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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

THE INFLUENCE OF COAGULANTS IN COLLOIDAL PARTICLES REMOVAL FROM DISPERSIONS

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ABSTRACT. This study describes the physicochemical treatment applied to colloidal dispersion of carboxymethylcellulose (CMC) in order to improve the removal of colloidal particles from aqueous solution by sedimentation and pressure filtration. The physicohemical treatment consists in coagulation/flocculation with different coagulants/flocculants at different concentrations. By coagulation-sedimentation combination the optimal parameters were established to be 5.9 for pH and 200 mg/g ($FeCl_3$/CMC) for coagulant concentration. By coagulation-filtration the best result were obtained with the coagulant concentration of 200 mg/g ($FeCl_3$/CMC) and pressure difference of 4 bar.

Keywords: *physicochemical treatment, coagulation, flocculation, sedimentation, pressure filtration, carboxymethylcellulose.*

INTRODUCTION

The application of physicochemical treatment in removing micron-size or colloidal particles is widespread in wastewater treatment, before sedimentation and membrane (micro-, ultra- and nano-) filtration when the fouling of filtering surface occurs [1].

Coagulation by chemical additives and flocculation by natural or synthetic materials are the most important physicochemical pretreatment steps in industrial wastewater used to reduce the suspended and colloidal materials responsible for color and turbidity of the wastewater. A well-chosen pretreatment process can change the structure of the system improving the sedimentation and membrane filtration processes.

Removal of colloidal and micro-size particles by coagulation/flocculation, precipitation and neutralization involves particle destabilization and particle transport [2, 3]. Coagulants destabilize colloidal suspensions allowing particles to agglomerate into microflocs, while flocculants bring the microflocs into contact with each other forming large flocs.

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Experimental determination have shown that destabilization in filtration is similar to destabilization in coagulation; effective coagulants/ flocculants are observed to be effective “filter aids”. In the same time, particles transport in filtration is analogous to transport in coagulation/ flocculation processes [4].

A great variety of destabilizing chemicals is currently available for this purpose, including metal salts (e.g., salts of Al(III), Fe(III)) and natural and synthetic polymers, which may be organic or inorganic.

The effect of a coagulation/flocculation treatment depends on the pH, the type and concentration of the used additives, and the characteristics of the feed suspension [5].

The objectives of the present work are: a). evaluation of the physicochemical pretreatment procedure in removal of colloidal particles of carboxymethylcellulose by filtration; b). optimization of pH and coagulant concentration by jar test apparatus; and c). determination of filtration kinetics by pressure filtration tests.

RESULTS AND DISCUSSION

a). Carboxymethylcellulose (CMC) solution contains colloidal particles that not settle if no coagulant is added, causing turbidity. In order to destabilize the system and to remove the colloidal particles of CMC from solution, preliminary tests are conducted in this work using different coagulants as ferric chloride $FeCl_3$, calcium chloride $CaCl_2$, and polyacrilamide (PAA) as flocculant, and a combination of these.

Considering the mean filtration rate of coagulated/flocculated 5 g/L CMC solutions as performance parameter, the best results obtained by vacuum filtration are shown in Table 1.

Table 1. Results of preliminary tests

Sample	Coagulant concentration [mg/g]	V_f [m^3/m^2]	τ [s]	$w_f \cdot 10^6$ [m/s]	Observation
Solution CMC 3%	0	-	-	-	Rapid fouling
Solution CMC 1%	0	0.00071	900	0.79	Rapid fouling
Solution CMC 0.5%	0	0.00116	900	1.29	Rapid fouling
Solution CMC 0.5% + $FeCl_3$	75	0.0174	900	16.4	Small flocs

Sample	Coagulant concentration [mg/g]	V_f [m^3/m^2]	τ [s]	$w_f \cdot 10^6$ [m/s]	Observation
Solution CMC 0.5% + $FeCl_3$	150	0.0358	900	39.4	Large flocs
Solution CMC 0.5% + $CaCl_2$	2980	0.0076	900	8.43	No structural modification
Solution CMC 0.5% + $CaCl_2$	5960	0.0063	900	7.03	No structural modification
Solution CMC 0.5% + PAA	120	0.0093	900	10.3	Small flocs
Solution CMC 0.5% + PAA	240	0.0109	900	12.18	Small flocs
Solution CMC 0.5% + $FeCl_3$ + PAA	75 120	0.0542	900	60.22	Large flocs
Solution CMC 0.5% + $FeCl_3$ + PAA	75 240	0.035	900	38.88	Gelling aggregates

As Table 1 shows, the filtration of initial samples (with CMC concentration 0.5 %, 1% or 3 %) leads to the rapid fouling of filter medium, without the possibility to measure the filtration rate for 3% CMC solution sample. The rapid fouling of filtering surface caused by blocking and internal clogging justifies the pretreatment of CMC solution using coagulants and/or flocculants.

Comparing the values of obtained filtration rate it was concluded that, in spite that addition of polyacrylamide (PAA) can accelerate the filtration process, for the next experiments only $FeCl_3$, which is friendlier with the environment than (PPA), will be used as coagulant.

b). In order to optimize the pH and the $FeCl_3$ dosage, considering coagulation procedure before a conventional sedimentation, the methods of A. Koohestanian [6] and S. W. Krasner [7] were applied. The variation of supernatant turbidity after sedimentation in jar test apparatus for different pH values and constant coagulant concentration of 200 mg/g plotted in Figure 1 shows the minimal values for pH of 5.9.

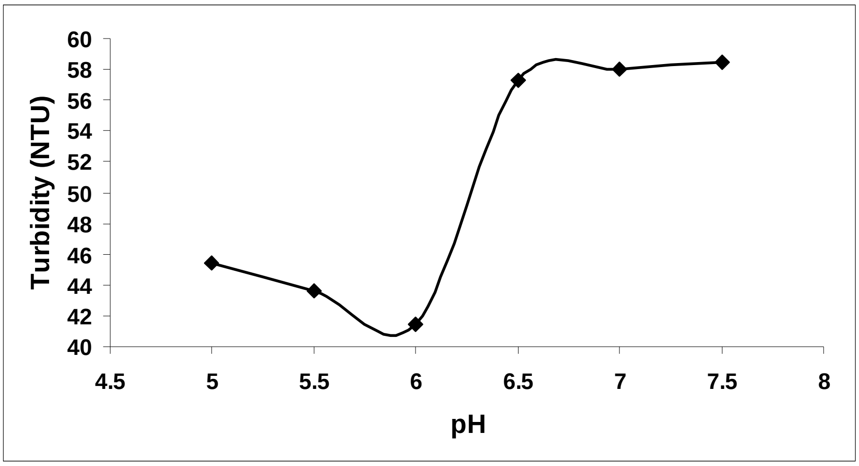

Figure 1. pH effect on the turbidity removal for 5 g/L CMC dispersion.

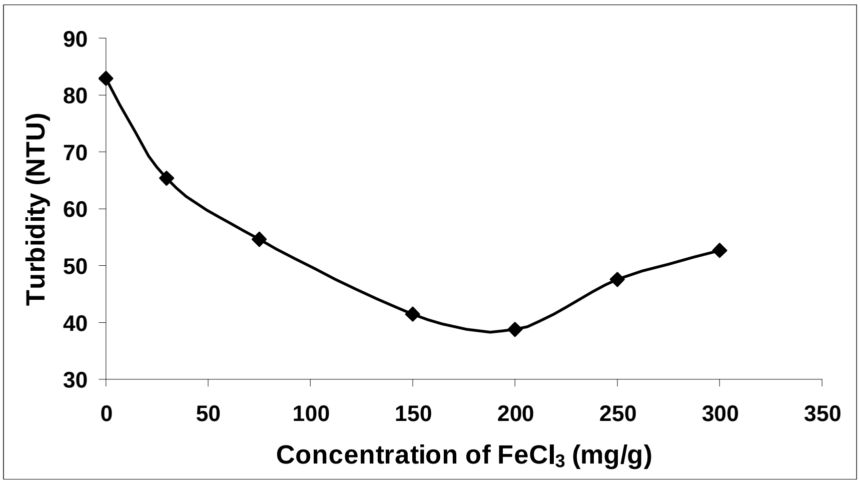

Figure 2. Coagulant concentration effect on the turbidity removal for 5 g/L CMC dispersion.

The influence of different concentrations of $FeCl_3$ added to CMC solution at constant pH = 5.9 is presented in Figure 2. As can be seen, by increasing the coagulant concentration, the supernatant turbidity decreases until the experimental concentration of coagulant is equal to 200 mg/g ($FeCl_3$/CMC). After this concentration the turbidity increases again. This means that for a concentration higher than 200 mg/g ($FeCl_3$/CMC) a re-dispersing of the flocs occurs, enhancing in this way the turbidity of solution.

Considering the combination coagulation-sedimentation at 200 mg/g ($FeCl_3$/CMC), the turbidity decreases from 83 NTU in initial solution to 38.76 NTU in supernatant, which means a turbidity removal with more than 53 %.

The progress of sedimentation, at optimal concentration of $FeCl_3$ equal to 200 mg/g ($FeCl_3$/CMC) and pH equal to 5.9 is shown in Figure 3. The mean settling rate of 0.63 mm/min was obtained by the typical curve.

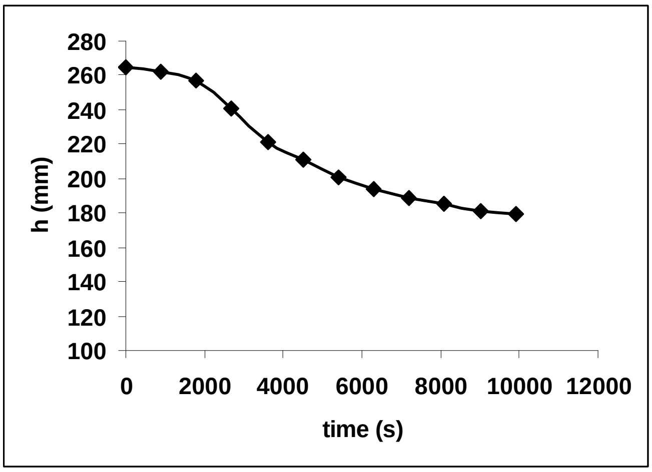

Figure 3. Sedimentation curve at optimal conditions.

c). To describe the pressure filtration, Darcy's law written as Equation 1, is proposed:

$$\frac{dV}{A \cdot dt} = \frac{\Delta p}{\eta \left(r_c \cdot c \cdot \frac{V}{A} + R_m \right)} \qquad (1)$$

where V is the volume of filtrate (m^3), Δp – pressure difference (Pa), A - filtering surface (m^2), η - the liquid viscosity (Pa.s), r_c - specific resistance of the filter cake (m/kg), R_m - the resistance of the filter medium (m^{-1}), c – weight of solids/volume of filtrate (kg solid/m^3 filtrate).

Considering V/A = V_f (m^3/m^2) the specific filtrate volume, and integrating Equation (1) with the assumption of constant pressure, a linear dependence of t/V_f versus V_f is resulting (Equation 2):

$$\frac{t}{V_f} = \frac{\eta \cdot r_c \cdot c}{2 \cdot \Delta p} \cdot V_f + \frac{\eta \cdot R_m}{\Delta p} \tag{2}$$

The mean value of cake resistance r_c and the resistance of the filter membrane R_m determined from the slope *a* and the intercept *b* of linear plot t/V_f versus V_f are given by Equations (3) and (4):

$$r_c = \frac{a \cdot 2 \cdot \Delta p}{\eta \cdot c} \tag{3}$$

$$R_m = \frac{\Delta p \cdot b}{\eta} \tag{4}$$

Considering the results obtained by the combination coagulation-sedimentation procedure, pressure filtration tests were conducted after the coagulation with ferric chloride concentration between 150 mg/g and 200 mg/g ($FeCl_3$/CMC). Figures 4a and 4b show the influence of coagulant concentration on the filtration kinetics of 5 g/L CMC solution.

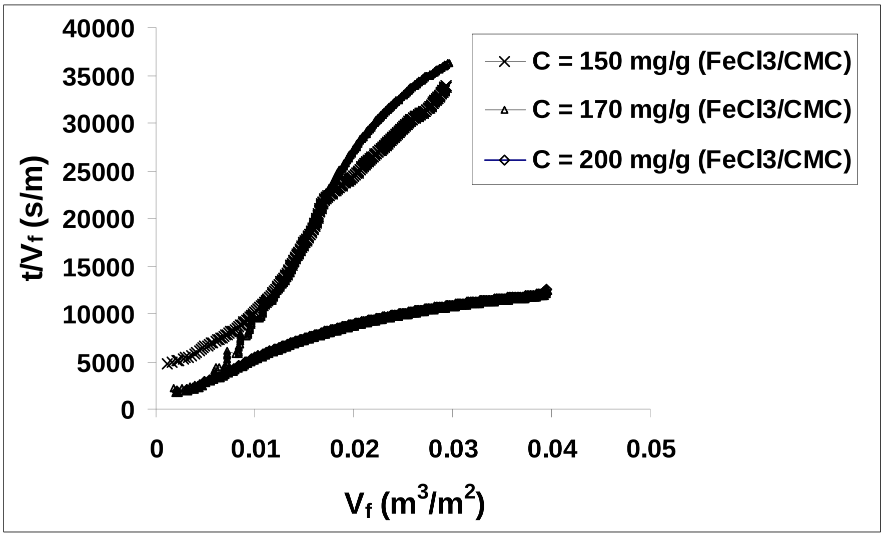

Figure 4a. Comparison of filtration behavior at 2 bar and different $FeCl_3$ dosage.

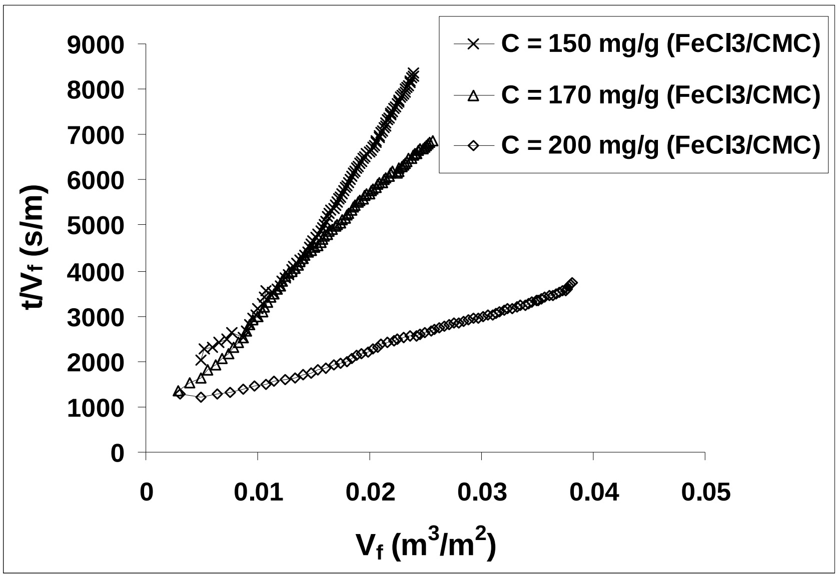

Figure 4b. Comparison of filtration behavior at 4 bar and different $FeCl_3$ dosage.

As it can be seen, an acceleration of the filtration process with the increase of the coagulant concentration is observed for experimental measurements at 2 bar and at 4 bar. In both cases a lower slope of the curves t/V_f vs. V_f was obtained when before pressure filtration a coagulant concentration of 200 mg/g ($FeCl_3$/CMC) was used.

Considering the effect of the coagulant concentration on the pressure filtration of 5 g/L CMC solutions, next results were determined from experimental data, using Equations (3) and (4): specific filter cake resistance of $r_c \approx 13.0 \cdot 10^{13}$ m/kg for coagulant concentration of 150 mg/g ($FeCl_3$/CMC), $r_c \approx 8.3 \cdot 10^{13}$ m/kg for 170 mg/g ($FeCl_3$/CMC), and $r_c \approx 2.0 \cdot 10^{13}$ m/kg for 200 mg/g ($FeCl_3$/CMC), and a mean medium resistance of $R_m \approx 3.0 \cdot 10^{11}$ m^{-1}, when the experiments were conducted at Δp = 4 bar.

Coagulant effect on turbidity removal by pressure filtration has shown a decrease from 83 NTU in initial samples to 6 - 8 NTU in filtrate, which means a turbidity removal with more than 90 %. This can be explained by adsorption phenomena and the retention of small particles on filter cake.

The influence of the pressure difference on the filtration test at coagulant concentration of 200 mg/g ($FeCl_3$/CMC) is shown in Figure 5. It can be seen an acceleration of filtration process with the increase of pressure difference from 1 bar to 4 bar.

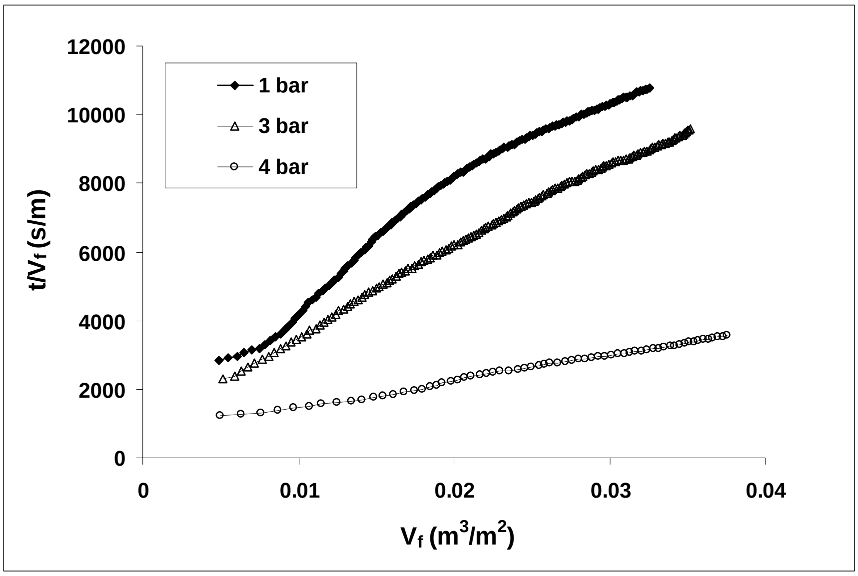

Figure 5. Comparison of filtration behavior at different pressure.

Specific filter cake resistances of $r_c \approx 6.0 \cdot 10^{13}$ m/kg for a difference pressure Δp = 1 bar, $r_c \approx 4.8 \cdot 10^{13}$ m/kg for Δp = 3 bar and $r_c = 2.0 \cdot 10^{13}$ m/kg for Δp = 4 bar were calculated considering experimental data at different pressures and constant coagulant concentration of 200 mg/g.

The results show that the specific filter cake resistance decreases with the increase of coagulant dosage and with the increase of pressure difference.

Considering the combination coagulation-filtration the best results were obtained for coagulant concentration of 200 mg/g ($FeCl_3$/CMC) and Δp = 4 bar. The mean filtration rate for these conditions, considering the calculated cake resistance, is $w_f = 20.5 \cdot 10^{-5}$ m/s, which is 3.5 times higher than filtration rate obtained for coagulant concentration of 150 mg/g ($FeCl_3$/CMC) and Δp = 4 bar ($w_f = 6.0 \cdot 10^{-5}$ m/s), and 10 times higher than filtration rate obtained for 200 mg/g ($FeCl_3$/CMC) and Δp = 1 bar ($w_f = 2.0 \cdot 10^{-5}$ m/s).

CONCLUSIONS

In this study coagulation with ferric chloride as physicochemical pretreatment before conventional sedimentation and before pressure filtration was applied to 5 g/L CMC solution samples in order to improve the removal of colloidal particles and to avoid membrane-fouling.

The optimal experimental parameters were obtained combining coagulation with settling in a jar test apparatus and coagulation with pressure filtration in Filtratest.

By coagulation-sedimentation combination the optimal parameters were established to be 5.9 for pH and 200 mg/g ($FeCl_3$/CMC) for coagulant concentration. The influence of coagulant concentration and pressure on filtration has shown an acceleration of filtration kinetics with the increase of the concentration of $FeCl_3$ from 150 mg/g to 200 mg/g and with the increase of pressure from 1 bar to 4 bar, by the reduction of the specific cake resistance.

After coagulation the turbidity of carboxymethylcellulose solution was found to be reduced by more than 53 % considering the combination coagulation-sedimentation and by more than 90% for the combination coagulation-filtration. This means that the procedure coagulation-filtration is more efficient for the removal of CMC particles due to adsorption phenomena and better retention of small particles on filter cake.

EXPERIMENTAL SECTION

Colloidal synthetic solutions of carboxymethylcellulose 5 g/L were obtained dissolving sodium carboxymethylcellulose, a white powder, in cold distillated water (initial turbidity was equal to 83 NTU).

Preliminary tests have been made using the laboratory vacuum equipment (Δp = 400 mm Hg).

A jar test apparatus model JLT 6 was used for the optimization of pH and dosage of coagulants/flocculants. Samples of 500 mL of 5 g/L CMC solution were placed in six beakers. To optimize the pH, solutions of 1.0 N NaOH and 1.0 N H_2SO_4 were added in each beaker containing the CMC solution and 200 mg/mg ($FeCl_3$/CMC), determined by preliminary tests.

After pH adjustment different concentrations of ferric chloride (30, 75, 150, 200, 250, 300 mg/g) were tested by stirring at 100 rpm for 1 min, and then at 30 rpm for 15 min. Then, the stirrer was turned off in order to let the sample to settle for 30 min. Supernatant was sampled 10 mm below the water surfaces, and the turbidity and pH were measured. The procedures were repeated at fixed dosage to examine the optimum pH.

Turbidity was measured by an Analytic turbidimeter Hanna type C-102 with a range of 0 – 100 FTU.

The pH was measured with a pH/mV meter type Orion 4 STAR from Thermo Electron Corporation.

Pressure filtration tests were performed with the laboratory filtration equipment FITRATEST from BOKELA GmbH having a pressure filter cell of steel with the capacity of 400 mL and the filtering surface of 20 cm^2. For each experiment sample of 100 mL 5g/L CMC solution was tested. FILTRATEST apparatus was operated at constant pressure; pressure difference Δp was chosen between 1 bar and 4 bar. The cumulative filtrate weight was recorded online by the computer and analyzed using Excel software. Three replicate experiments were carried out for each set of experimental conditions. The reproducibility of experiments was higher than 95 %. A SEFAR filter medium with pore size of 1.0 microns was tested during the pressure filtration.

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