jar test results, the optimum coagulant doses for PACl and ALS were stated. Three minutes of rapid mixing at 200 rpm, followed by slow mixing at 30 rpm for 30 min and 30 min sedimentation were applied. The tested doses were in the range of 1–6 mg Al/dm^3. The optimal PACl dose was stated at 4 mg Al/dm^3 and for ALS at 5 mg Al/dm^3.

The dosing sequence of the PAC and the coagulant was then examined, mainly in terms of NOM removal and flocs strength. The experiments were carried out using an SW1 six-beaker flocculator (Stuart Scientific). Three PAC and coagulant dosing strategies were assessed in coagulation–adsorption tests. The first strategy was the PAC dosing at the beginning of the rapid mixing stage, which lasted 3 min. After 120 s of the PAC mixing with water, the coagulant was dosed. Rapid mixing was carried out at 200 rpm, followed by slow mixing at 30 rpm for 30 min, and then the water sample was subjected to 30 min sedimentation. Flocculation and sedimentation procedures were the same for all tested strategies. The second strategy was the simultaneous dosing of coagulant and adsorbent at the beginning of 3 min of rapid mixing. In the third strategy, the process parameters were the same as in the first variant, while the order of reagents dosing during rapid mixing was the opposite. The PAC dose in all strategies was stated at 40 mg/dm^3.

In the floc strength experiments, after the flocculation stage the sample was vigorously mixed at 200 rpm for 60 s and then left for 30 min sedimentation. The effectiveness of coagulation–adsorption and flocs strength was determined by measuring color, turbidity and absorbance UV254 in raw and clarified water.

3. Results and discussion

3.1. Impact of PAC and coagulant dosing sequence on the quality of treated water

In practice, in conventional coagulation–adsorption, it is often suggested to use the procedure of PAC dosing followed by coagulant in order to increase sorption efficiency before PAC grains are incorporated into flocs structure. In such a dosing strategy both susceptible and non-susceptible to coagulation impurities are adsorbed.

The results of the tests presented in the paper show that the removal of the dissolved organic matter determined as absorbance UV254 in the filtered samples was not dependent on PAC and coagulant dosing strategy. However, the dosing sequence affected the other parameters, as shown in Figs. 1–3.

The analysis of Fig. 1 indicates that when PAC was dosed before the coagulant, regardless of the type of coagulant, the effectiveness of contaminants removal was high, but better-treated water quality was demonstrated using alum. Absorbance UV254 in filtered samples decreased from 21.05 m^{-1} in raw water to 2.95 and 2.0 m^{-1} for PACl and ALS, respectively. Turbidity remained at the level close to raw water for alum (4.34 NTU), while it increased from 4.18 to 6.12 NTU for PACl. Hence, it may be concluded that the increase of turbidity observed in PACl samples resulted from PAC particles in clarified water which were not incorporated into flocs structure. Color was lowered from 110 to 39 CU for polyaluminium chloride and to 25 CU for aluminum sulfate. The above results indicate that both coagulants coped well with the removal of organic compounds.

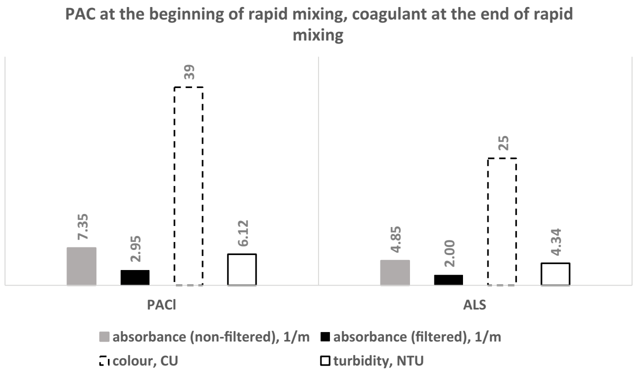

Fig. 1. Effect of coagulation–adsorption–strategy 1.

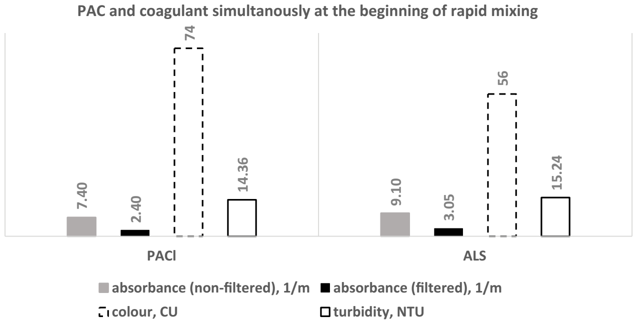

Fig. 2. Effect of coagulation–adsorption–strategy 2.

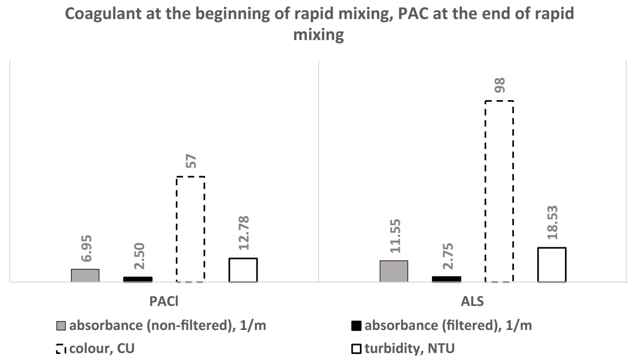

Fig. 3. Effect of coagulation–adsorption–strategy 3.

A significant decrease in absorbance in non-filtered samples, which illustrate the content of dissolved organic compounds and suspensions and colloids in water, was also observed. The observed changes in turbidity and a decrease in absorbance values in non-filtered samples from 23.35 to 7.35 m^{-1} and 4.85 m^{-1} for PACl and ALS, respectively, suggest a decrease in the concentration of suspensions in the water of the particle of a size larger than 1 μm. These particles had no direct influence on turbidity measurement because turbidimeters are the most sensitive to measure particles with sizes much smaller than 1 μm. As a result, there was no relationship between turbidity and the total suspended solids in the samples.

The obtained results show that such PAC and coagulant dosing sequence is more advantageous when using hydrolyzing coagulant. The precipitation of post-coagulant suspension during perikinetic coagulation and the initial phase of orthokinetic coagulation for alum generates fewer particles of larger size than in the case of PACl, which results in lower turbidity after the coagulation–adsorption–sedimentation process. It also facilitates the incorporation of PAC grains into the floc structure due to similar particle sizes of suspension and activated carbon. In the case of PACl, when a large number of fine particles are present in water, this process is less effective and often requires the use of reagents enhancing flocculation. However, coagulation without PAC addition resulted in residual turbidity at 5.06 NTU for ALS and 2.14 NTU for PACl. This was due to the fact that in the case of ALS not all small particles (up to 1 μm) were incorporated into the floc structure, that is, the bridging mechanism was not effective enough and only PAC dosing enhanced their agglomeration.

Changing the dosing sequence into a simultaneous dosing strategy caused the phenomena occurring during rapid mixing and flocculation have changed in comparison to the previous sequence. The turbidity of treated water was significantly higher than in raw water and it was at 14.36 NTU for PACl and 15.24 NTU for ALS. The analysis of the sludge retained on membrane filters (used in absorbance UV254 measurement), demonstrated that it mainly consisted of activated carbon particles.

Despite the difficulties with incorporating PAC particles into the floc structure, the simultaneous dosing of PAC and coagulant did not change the effectiveness of reducing organic compounds (absorbance UV254 in filtered samples) for both tested coagulants. The color after the process was 74 and 56 CU for F1.2A and ALS, respectively. This means that NOM was adsorbed on PAC and removed during coagulation, but post-coagulation aggregates susceptible to separation could not be obtained.

Similarly, low treatment efficiency was achieved in the tests with PAC dosing after coagulant (strategy 3). However, it should be noted that the quality of treated water was affected by the type of coagulant. Lower turbidity, absorbance in non-filtered samples and color after treatment were noted in samples where pre-hydrolyzed coagulant was used. However, this does not change the fact that the coagulation–adsorption process was ineffective regardless of the coagulant used, in terms of water clarification effects. That strategy, as in the case of simultaneous dosing of PAC and coagulant, did not allow the formation of permanent, well-sedimenting flocs.

The test results obtained in different coagulant and PAC dosing sequences indicate that the PAC dosing before the coagulant is the most effective. In practice, if PAC was applied simultaneously or after coagulant, the residual turbidity in the clarified water would supply rapid filters and due to the size of PAC particles, it could deteriorate filtrate quality.

3.2. Impact of PAC and coagulant dosing strategy on the floc strength

The analysis of the obtained results indicates that after flocs breakage the quality of water after sedimentation clearly depended both on the type of coagulant and the dosing sequence of the reagents (Figs. 4–6). Flocs containing polymeric Al species were definitely less sensitive to breakage. This was confirmed by the values of the color of purified water. In breakage tests in which PAC was dosed at the beginning of the rapid mixing color was 107 CU for PACl and 155 CU for ALS. The values of turbidity and absorbance in non-filtered samples increased significantly after disruption compared to samples without flocs breaking, but they were similar regardless of the type of coagulant. However, there was a clear effect of the coagulant type for the other two PAC and coagulant dosing sequences. The positive effect of polymeric aluminum forms was also visible.

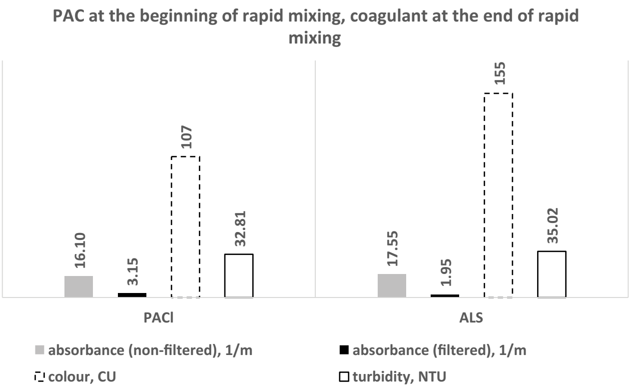

Fig. 4. Effect of flocs breakage and regrowth on treatment effectiveness–strategy 1.

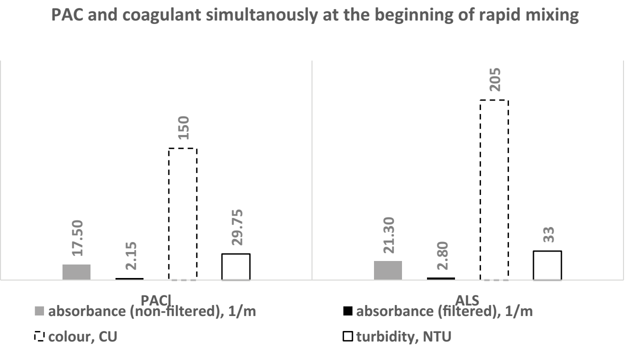

Fig. 5. Effect of flocs breakage and regrowth on treatment effectiveness–strategy 2.

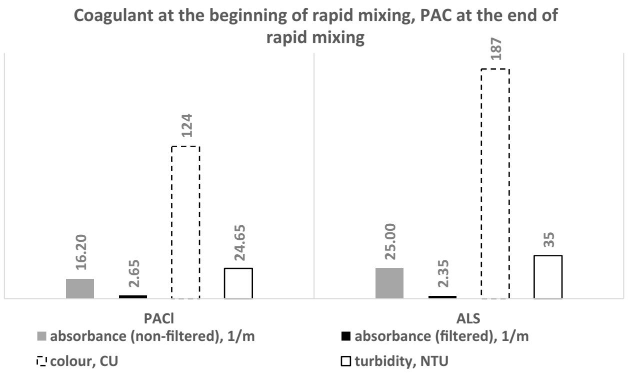

Fig. 6. Effect of flocs breakage and regrowth on treatment effectiveness–strategy 3.

In the case of the simultaneous sequence of coagulant and PAC dosing in the water after sedimentation of broken flocs, absorbance values for non-filtered samples, color and turbidity were 17.5 and 21.3 m^{-1}, 150 and 205 CU, 29.75 and 33 NTU for PACl and ALS, respectively.

In tests in which PAC was dosed after coagulant, the absorbance values in non-filtered samples, color and turbidity for PACl and ALS were 16.2 and 25 m^{-1}, 124 and 187 CU, 24.65 and 35 NTU, respectively.

Generally, there were no changes in absorbance in filtered samples, irrespective of the reagents dosing sequence and type of coagulant, which means that flocs breakage did not cause the desorption of organic pollutants into water.

The results of the strength tests indicate that the use of pre-hydrolyzed coagulant after PAC dosing was the most beneficial due to the criterion of aggregate strength. Such a sequence, when using a coagulant containing polymeric Al species, had the least negative effect on the quality of treated water, despite the disintegration of flocs, which can occur while recycling of post-coagulation sludge.

4. Conclusions

The removal of the dissolved organic matter determined in the coagulation–adsorption process was not dependent on PAC and coagulant dosing sequence. However, the dosing sequence had an impact on the formation of post-coagulation aggregates and further flocs sedimentation resulting in various turbidity removal. The most effective strategy was PAC dosing before coagulant except the residual turbidity which was at the level close to raw water. Probably, the longer sedimentation time would have been required. In other dosing strategies turbidity of treated water increased in comparison to raw water.

When PAC was dosed before coagulant, regardless of the type of coagulant, the effectiveness of organic contaminants removal was high. However, in that dosing strategy, the better-treated water quality was demonstrated using aluminum sulfate than pre-hydrolyzed coagulant.

Water quality after sedimentation of broken flocs clearly depended both on the type of coagulant and the dosing sequence of the reagents. Flocs containing pre-hydrolysis products were definitely less sensitive to rupture.

Flocs breakage, independently of PAC and coagulant dosing sequence and the type of coagulant did not cause the desorption of organic pollutants into water.

Dosing of pre-hydrolyzed coagulant after PAC had the least negative effect on the quality of treated water, despite flocs breakage. Such a phenomenon can occur, for example, while recycling of post-coagulation sludge to improve the efficiency and stability of the flocculation process.

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