

ANDRZEJ M. DZIUBEK*, JOLANTA MAĆKIEWICZ*

ON THE EFFICIENCY OF IRON COAGULANTS IN THE TREATMENT OF THE ODRA RIVER WATER

Two novel ferric coagulants, Roflok-WP (ferric chloride, manufactured by Rokita-Brzeg Dolny) and PIX (ferric sulfate, made by Kemipol-Police), were tested for their efficiencies in the coagulation of the Odra River water at natural and adjusted pH. Roflok-WP was found to yield better flocculation effects than PIX, particularly in natural and alkaline water. Following adjustment of pH to the optimum value (6.5-6.8), the efficiencies of both coagulants were similar.

1. INTRODUCTION

Iron salts have long been in use as flocculating agents. In Finland, attempts were made to intensify the water treatment process by adding iron salts at the first stage of coagulation (carried out in a two-stage system), thus accounting for considerable abatement of the THM content in the water [1]. In Poland, the advantages of using iron salts as flocculants in water coagulation, particularly when organic matter is to be removed, have been reported in specialized literature for over than 20 years [2], [3]. But it is only recently that the interest in iron salt coagulants has increased noticeably, primarily because of the low cost of their manufacture, as well as because the admissible level for aluminium concentration in drinking water has already been established.

2. CHARACTERIZATION OF THE COAGULANTS

Two inorganic Fe(III)-based coagulants, PIX and Roflok-WP, are marketed in Poland. According to the manufacturer's specifications, PIX is a Fe(III) sulfate

*Institute of Environment Protection Engineering, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

solution of a yellowish-brown colour, the density approaching 1.5 g/cm^3 , and the viscosity ranging between 5 and 20 cP. The pH of the solution does not exceed 1.0. Free-acid content varies from 0 to 20 g/dm^3 , and active-substance concentration amounts to 3.1 mol/dm^3 . Trace elements occur at the following concentrations: cadmium, 0.5 mg Cd/kg; copper, 10 mg Cu/kg; nickel, 40 mg Ni/kg; zinc, 1,000 mg Zn/kg; chromium, 30 mg Cr/kg; mercury, 0.05 mg Hg/kg and lead, 1.0 mg Pb/kg. The coagulant should not be dosed in dilution: 10 cm^3 are equivalent to 14.7 g of PIX, i.e. to 1.75 g Fe. The concentrations of Fe(III) and Fe(II) in the PIX solutions amount to $173 \pm 3 \text{ g Fe/dm}^3$, respectively. PIX is manufactured by Kemipol-Police, Poland.

Roflok-WP is an aqueous solution of ferric chloride. It has a red-brown colour, the density of about 1.4 g/cm^3 , the viscosity of about 7 cP, and pH below 1.0. The Roflok-WP solution contains Fe(III) at concentrations ranging between 177 and 190 g Fe/dm³; the maximum concentration of Fe(II) being 0.5%. The coagulant is manufactured by Rokita-Brzeg Dolny, Poland, in solutions of at least 37% concentration (grade I), and at least 33% concentration (grade II), the concentrations of free HCl being $\leq 2\%$ and $\leq 3\%$ for grade I and grade II, respectively.

The hydrolysis of the two coagulants accounts for the decrease of pH and alkalinity levels in the water, but this decrease is greater in the presence of Roflok-WP [4].

3. EXPERIMENTAL

3.1. METHODS

The coagulation process was run on a laboratory scale with standard samples of the Odra River water. The efficiency of Fe(III) salts as coagulating agents was determined as natural and adjusted pH of the water sample. Adjustment was carried out in the pH ranges from low to natural and from natural to high, using HCl and KOH or Ca(OH)_2 , respectively. The efficiencies of the two coagulants were assessed by taking into account the treatment effects and the iron concentration persisting in the effluent from the coagulation process [4].

3.2. COMPOSITION OF THE RIVER WATER

The parameters of the water samples measured in the course of the study are listed in the table.

Table

Parameters of the Odra River samples

Parameter, unit	Summer 1992	Winter 1992/1993	Spring 1994
Alkalinity, val/dm ³	2.3-2.5	1.3-1.9	1.4-2.0
pH	7.3-8.3	7.2-7.4	7.2-7.9
Colour, g Pt/m ³	20-35	15-20	10-30
Turbidity, g/m ³	15	5-15	10-30
COD (permanganate), g O ₂ /m ³	6.8-8.3	3.3-4.4	3.9-10.2
Total iron, g Fe/m ³	0.1-0.8	0.3-0.8	0.3-1.9

As shown by these data, the pollution load of the Odra River water was not very high. In the winter season it was even lower than in the summer season, and so were alkalinity and pH.

4. RESULTS

4.1. EFFICIENCY OF PIX

The results are plotted in figure 1. To eliminate the adverse effect of winter temperature on the course of the coagulation process, the temperature of the water samples was adjusted to room temperature. Consideration was also given to the proneness of the water pollutants to removal in the summer and winter seasons.

As shown by the plots in figure 1, removal efficiency for turbidity was higher in summer than in winter, unlike that for colour or COD_p, which was higher in the winter season. The optimum PIX doses amounted to 30 g/m³ and 50 g/m³ in summer and winter, respectively, even though the pollution level in the river water was noticeably lower in the winter season. It was

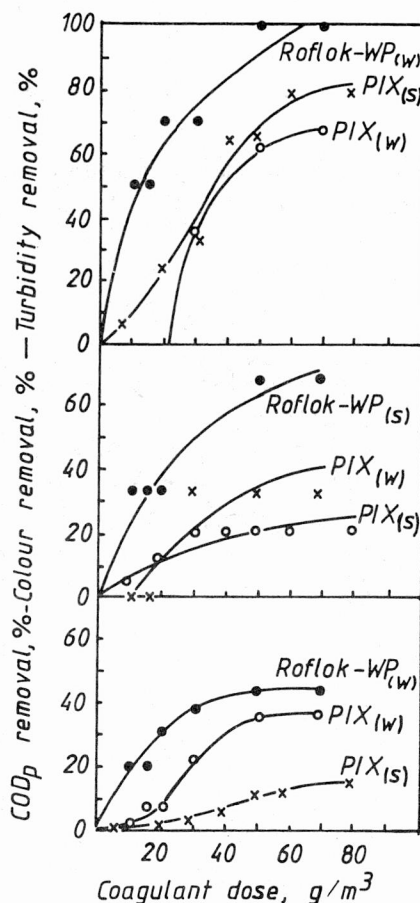


Fig. 1. Removal efficiencies obtained by iron-salt coagulation of the Odra River water

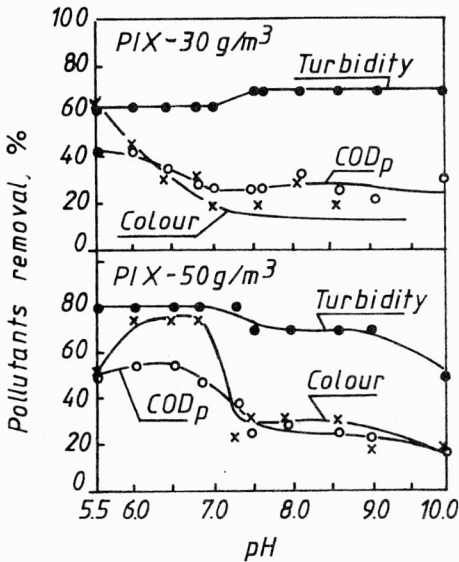


Fig. 2. Efficiency of PIX in the winter season versus pH

pH = 6.7 and the application of 30 g/m^3 dose provided efficiencies similar to those obtained with the 50 g/m^3 dose without pH adjustment.

found that in winter the PIX doses of up to 20 g/m^3 had no coagulating effects. There was a concomitant considerable rise in both turbidity and colour intensity, which might be indicative of the formation of complexes with the iron salts added. The need of applying a higher PIX dose in the winter season, in spite of the decreased pollution level, should be attributed to the increased stability of the colloids in the Odra River, because the winter temperature effect (as already mentioned) was eliminated in our study [3].

For water less prone to treatment, the effect of pH adjustment on the coagulation efficiency in the winter season (PIX dose, 50 g/m^3) is plotted in figure 2. As shown by these data, pH < 6.7 created evidently favourable conditions, particularly for the removal of organic pollutants. Adjustment to

4.2. EFFICIENCY OF ROFLOK-WP

The experiments were carried out in the winter season, when the river water was characterized by an increased stability of the colloidal system. The removal of the polluting species by coagulation increased with the increasing Roflok-WP dose (its optimum being 30 g/m^3 , figure 1).

The effect of pH adjustment on the efficiency of the Roflok-WP coagulation at the dose of 30 g/m^3 is shown in figure 3. Thus the efficiency of colour removal increased when pH decreased, COD_p removal was almost identical in the entire pH range investigated,

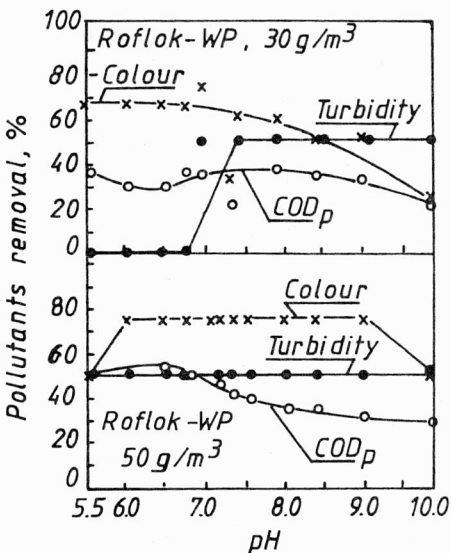


Fig. 3. Efficiency of Roflok-WP in the winter season versus pH

whereas the efficiency of turbidity removal increased with the increasing pH. The increase of the coagulant dose to 50 g/m^3 brought about a colour removal of approximately 75% at pH range from 6.0 to 9.1, and a turbidity removal of approximately 50% at pH range from 5.5 to 10.0. The efficiency of COD_p removal was noticeably better, even amounting to over 50% at pH between 6.0 and 6.8.

4.3. EFFICIENCY OF ALUM

For the purpose of comparison, standard tests were carried out on the Odra River water samples (collected in the spring season) which were treated by alum coagulation [5], since alum is preferable to iron salts in Poland's water treatment plants. The physicochemical parameters of the water samples did not substantially differ from those measured during two characteristic seasons – summer and winter. The removal efficiencies are plotted in figure 4.

The optimum alum dose amounted to 30 g/m^3 and was identical to that of Roflok-WP in terms of quantity. The difference in the efficiencies of turbidity and colour removal between alum and Roflok-WP was found to be small, but alum provided higher efficiency of COD_p removal.

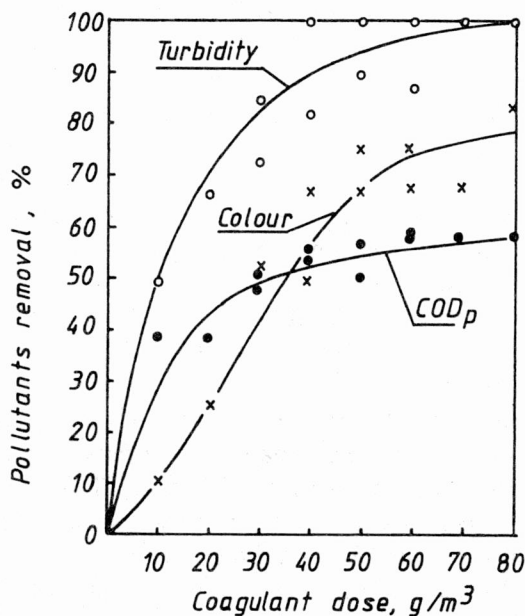


Fig. 4. Removal efficiencies obtained by alum coagulation of the Odra River water

4.4. COMPARISON OF REMOVAL EFFICIENCIES PROVIDED BY ROFLOK-WP AND PIX

The efficiencies of the two coagulants were compared in the winter season (figure 1) and the coagulating effect was found to be far better when Roflok-WP was used. The minimum doses required to achieve the coagulating effect amounted to 10 g/m^3 and $>20 \text{ g/m}^3$ for Roflok-WP and PIX, respectively. The removal efficiencies obtained with Roflok-WP were by 30% higher for turbidity, by 20–25% higher for coloured matter and by 10–20% higher for COD_p than those achieved with PIX (figure 1). In other words, a 10 g/m^3 Roflok-WP dose yields the same treatment effects as the dose of 30 g/m^3 of PIX. Taking into account the optimum pH range,

which is almost the same for the two coagulants, as well as the treatment effects, Roflok-WP should be recommended rather than PIX as a flocculating agent.

In terms of iron content, the efficiency of Roflok-WP was about 1.5 times as high as that of PIX. In terms of the coagulating effects obtained with the optimum coagulant doses (30 g/m³ and 50 g/m³ for Roflok-WP and PIX, respectively) at pH adjusted to the optimum level, PIX was found to be more efficient. However, relating this efficiency to 1 g of Fe in the coagulant, the difference in the efficiencies of the two coagulants at optimum pH of water was not so distinct as before any longer. Roflok-WP was found to be more effective than PIX in water of high pH. The increase of the dose to 50 g/m³ increased the efficiency of colour removal more than twice as compared to PIX (COD_p removal being similar for the two coagulants). The efficiency of turbidity removal was noticeably deteriorated in the entire investigated pH range. The fact that the coagulating effects obtained with Roflok-WP were better than those achieved with PIX should be attributed to the amount of free acids in Roflok-WP. This finding seems to be corroborated by the increased drop of pH and alkalinity of the water (as compared to that produced by PIX) and by the almost equal removal efficiencies obtained at optimum pH, irrespective of the coagulant applied.

The amount of iron persisting in the effluent from the coagulation process approached 1.0 to 2.0 g Fe/m³. The concentrations measured after filtration of the samples were much lower, ranging between 0.06 and 0.20 g Fe/m³ at natural pH (or between 1.5 and 1.8 g Fe/m³ when no filtration was applied). Adjustment of pH brought about an abatement of persisting iron concentrations after sample coagulation with the optimum PIX dose. Thus, at high pH of water and a 30 g/m³ PIX dose, persisting iron concentrations varied from 0.1 to 0.3 g Fe/m³ after filtration of a water sample, and from 1.6 to 2.1 g Fe/m³ in the case when the sample was not filtrated. At high pH of water containing 50 g/m³ of PIX, they ranged from 0.05 to 0.10 g Fe/m³ and from 1.6 to 2.5 g Fe/m³, respectively. At low pH of water, the concentrations of persisting iron were found to be slightly higher (especially at increased coagulant doses), approaching 0.14 g Fe/m³ for the 30 g/m³ dose, and ranging from 0.1 to 0.2 g Fe/m³ for the 50 g/m³ dose. At pH = 5.5, iron content after filtration approached 1.0 g Fe/m³.

Persisting iron concentrations after coagulation with Roflok-WP at natural pH ranged between 0.05 and 0.15 g Fe/m³ in samples after filtration. At optimum Roflok-WP dose (30 g/m³) and pH adjusted to acidic range, persisting iron concentrations were very low, varying from 0.06 to 0.08 g Fe/m³. Equally low concentrations (0.05–0.08 g Fe/m³) were measured for alkaline water solutions and 30 g/m³ Roflok-WP dose. The increase of the coagulant dose to 50 g/m³ accounted for a rise in the amount of persisting iron which varied between 0.1 and 0.2 g Fe/m³ at acidic pH. Thus, at pH = 6.0, the persisting iron content was 1.1 g Fe/m³ and reached the value of 3.5 g Fe/m³ at pH = 5.5. In alkaline solution, persisting iron concentrations remained low, ranging from 0.08 to 0.11 g Fe/m³.

In terms of persisting iron concentrations, coagulation with optimum dose of Roflok-WP was slightly more effective than the one with the optimum PIX dose.

5. SUMMARIZING COMMENTS

Both PIX and Roflok-WP can be applied to the coagulation of pollutants in surface water over a wide pH range (from acidic to alkaline solutions). Roflok-WP proved to be a more effective coagulant than PIX. The efficiencies of both coagulants can be improved by pH adjustment to the optimum value which, in the case of the Odra River, varied between 6.6 and 6.7. Persisting iron concentrations after filtration of the samples were far below the admissible level for drinking water, irrespective of whether PIX or Roflok-WP was applied.

The treatment effects obtained with iron salts (which are very similar to those achieved with alum), as well as their competitive price (which is approximately half that of alum) suggest the preference for iron salts as coagulants. Another advantage of using iron salts is that they produce heavier flocs which are easier to settle, and the admissible level of iron ion concentration persisting in the treated water is easier to achieve. Persisting aluminium ion concentrations are often found to exceed the admissible values, particularly at an increased pH of raw water.

Even though the results obtained corroborate the preference for iron coagulants, their widespread implementation cannot be too hasty. One should remember that, in some instances, iron salts not only fail to remove coloured matter, but they may even raise its concentration as a result of chemical reactions. Iron salt coagulation of water pollutants can also be a failure during algae blooming.

With these thoughts in mind, many waterwork managers in Poland attempt to include iron coagulants into the treatment train.

REFERENCES

- [1] *Nowoczesne metody koagulacji i chemicznego strącania w oczyszczaniu wody i ścieków (doświadczenia skandynawskie)*, praca zbiorowa, Kemipol, Kemira Kemwater, Politechnika Krakowska, MPWiK w m.st. Warszawie.
- [2] KOWAL A.L., ŚWIDERSKA-BRÓŻ M., *Intensyfikacja procesu koagulacji w wodzie*, Prace Nauk. Inst. Inż. Ochr. Środow. PWR., nr 27 (1974).
- [3] MAĆKIEWICZ J., *Flokulacja w procesie koagulacji i filtracji wód*, PWN, Warszawa 1987.
- [4] DZIUBEK A.M., MAĆKIEWICZ J., *Ocena skuteczności technicznych soli żelaza w koagulacji domieszek wody odrzańskiej*, Ochrona Środowiska, nr 3(50) (1993).
- [5] DZIUBEK A.M., KASPRZAK M., *Wykorzystanie nowych koagulantów żelazowych do usuwania wybranych domieszek wód*, PWR., unpublished report, 1994.

PRZYDATNOŚĆ SOLI ŻELAZA DO KOAGULACJI DOMIESZEK WODY ODRZAŃSKIEJ

Omówiono wyniki zastosowania nowych koagulantów żelazowych do oczyszczania domieszek wód powierzchniowych i odniesiono je do efektów, jakie uzyskiwano stosując siarczan glinu. W badaniach ustalono przydatność Rofloku-WP i PIX-u w procesie oczyszczania wody odrzańskiej o naturalnym oraz korygowanym pH. Stwierdzono, że lepsze efekty koagulacji uzyskano stosując Roflok-WP, zwłaszcza przy naturalnym i zasadowym pH wody, przy czym korekta pH do wartości optymalnej 6,5–6,8 niwelowała różnice w efektach koagulacji obydwoma koagulantami, zwłaszcza w odniesieniu do zawartego w nich żelaza.

ПРИГОДНОСТЬ ЖЕЛЕЗНЫХ СОЛЕЙ ДЛЯ КОАГУЛЯЦИИ ПРИМЕСЕЙ ВОДЫ ИЗ ОДЕРА

Обсуждены результаты применения новых железных коагуляторов для очистки примесей поверхностных вод, которые были отнесены к эффектам, полученным при применении сульфата алюминия. В исследованиях была установлена пригодность Рофлока-ВП (Roflok-WP) и ПИКС-а (PIX) в процессе очистки воды из Одера натурального и скорректированного pH. Было установлено, что лучшие эффекты коагуляции получены с применением Рофлока-ВП, особенно в натуральной и щелочной среде, при чем корректировка pH к оптимальному значению 6,5–6,8 удаляла разницы в эффектах коагуляции обоими коагуляторами, особенно в отнесении к содержащемуся в них железу.