Environment Protection Engineering

Vol. 30 2004 No. 1–2

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CHEMICAL COAGULATION OF MODEL WASTEWATER

The results of studies on model wastewater coagulation are presented. Coagulation–flocculation tests were performed in five replications each, which allowed us to compare four inorganic coagulants used most often in practice. Model wastewater samples showed satisfactory treatability by coagulation with aluminum and iron(III) salts. It was found that aluminum coagulants were characterized by higher coagulating ability than iron coagulants, and that coagulating abilities of the coagulants tested were as follows: PAC > $Al_2(SO_4)_3$ and $FeCl_3$ > PIX.

1. INTRODUCTION

The need to combine biological wastewater treatment with chemical coagulation results first of all from strict restrictions imposed on the phosphorus content in effluents. The most common inorganic coagulants are: PIX [1], [2]; $Al_2(SO_4)_3$ [1], [3], [4]; PAC [1], [4], [5]; $FeCl_3$ [6], and more and more popular potassium ferrate(VI) [7]. Theoretically hydrolysis of (Al and Fe) chlorides offers a wider possibility of forming cations, whose valence exceeds +3, than hydrolysis of sulfates(VI). Taking into account the Schulz–Hardy rule, this may indicate higher coagulating ability of chloride coagulants compared with sulfate coagulants. This hypothesis may be also confirmed by the presence of polycations $\{Al_{13}\}^{7+}$ in fresh floccules of post-coagulation sludge obtained due to destabilization of a "sensitive" model system (silica suspension) by PAC, as reported by BOTTERO et al. [8]. The extrapolation (underlined) of the effect of coagulant-ion valence on coagulation efficiency:

$$\mathrm{I : II : III : IV} : \underline{\mathrm{V : VI : VII}} = 1 : 20 : 500 : 10000 : \underline{200000 : 4000000 : 80000000}$$

may lead to the following conclusion: *0.1% contribution of* $\{Al_{13}\}^{7+}$ *to coagulation with* Al^{3+} *ions increases 10 times the process efficiency.*

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Therefore, a question arises whether these theoretical speculations can be verified practically [9]? It would be difficult to answer this question by performing coagulation–flocculation tests on natural wastewater, not only due to its diversity, but first of all due to a low reliability of such tests, connected with changes in wastewater properties and the lack of reproducibility of relevant laboratory tests. In the circumstances, the best solution is to use model wastewater, treatable by both biological and chemical processes. This allows us to conduct experiments in many replications and to obtain reliable results that can be analyzed statistically.

The paper presents the results of comparative coagulation–flocculation tests carried out on model wastewater with the most commonly applied inorganic coagulants, i.e.: PIX, $FeCl_3$, $Al_2(SO_4)_3$, and PAC.

2. METHODS

The wastewater samples were obtained by dissolving a precisely weighed (+/–1 mg) analytical sample of milk powder (Nestle) in distilled water. 200 cm^3 of carefully stirred fresh wastewater was poured into nine 350 cm^3 beakers.

Table 1

Parameters of crude model wastewater – mean for 20 replications

Parameter	Mean value ($mg\ dm^{-3}$)	Standard deviation ($mg\ dm^{-3}$)
COD	14580	1120
Suspended solids	224	15
Turbidity	258	16
Colour	>550	not determined

Table 1 presents the mean values (for 20 replications) of the basic parameters of crude model wastewater, with standard deviations (SD). The highest standard deviation (ca. +/–7%) was calculated for the determinations of chemical oxygen demand. Colour intensity of crude model wastewater exceeded 550 mg dm^{-3} and due to the lack of colour can be considered an apparent colour.

Ambient and wastewater temperature, controlled each time, was 291 K +/–2 K. The coagulants were dosed using bulk solutions obtained from the analytical sample of $Al_2(SO_4)_3$ and $FeCl_3$, or on the basis of the information provided by the manufacturer of PIX and PAC. After introducing the coagulant to a wastewater sample, the time of rapid mixing was ca. 60 s, the time of slow mixing – 600 s, and the time of sedimentation – 1500 s. After that time the samples were collected from above the sludge for physicochemical analyses and determinations.

Coagulation tests were carried out for each coagulant in five replications. Figures present mean values for five replications, or means with standard deviations.

The following coagulants were used:

a) low-polymerized PAC obtained from Anorthosite [5] with $[OH]/[Cl] \approx 1$,

b) PIX 110S with $d = 1.50$ g cm^{-3} and Fe^{3+} content of 12.5% (+ ca. 1% of Fe^{2+}),

c) $Al_2(SO_4)_3$ and $FeCl_3$, both obtained by dissolving an analytical sample (+/–1 mg) of salt in 2000 cm^3 of distilled water.

The following parameters were determined in samples of crude and coagulated wastewaters: chemical oxygen demand (COD), suspended solids' concentration, turbidity, colour intensity and pH. The measurements and analyses were made by standard methods [10] with a HACH instrument and a pH-meter HANNA Hi8424.

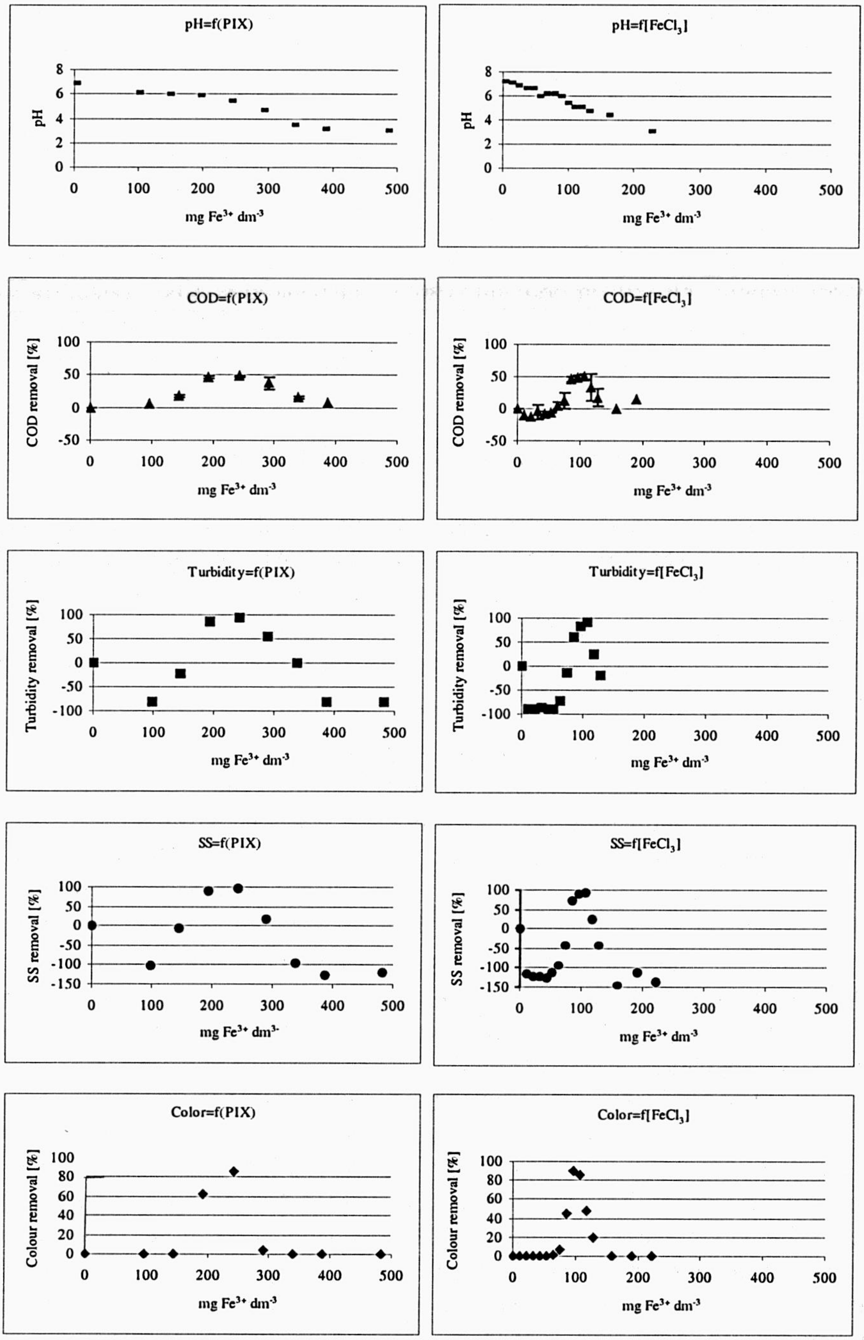
3. RESULTS AND DISCUSSION

Figure 1a presents the changes in pH and removal of COD, turbidity, suspended solids and colour, depending on the dose of iron(III) ions coming from PIX. The dose of 100–200 mg Fe^{3+} dm^{-3} caused a decrease in wastewater pH from $pH_0 \approx 7.0$ to pH ≈ 6.0. The highest doses (400–500 mg Fe^{3+} dm^{-3}) allowed us to reduce pH value to ≈ 3.0. It is obvious that iron(III) salt in a water solution (sewage) decreases pH of the system:

$$Fe^{3+} + HOH \leftrightarrow FeOH^{2+} + H^+.$$

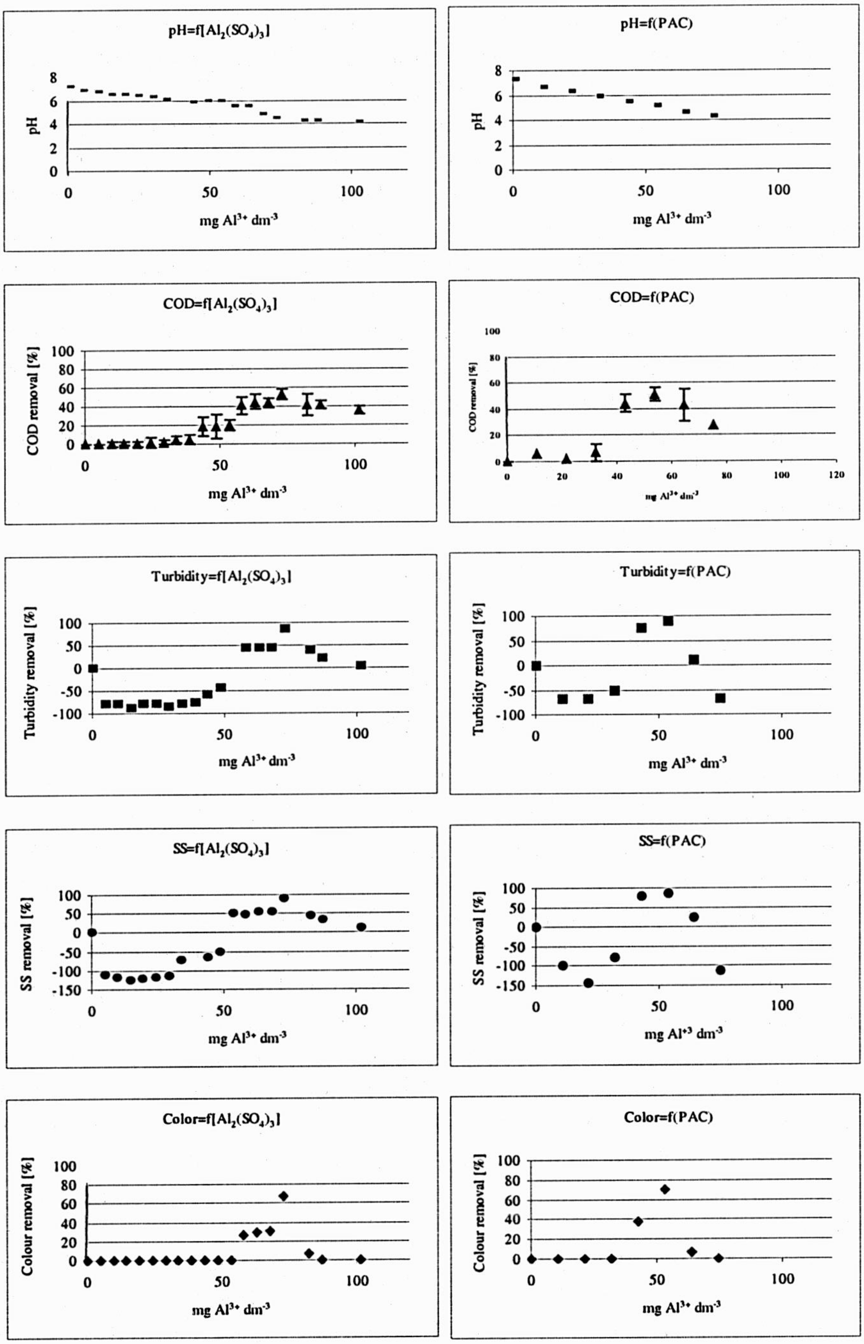
Analysis of figure 1a shows that the initial dose of 97 mg Fe^{3+} dm^{-3} did not cause any changes in COD and colour of wastewater and had a negative effect on its turbidity and concentration of suspended solids. An increase in turbidity and concentration of suspended solids was probably connected with the sampling technique (sample collection from above the sludge). This technique ensures close comparability of laboratory analyses and real situations at sewage treatment plants, because it may be applied both under conditions of coagulant deficiency, with the lack of the so-called visible coagulation, and in a system enriched with colloidal hydroxide formed due to hydrolysis of coagulant, i.e. $\{Fe(OH)_3\}_n$.

At PIX doses of 145, 193 and 241.5 mg Fe^{3+} dm^{-3} visible coagulation took place in wastewater samples, which resulted in COD elimination of up to 50% of its initial value. The dose of 241.5 mg Fe^{3+} dm^{-3} enabled total (100%) removal of turbidity and suspended solids, and colour removal in almost 90%. A high correlation between the changes in COD and colour of coagulated wastewater was observed by RATNAWEERA et al. [12]. An increase in the PIX dose above 241.5 mg Fe^{3+} dm^{-3} (to almost 500 mg Fe^{3+} dm^{-3}) results in a successive decrease in the removal of COD, turbidity and suspended solids, whereas at 338 mg Fe^{3+} dm^{-3} the colour of the system "returns" to its initial value.



a) b)

Fig. 1. Wastewater coagulation by ferric coagulants: PIX (a) and $FeCl_3$ (b)



a) b)

Fig. 2. Wastewater coagulation by aluminium coagulants: $Al_2(SO_4)_3$ (a) and PAC (b)

A detailed analysis of the diagrams shown in figure 1a indicates that the optimum dose of PIX is 241.5 mg Fe^{3+} dm^{-3}. The diagrams in figure 1b represent coagulation caused by $FeCl_3$. The dependence pH = $f(FeCl_3)$ is similar to that recorded for PIX. In this case, coagulation was visible, therefore the range of coagulant doses was limited to 222.5 mg Fe^{3+} dm^{-3}. Similarly as shown in figure 1a, the lowest coagulant doses (to ca. 60–70 mg Fe^{3+} dm^{-3}) affected negatively turbidity, suspended solids concentration, and even COD, producing no effect on wastewater colour. It seems that a small amount of substances determined in terms of COD became "suspended" on colloidal $\{Fe(OH)_3\}_n$ during latent coagulation, in this way penetrating into the samples collected from above the sludge. In the dose range from 74 to 106 mg Fe^{3+} dm^{-3}, the level of COD removal increased to ca. 50% of its initial value, which was accompanied by total removal of turbidity and suspended solids, and a 85–90% decrease in colour intensity. Similarly as in the case of PIX, an increase in the coagulant dose above 106 mg Fe^{3+} dm^{-3} had a negative effect on wastewater treatment efficiency.

A detailed analysis of the diagrams shown in figure 1b revealed that the optimum dose of $FeCl_3$ was 106 mg Fe^{3+} dm^{-3}.

Figure 2a presents diagrams for an aluminum coagulant in the form of $Al_2(SO_4)_3$. PH =f [$Al_2(SO_4)_3$] approaches here its final value higher than 4.0, i.e. by at least one unit higher compared to that in the case of iron coagulants. Similarly as for Fe^{3+}, also after adding aluminum salt to wastewater samples, pH of the system has to decrease:

$$Al^{3+} + HOH \leftrightarrow AlOH^{2+} + H^+.$$

Figure 2a shows that no visible coagulation was observed for the coagulant doses ranging from 5 to ca. 50 mg Al^{3+} dm^{-3}, and the level of turbidity and concentration of suspended solids suggested the presence of colloidal $\{Al(OH)_3\}_m$ in the samples collected from above the sludge. Similarly as in figures 1, no colour changes were observed at the above doses of $Al_2(SO_4)_3$. In the dose range from ca. 50 to 73 mg Al^{3+} dm^{-3}, COD removal reached 60% of its initial value. Similarly as in the case of PIX and $FeCl_3$, these doses enabled total removal of turbidity and suspended solids, whereas colour was eliminated in 70% only. An increase in the coagulant dose to 102 mg Al^{3+} dm^{-3} resulted in lower treatment efficiency. However, aluminium coagulant compared with iron coagulants allowed turbidity, suspended solid concentration and colour intensity to assume only their previous values, whereas at its highest dose COD still constituted only 40% of its initial value. This indicated that the negative effect of the so-called overdosing was less adverse for the aluminium coagulant than for the iron coagulants.

A detailed analysis of the diagrams shown in figure 2a indicates that the optimum dose of $Al_2(SO_4)_3$ was 73 mg Al^{3+} dm^{-3}. The diagrams in figure 2b represent coagulation due to PAC. A final pH value – slightly above 4.0 – is similar to that obtained for $Al_2(SO_4)_3$. No visible coagulation was observed at the coagulant doses ranging from 11 to 32 mg Al^{3+} dm^{-3}, and the levels of turbidity and concentration of suspended solids suggested an appearance of an additional colloid, i.e. $\{Al(OH)_3\}_m$, in the system. Similarly as in the case of PIX, $FeCl_3$ and $Al_2(SO_4)_3$, no colour changes were observed at these doses of PAC. The dose as small as 53.5 mg Al^{3+} dm^{-3} proved to be optimum for this polyaluminum coagulant, enabling over 50% removal of the substances in terms of COD, and almost 100% elimination of turbidity and suspended solids, with a decrease in colour intensity exceeding 70%. Similarly as in figures 1 and 2a an increase in the coagulant dose above the optimum value resulted in lower treatment efficiency.

Table 2

Optimum coagulant doses

Coagulant	Optimum dose	
	mg Fe^{3+} (Al^{3+}) dm^{-3}	mmole Fe^{3+} (Al^{3+}) dm^{-3}
PIX	241.5	4.3
$FeCl_3$	106.0	1.9
$Al_2(SO_4)_3$	73.0	2.7
PAC	53.5	2.0

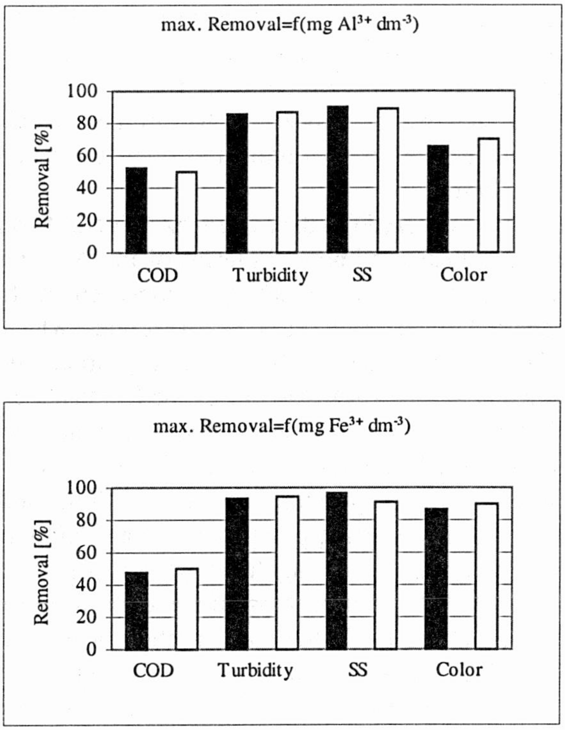


Fig. 3. Wastewater coagulation by the optimum doses of $Al_2(SO_4)_3$ and PIX – black columns and PAC and $FeCl_3$ – white columns

Table 2 presents the optimum doses of coagulants. The experiments revealed that $FeCl_3$ and PAC enabled minimal consumption of coagulating ions, i.e. 1.9 and 2.0 millimoles of Fe^{3+} and Al^{3+}, respectively, per 1 dm^3 of treated wastewater. $Al_2(SO_4)_3$ and PIX required a much higher amount of coagulating ions, i.e. 2.7 and 4.3 mmoles dm^{-3}, respectively.

The results in table 2 and figure 3 show that in order to obtain almost identical results of treating the wastewater by $Al_2(SO_4)_3$ and PAC, i.e. 50% removal of COD and over 90% elimination of suspended solids, turbidity and colour, 2.1 times as many ions from PIX as from $FeCl_3$ are necessary. Simultaneously 2.7 mmoles of Al^{3+} from $Al_2(SO_4)_3$ ensured almost the same results of coagulation as 2.0 mmoles of Al^{3+} from PAC, i.e. over 50% removal of COD, ca. 90% elimination of suspended solids and turbidity, and over 70% colour removal. It may be stated that the optimum coagulant doses presented in table 2 allowed us to achieve similar results of model wastewater coagulation (treatment).

4. CONCLUSIONS

The experimental results confirm a satisfactory treatability of model wastewater samples by coagulation–flocculation. Such wastewater makes it possible to perform laboratory experiments in any number of replications.

The range of measurements and analyses applied in the tests allowed us to present the results in a clear and legible way, to indicate trends and differences, and to analyze statistically the database.

Several regularities were observed in the system examined. It was confirmed that the dose of the aluminium coagulant estimated in terms of the Al^{3+} ion consumed was ca. two–four times lower than the Fe^{3+} dose, which is consistent with the Schultz–Hardy rule and the results reported by BOTTERO et al. [8], RAK and ŚWIDERSKA-BRÓŻ [4], and AGUILAR et al. [1]. The optimum doses of PAC and $FeCl_3$ turned out to be 1.3–2.1 times lower than the optimum doses of $Al_2(SO_4)_3$ and PIX. The fact that the Al^{3+} dose (mg dm^{-3}) was half that of Fe^{3+} can be easily explained, as the iron mole is twice as large as the aluminium mole. However, the fact that the optimum doses of PAC and $FeCl_3$ turned out to be 1.3–2.1 times lower than the optimum doses of $Al_2(SO_4)_3$ and PIX should be explained in different manner. The starting point for our considerations is the presence of aluminum polycations $\{Al_{13}\}^{+7}$ in PAC-coagulated systems [8]. Adjustment of Bottero's idea [8] to the above quantitative relationships allows us to form the hypothesis that in a system coagulated by PAC and $FeCl_3$ the concentration of polyiron or polyaluminum ions of electrovalence higher than +3 is greater than in a system coagulated by $Al_2(SO_4)_3$ and PIX. However, it would be better to use this hypothesis and to take into consideration at the same time a function being the product of concentration and electrovalence, i.e. ionic strength of a polycation. Despite the fact that the theory of polyaluminum cations is much more developed than the theory of polyiron cations, the results of the present studies reveal higher concentration of specific polyiron cations in a system coagulated by $FeCl_3$ compared with a system coagulated by PIX.

The results obtained allow us to formulate the following conclusions:

1. Model wastewater samples show satisfactory treatability by coagulation–flocculation with aluminium and iron (III)salts, and make it possible to conduct laboratory tests in many replications.
2. The coagulating ability of inorganic flocculants can be determined based on the following parameters: pH, COD, suspended solids concentration, turbidity and colour intensity.
3. Aluminium coagulants are characterized by higher coagulating ability than iron coagulants.
4. The coagulating abilities of the coagulants tested are as follows: PAC > $Al_2(SO_4)_3$ and $FeCl_3$ > PIX.

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KOAGULACJA CHEMICZNA ŚCIEKÓW MODELOWYCH

Przedstawiono i zinterpretowano wyniki badań koagulacji ścieków modelowych. Przeprowadzenie testów koagulacyjno-flokulacyjnych, każdy w 5 powtórzeniach, umożliwiło porównanie 4 koagulantów nieorganicznych najczęściej stosowanych w praktyce. Uzyskano potwierdzenie właściwej podatności użytych ścieków modelowych na koagulację solami glinu i żelaza(III). Koagulanty glinowe miały lepsze zdolności koagulacyjne niż żelazowe. Stwierdzono też zróżnicowanie skuteczności w następujących parach koagulantów: PAC > $Al_2(SO_4)_3$ oraz $FeCl_3$ > PIX.