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TREATMENT OF LOW-SALINITY MOUNTAINOUS WATERS

Low-alkalinity and low-hardness mountainous waters are considered to be unsusceptible to coagulation. For many months these waters reveal low turbidity and low temperature. This paper evaluates the influence of pH adjustment downwards before coagulant and lime addition on flocculation and the effectiveness of water treatment. The effects of high-turbidity or intense colour on coagulation were also examined.

1. INTRODUCTION

Mountainous waters usually reveal low temperature, low hardness, low alkalinity and low pH. They are also seasonally rich in humic substances [1]. For such waters the use of chlorine as a disinfectant is under scrutiny because of its potential to form trihalomethanes. In order to reduce the risk of THMs (trihalomethanes) formation, humic substances should be removed before chlorination or chlorine should not be used in water treatment.

The basic process of organic matter removal is coagulation. This process involves several mechanisms, which may overlap so more than one mechanism may be responsible for organic matter removal. Charge neutralisation is the mechanism that explains the precipitation of organic matter in operational regions, where precipitation of metal hydroxide is minimal. Cationic aluminium or iron interacts electrostatically with anionic organic compounds to form insoluble charge-neutral products. In operational regions, insoluble iron and alum hydroxides form organic contaminants, which can be removed by entrapment or surface adsorption. Colloidal organic matter can act as nuclei for precipitate formation, or can become entrapped during floc aggregation [2].

Under the pH conditions of the most natural waters humic acids occur as negatively charged macromolecules. Their negative charge results from the presence of functional groups, i.e. carboxyl and phenol groups. As pH increases, the stability of the functional groups increases. At pH 4.0–6.0 the efficiency of organic matter removal is the best, because positively charged products of metal hydrolysis exist at this

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pH range. For iron coagulants some authors suggest pH <4.0. For pH>6, at the range of aluminium and iron hydroxides' precipitation, sorption has a decisive influence on the efficiency of removal and dominates over the charge neutralisation [3], [4].

Taking into consideration the fact that the form of humic acids depends on pH, the preliminary acidifying of raw water to pH = 4.0–5.0 should precede a coagulant addition, and should be followed by lime addition. Lime is expected not only to increase pH to optimum, but also to act as nuclei in a flocculation process. The aim of pH adjustment downwards prior to coagulant addition was to obtain the colloidal coagulant, organic complexes, more susceptible to coagulation.

The objective of the investigation was to estimate the influence of pH lowering before the coagulant addition on organic matter removal from low-salinity mountainous waters.

2. MATERIALS AND METHODS

2.1. WATER SAMPLES

The investigation was carried out for three different water sources, whose characteristics are presented in the table:

- Natural water from the mountainous water intake.
- Intensively coloured water (80 mg/dm³) prepared on the basis of natural water.
- High-turbidity water (60 mg/dm³) prepared on the basis of natural water.

Table

Water characteristics

Measurements	Unit	Natural water	Intensively coloured water	High-turbidity water
pH	–	6.5–6.85	6.77	6.85
Acidity	mval/dm ³	0.3–0.9	0.4	0.3
Alkalinity	mval/dm ³	0.3–0.4	0.4	0.4
Colour	mg/dm ³	30–35	80	30
Turbidity	mg/dm ³	<5	<5	30
Permanganate oxygen demand	mg O ₂ /dm ³	1.6–4.8	7.5	3.0
Iron	mg Fe/dm ³	0.0–0.6	–	–
Aluminium	mg Al/dm ³	0.0–0.26	0.0	0.1
Total hardness	mg CaCO ₃ /dm ³	40–125	40	40
Conductivity	μS/cm	68–75.7	95	74.5
Absorbance UV ₂₅₄	cm ⁻¹	0.1–0.12	0.2	0.1

Intensively coloured water was prepared by peat extract addition to natural water, while high-turbidity water – by addition of kaolin and bentonite suspension. It was necessary to use prepared water, because in the period of this study natural water lacked any intensively coloured contaminants of high turbidity (which periodically occur in natural water).

2.2. NATURAL WATER

This water was taken from one of mountainous water intakes. During the studies natural water was basically contaminated by colouring matter approaching 30–35 mg/dm³. Turbidity was lower than 5 mg/dm³. pH ranged from 6.5 to 6.85, but occasionally much lower values were measured (pH 5.2). Alkalinity was very low, i.e. 0.3–0.4 mval/dm³; hardness, 40–125 mg CaCO₃/dm³; conductivity, 68–75.7 μS/cm. Absorbance UV₂₅₄ ranged from 0.1 to 0.12 cm⁻¹, permanganate oxygen demand varied from 1.6 to 4.8 mg O₂/dm³. In spite of apparently good quality of raw water, large quantities of THMs appeared after water disinfection with chlorine. Their concentration after 30 min chlorination exceeded the values acceptable for drinking water. During 30 min chlorination with the dosage of 1.2 mg Cl₂/dm³ THMs concentration reached 60 μg/dm³. The potential of THMs formation (THMPF) was also determined. THMs concentration after 24 hour chlorination with the dosage of 10 mg Cl₂/dm³ was 140 μg/dm³.

2.3. INTENSIVELY COLOURED WATER

Water with artificially intensified colour was characterised by colour of 80 mg/dm³, POD of 7.5 mg O₂/dm³, absorbance of 0.22 cm⁻¹, hardness of 40 mg CaCO₃/dm³ and conductivity of 95 μS/cm. Other parameters did not exceed the permissible values established for drinking water (table).

2.4. HIGH-TURBIDITY WATER

Water with artificially increased turbidity was characterised by the colour of 60 mg/dm³ (in a filtered sample it was much lower, i.e. 30 mg/dm³); POD was 3.0 mg O₂/dm³; hardness, 40 mg CaCO₃/dm³; and conductivity, 74.5 μS/cm. Other parameters similar to those of other waters tested did not exceed the permissible values established for drinking water (table).

2.5. JAR TEST PROCEDURES

Coagulation experiments were carried out in a series:

1. Coagulation without preliminary pH adjustment before coagulant and lime addition.
2. Coagulation with preliminary pH adjustment before coagulant and lime addition.

All tests were conducted at a room temperature. In laboratory-scale studies a kind of coagulant as well as its optimum dose and optimum coagulation pH were determined (series 1). For an optimum coagulant dose and optimum pH the influence of water acidification before coagulant addition on the effectiveness of contaminants'

removal was also investigated. Two different coagulants were tested. In this study, the range of coagulant dose varied in the range of 10–60 mg/dm³. In a series 2, where pH was preliminary adjusted downwards, the time of reaction of water with acid was 2 minutes. Afterwards, immediately after the coagulant addition, pH was increased up to the optimum value established in a series 1 by lime slurry addition.

Coagulation experiments were carried out using "jar tests" (1.5 dm³ water sample). After coagulant addition the solutions were rapidly stirred for 1 min at 200 rpm, followed by lime addition, and rapidly stirred for next 2 min at 200 rpm. Finally, the solutions were slowly stirred at 10 rpm for 30 min, followed by 30-min sedimentation. Visual observations of flocculation were made using a conventional scale [3], [4]:

- 1 – opalescence,
- 2 – beginning of flocculation,
- 3 – very small flocs,
- 4 – small flocs,
- 5 – middle-size flocs,
- 6, 7 – quite large flocs,
- 8 – large flocs,
- 9, 10 – very large flocs,
- ↓ – beginning of flocs' settling,
- ↓↓ – quick flocs' settling,
- ↓↓↓ – very quick flocs' settling.

The obtained treatment effects were estimated on the basis of water analyses. The following parameters were determined: pH, acidity, alkalinity, colour, turbidity, permanganate oxygen demand (POD), total hardness and residual soluble coagulant. Measurements of turbidity were noted only for high-turbidity water, because too low turbidity of other water tested made the discussion of the changes impossible. Changes of hardness, if any, allowed us to determine insoluble lime salts formed in the process. All measurements were carried out in filtered samples. The samples were filtered through a 45- μ m membrane and also their absorbance was measured at 254 nm using UV-VIS spectrophotometer. The values of absorbance were treated as an indicator of organics in water. All the analyses were made in accordance with standard methods.

During the studies there were a lot of problems with pH control. A set of classical electrodes did not work properly. For the water of such low alkalinity it was necessary to use a special electrode and to establish constant time of exposure.

2.6. REAGENTS

There were two coagulants tested in the studies: Al₂(SO₄)₃·18 H₂O and FeSO₄·7 H₂O. The coagulants were dosed as 2% solutions. pH was adjusted downwards by addition of 2% sulphuric acid. To increase pH to the optimum level, 1% lime slurry was supplied into water samples.

Because waters tested had poor buffer properties, an exact dosage of acid and lime was a crucial condition for maintaining proper pH for coagulation.

There are a lot of suggestions to use polyelectrolytes in waters, which are unsusceptible to coagulation. However, it would not be a good idea in this case, because it is said that polyelectrolytes increase the quantity of trihalomethanes in water after its chlorination [3].

3. RESULTS AND DISCUSSION

3.1. NATURAL WATER

Coagulation with aluminium sulphate. Taking into consideration the results of contaminants' removal and minimum soluble aluminium residue, the optimum coagulant dose in a series 1 (without preliminary pH adjustment) was 4.8 mg Al/dm^3 (60 mg/dm^3). The order of chemical dosage significantly influenced flocculation in this series. Lime addition prior to coagulant addition improved both flocculation and the effects of contaminant removal. In order to assess the influence of acidifying before coagulant and lime addition, the same dose of $\text{Al}_2(\text{SO}_4)_3$ was used in a series 2 with preliminary pH adjustment downwards.

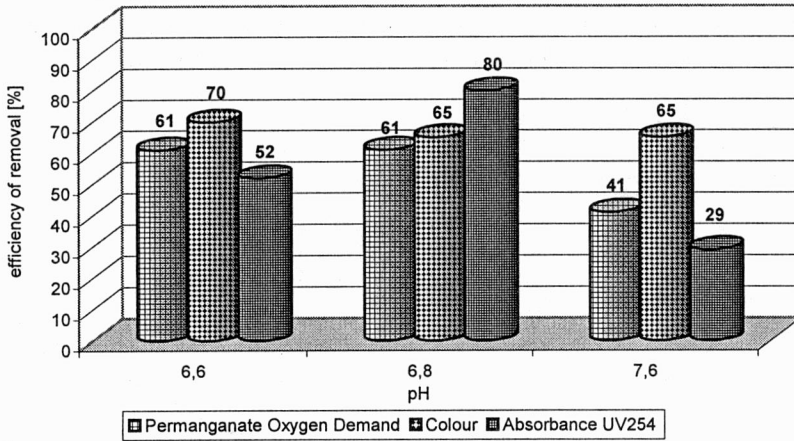


Fig. 1. The influence of pH on the efficiency of pollutants' removal during natural water coagulation without preliminary acidifying (4.8 mg Al/dm^3)

The optimum pH in both series was 6.8. It allowed the most effective removal of colour, POD and absorbance UV_{254} . At pH 6.6, 6.8 and 7.6 in a series 1 the effectiveness of colour removal, POD removal and absorbance removal was 70%, 65%, 65%; 61%, 61%, 41% and 52%, 80%, 29%, respectively (figure 1). In a series 2 (where acid was added before coagulant and lime) at pH 6.6, 6.8 and 7.6 the effectiveness of colour removal, POD removal and absorbance removal was 50%, 83%, 50%, 44%, 56%, 62% and 57%, 88%, 31%, respectively (figure 2).

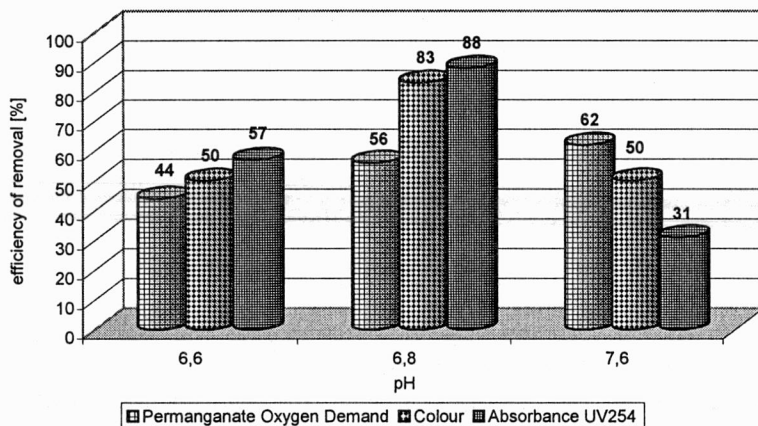


Fig. 2. The influence of pH on the efficiency of pollutants' removal during natural water coagulation with preliminary acidifying (4.8 mg Al/dm^3)

The above-mentioned results did not depend on flocculation course. At pH 6.8 acid addition caused deterioration of flocculation, so worse results of coagulation were expected in a series 1 with pH adjusted downwards (figure 3). Flocs were smaller in comparison with those in a series 1 and susceptible to flotation. However, the results proved that acid addition improved coagulation efficiency.

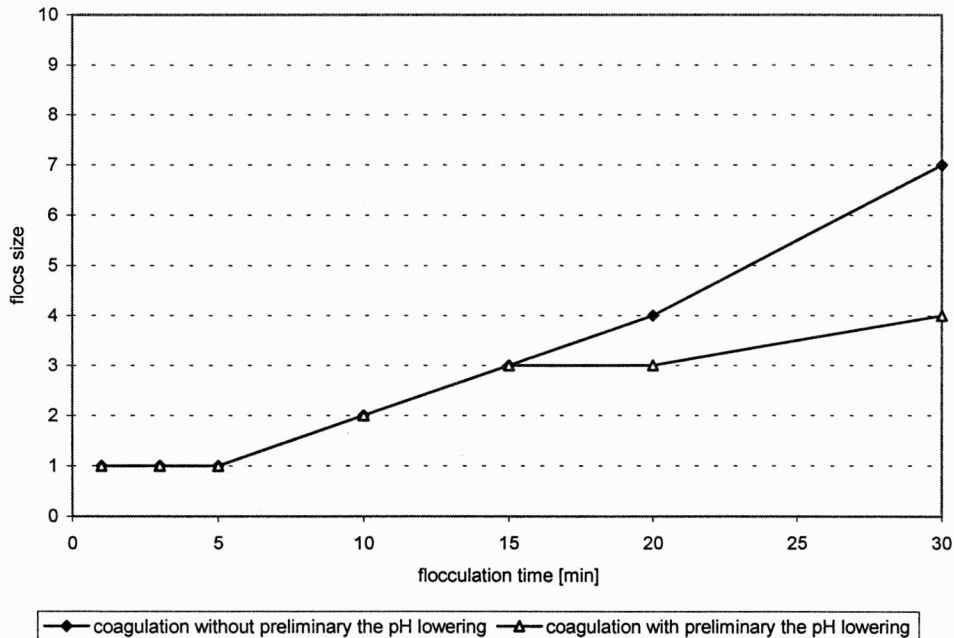


Fig. 3. The flocculation during natural water coagulation (4.8 mg Al/dm^3 , pH 6.8)

In a series 2 the increase of pH significantly influenced flocculation efficiency. During flocculation at pH 7.6 flocs were larger and susceptible to sedimentation (figure 4). However, the results of coagulation were much worse than at pH 6.8. Measurements of hardness proved that at pH 7.6 precipitation of insoluble lime salts started.

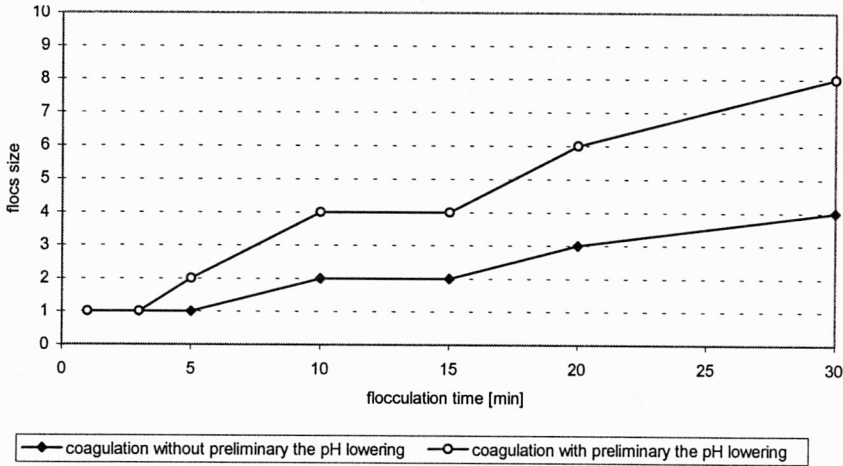


Fig. 4. The flocculation during natural water coagulation (4.8 mg Al/dm^3 , pH 7.6)

The attention should also be paid to the relationship between pH and residual aluminium in water after coagulation. The higher pH, the larger amounts of aluminium residual in a series 1 (figure 5). In a series 2 much smaller amounts of aluminium residual were noted in comparison with a series 1 (maximal value was 0.1 mg/dm^3).

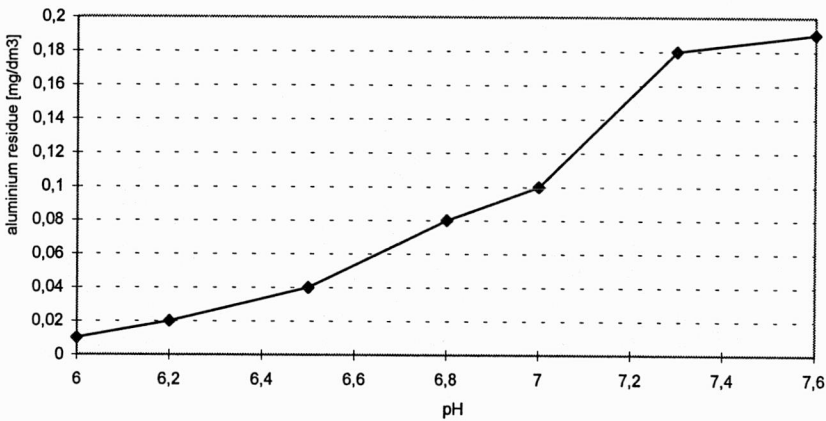


Fig. 5. The relationship between pH and aluminium residue after coagulation without preliminary acidifying (4.8 mg Al/dm^3 , pH 6.8)

Coagulation with ferrous sulphate. Mountainous waters are very well oxygenated, so the possibility of their coagulation by FeSO_4 was also tested. It was assumed that the concentration of oxygen was sufficient to oxidize iron(II) to iron(III). The results of tests proved that it was possible, even at pH 6.6, but required very high dose of coagulant (8 mg Fe/dm^3). A preliminary acidifying caused not only better flocculation (flocs were large and susceptible to sedimentation), but resulted in better water quality (figure 6). The preliminary acidifying and a successive coagulation at pH 6.6 ensured the highest effectiveness of coagulation, i.e. decrease in absorbance – 88%, and removal of colour – 83% as well as POD – 56% (figure 7). At the same pH coagulation in a series 1 was not so effective (figure 8).

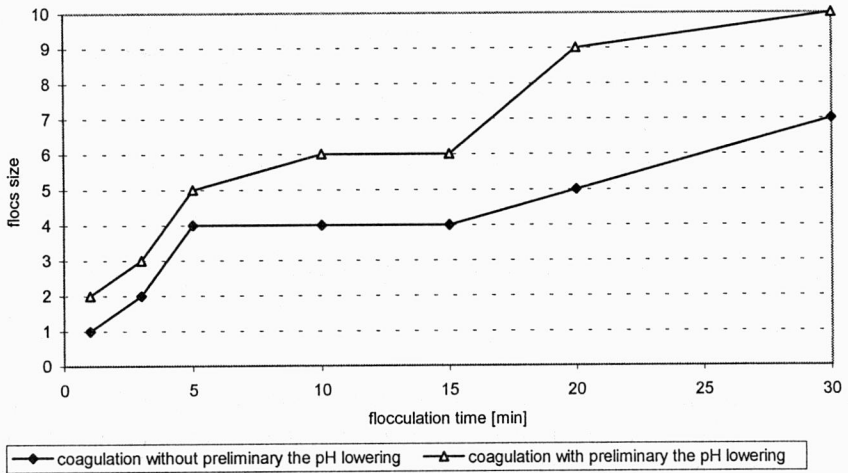


Fig. 6. The flocculation during natural water coagulation (8 mg Fe/dm^3 , pH 6.6)

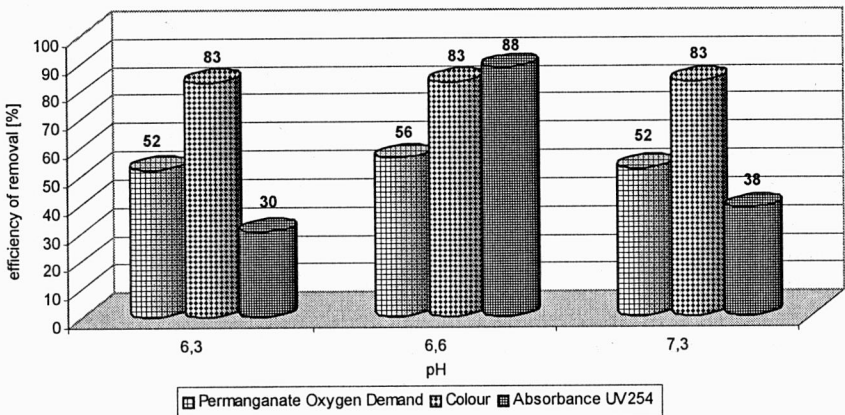


Fig. 7. The influence of pH on the efficiency of pollutants' removal during natural water coagulation with preliminary acidifying (8 mg Fe/dm^3)

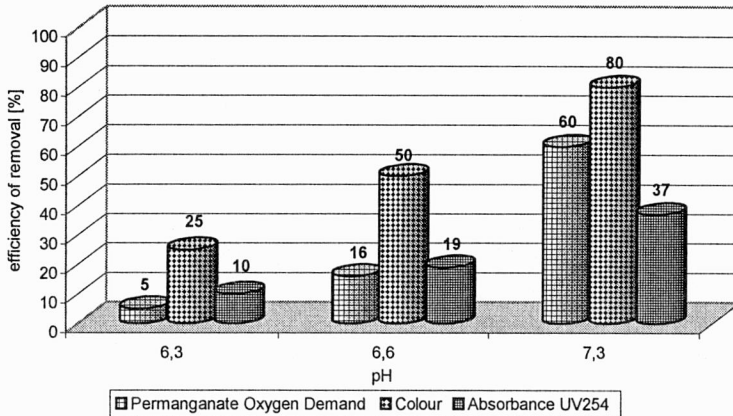


Fig. 8. The influence of pH on the efficiency of pollutants' removal during natural water coagulation without preliminary acidifying (8 mg Fe/dm^3)

In a series 1, as in the case of aluminium-based coagulant, the order of chemicals' dosage was very important. However, in contrary to aluminium sulphate, dosing of lime after coagulant addition was more favourable.

pH was a crucial parameter influencing the concentration of soluble iron residue. It was impossible to find out the relationship between pH and iron residue. In some tests iron residue did not exceed the permissible values established for drinking water, i.e. 0.5 mg Fe/dm^3 . In others tests, iron residue several times exceeded the permissible value. It was very difficult to explain the reasons of such uncontrolled growth of iron residue. It was supposed that it might be caused by the changes in oxygen concentration, while stored in a laboratory fridge. It was noticed that the longer time of water storage, the higher concentration of iron residue was noted. In order to prove this assumption these studies should be repeated directly at the water intake to avoid water storage and changes of oxygen concentration.

3.2. WATER OF INTENSIVE COLOUR AND HIGH TURBIDITY

Taking into consideration the fact that it was impossible to estimate the suitability of ferrous sulphate, intensively coloured waters of high turbidity were treated with aluminium sulphate only. The results of the investigation proved that in a series 1 the increase in the colour intensity or turbidity improved both flocculation (figure 9) and the effectiveness of coagulation (figure 10). After 20-minutes of flocculation flocs were large and susceptible to sedimentation. Coagulation of intensively coloured water at pH 6.8 resulted in 90% diminishing of absorbance, 91% removal of colour and 55% removal of POD. Coagulation of high-turbidity water at pH 6.8 was also very effective and caused 90% removal of turbidity, 70% diminishing of absorbance, 85% and 55% removal of POD. Because of high effectiveness of contaminants' removal in a series 1, it was no use to enhance coagulation by a preliminary pH lowering.

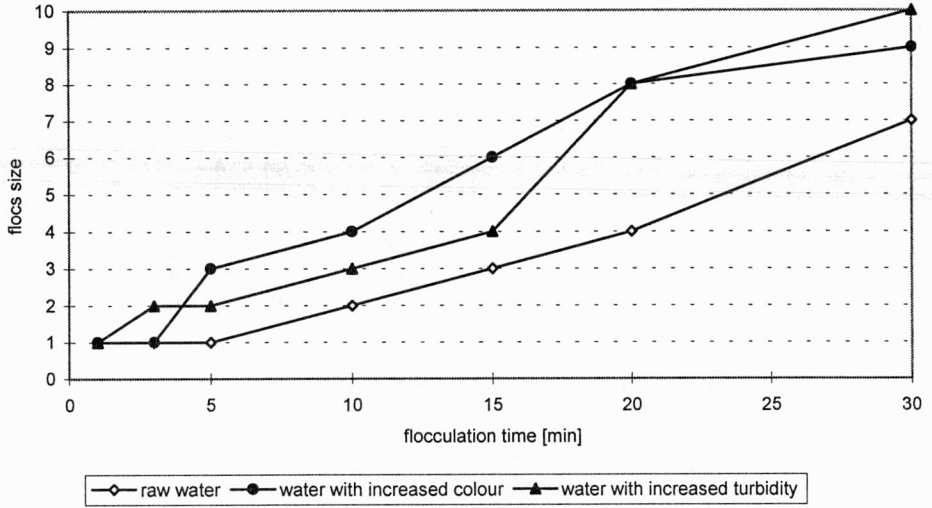


Fig. 9. The influence of intensive colour and high-turbidity on flocculation (3.2 mg Al/dm^3 , pH 6.8)

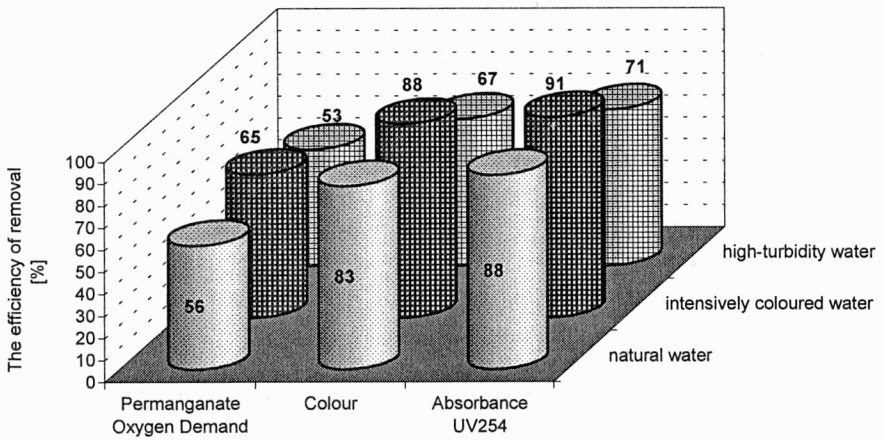


Fig. 10. The influence of intensive colour and high turbidity on coagulation without preliminary acidification (3.2 mg Al/dm^3 , pH 6.8)

4. CONCLUSIONS

- For low-alkalinity and low-hardness mountainous waters an effective coagulation by aluminium sulphate is possible. The optimum pH 6.8 is the crucial parameter, which ensures the best effects of contaminants' removal.

- Preliminary pH adjustment downwards before coagulant and lime addition improves the effectiveness of coagulation.
- Intensively coloured or high-turbidity waters are more susceptible to coagulation. Optimum coagulant doses for such waters are lower than for waters of better quality .

LITERATURE

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UZDATNIANIE WODY GÓRSKIEJ O MAŁYM ZASOLENIU

Miękkie i kwaśne wody górskie nie są podatne na koagulację. Wody te przez wiele miesięcy mają niską temperaturę i małą mętność. Oceniono wpływ wstępnego zmniejszenia pH wody przed dozowaniem koagulanta na przebieg procesu flokulacji oraz efekty uzdatniania tych wód. W toku badań określono wpływ zabarwienia i zmętnienia na przebieg procesu.

wody kwaśne
-u miękkie
koagulacja

