

Influence of Water Hardness on the Effectiveness of Coagulation of Humic Compounds

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ABSTRACT

The laboratory tests presented in the article aimed at determining the influence of water hardness on the effectiveness of humic substances removal in the coagulation process. The tests were conducted on three model solutions; very soft water, soft water and semi-hard water. The concentration of humic substances in each solution was equal to 20 mg/dm³. Calcium hydroxide, ferric(III)chloride and aluminium sulphate(VI) were applied as coagulants. On the basis of the conducted tests, it was found that the increased content of calcium, and particularly of magnesium in water, improves the effectiveness of humic substances removal. The process effectiveness expressed by changes in colour and permanganate index was the highest for semi-hard water. A decrease in colour equal to 88.8% and in permanganate index – 72.1% was observed in this case for the largest dose of calcium. Even better results were obtained by applying the remaining coagulants; a decrease in colour amounted to 99%, and in permanganate index to 95%.

Keywords: water hardness, humic substances, coagulation process

INTRODUCTION

Natural organic substances occurring in water include, inter alia, humic compounds (HC). They come from biochemical decomposition of plant and/or animal residues. They can also be leached from soils rich in humus and from lignite and coal deposits [Han et al. 2003, Lorenc-Grabowska and Gryglewicz 2004]. Despite long term studies, no unambiguous chemical formula of separate HC fractions was determined. The indicators which correlate with the HS content in water include colour, oxidisability (permanganate index), total organic carbon (TOC) and UV absorbance (at a wavelength of 254 nm) [Dębska et al. 2014, Kaleta and Elektorowicz 2009, Krupińska 2012, Pisarek and Głowacki 2015].

Humic compounds are not toxic substances and until recently they have been removed from the potable water primarily for aesthetic reasons [Kaleta et al. 2017]. However, due to their capability of absorbing other, often toxic admixtures,

their presence in water is inadvisable because it causes problems during its purification. There is also a potential danger of oxidation by-products formation and disinfection with carcinogenic and mutagenic properties, as well as the lack of biological stability of water [Kołodziej et al. 2008, Nawrocki and Biłozor 2010, Perchuć 2003].

Coagulation is one of the most popular technological processes applied in the removal of humic substances from water [Dąbrowska 2016]. The application of traditional coagulants (ferric or aluminium salts) is often connected to using increased doses and the need to support the coagulation process by chemical oxidation and/or poly-electrolytes. The effectiveness of the coagulation process increases along with water salinity, and particularly in its hardness [Oleksiak and Stępnik 2013, Świdorska-Bróż and Kowal 2009]. The initially hydrolysed coagulants, the use of which brings comparable results but at smaller doses, constitute an alternative to traditional coagulants. Their additional advantages involve lower

consumption of alkalinity, lower reduction of pH, and consequently, reduction or elimination of aggressive and corrosive water properties [Nowacka and Włodarczyk-Makuła 2015, Yan et al. 2010].

A high degree of HC removal is ensured through coagulation by calcium. Its effectiveness is directly proportional to the precipitation of calcium carbonate and magnesium hydroxide in water. The degree of HC removal is largely influenced by the carbonate hardness and purified water pH. At the high carbonate hardness and high water pH, the removal efficiency of these contaminations reached even 98% [Bob and Walker 2001, Świdorska and Anielak 2004].

The aim of the conducted tests was to evaluate the influence of water hardness on the removal effectiveness of humic compounds in the process of coagulation by calcium and with the use of ferric and aluminium salts.

RESEARCH METHODOLOGY

Tests were conducted on three model solutions A, B and C. Solution A was prepared on the basis of tap water diluted with distilled water (very soft water), solution B – on the basis of tap water (soft water), and solution C was obtained by adding magnesium chloride to tap water (semi-hard water). Humic acid in the amount of 20 mg/dm³ was added to all solutions. The following control indicators were determined in model solutions: pH, general hardness, calcium hardness, magnesium hardness, alkalinity, colour and permanganate index (PI). All indicators were marked in accordance with the applicable standards (Standard Methods for the Examination of Water and Wastewater, 18th edition, Washington 2002).

The coagulation process was conducted using calcium hydroxide – Ca(OH)₂, aluminium sulphate(VI) – Al₂(SO₄)₃ · 18 H₂O and ferric(III) chloride – FeCl₃ · 6H₂O.

Coagulation was conducted in a conventional manner (by volume); 1 dm³ of the appropriate model solution was measured to each of 6 beakers and those beakers were placed in a laboratory coagulator. Stirrers were very slowly set in motion and immediately increasing doses of the appropriate coagulant ranging from: for calcium 50–100 mg Ca/dm³, for the remaining coagulants 9–24 mg Al(Fe)/dm³ were measured to separate beakers. After this operation, quick mixing (100 rpm), lasting 3 minutes was started. Then,

the number of rotations was decreased to 10 rpm and slow mixing was conducted for 15 minutes.

RESULTS AND DISCUSSION

Due to the fact that model solutions were prepared on the basis of tap water, during the course of tests, their parameters displayed some variability. Average values (Table 1) were taken into account during the interpretation of results.

The prepared model solutions did not meet the requirements specified in the Regulation of Minister of Health of 7 December 2017 on the quality of water intended for consumption by humans (J. of Laws 2017, item 2294) due to the presence of humic compounds which were the cause of excessive colour and permanganate index (PI).

The water control parameters after the coagulation process for model solution A are presented in Table 2, for solution B in Table 3, and for solution C in Table 4.

The comparison of the coagulation effectiveness by calcium for model solution A, B and C is presented in Figures 1 and 2.

Dosage of increasing amounts of calcium into model solution A was ineffective. Both the colour and permanganate index did not reach the recommended and permissible values and indicated the high presence of humic compounds. At the largest dose of calcium, colour decreased by only 28.3% and permanganate index by 33.9%. Total hardness at the smallest dose of calcium slightly increased, and then it decreased along with an increase in the doses of calcium. Calcium hardness changed in a similar manner. Such a situation was caused by the occurring process of water decarbonisation, i.e. carbonate hardness removal; calcium carbonate CaCO₃ precipitated from water. Along with the increase in doses of calcium, the water pH increased and at doses of 80 mgCa/dm³ and 90 mgCa/dm³ it exceeded the admissible value for potable water which is below 9.5 pH.

The introduction of calcium into model solution B in the applied doses also did not bring the desired results. At the largest dose, the decrease in colour was equal to 40%, and permanganate index – 40.8%. Along with an increase in calcium, water pH increased and at the second dose in turn, it exceeded the normative value for potable water. At the same time, hardness (general and calcium), alkalinity m and alkalinity f slightly decreased. The process of partial water

decarbonisation occurred here similarly as in the case of solution A.

Coagulation by calcium of model solution C, which had higher magnesium hardness, was significantly more effective. At two largest doses, the recommended colour equal to 15 Hazen was obtained, and the percentage of its decrease ranged from 84.7–88.8%. Permanganate index below the permissible value ($5.0 \text{ mgO}_2/\text{dm}^3$) was obtained at the smallest dose of calcium. A decrease in this parameter changed from 65.5% to 72.1%. Similarly as in the case of model solutions A and B, along with the increase in the dose of calcium, water pH increased, whereas its hardness and alkalinity decreased, which was caused by the precipitation of calcium carbonate and magnesium hydroxide – $\text{Mg}(\text{OH})_2$.

Authors of other papers [Oleksiak and Stepniak 2013, Świdarska-Bróz and Kowal 2009] demonstrated that along with an increase in water hardness, the removal of humic substances in the coagulation process increases.

Effects obtained during coagulation by ferric(III)chloride are presented in figures 3 and 4.

Ferric(III)chloride dosed to model solution A caused the decrease in water colour from 14.1% (for the smallest dose) to 71.7% (for the largest dose). In the case of colour, the recommended value for potable water equal to $15 \text{ mgPt}/\text{dm}^3$ was not achieved. Permanganate index was also subject to a decrease from 8% to 66.9% and at the dose of $18 \text{ mg Fe}/\text{dm}^3$ it reached the permissible value for potable water equal to $5.0 \text{ mgO}_2/\text{dm}^3$. Along with an increase in doses of coagulant, the water pH decreased, and at two largest doses of coagulant, it was lower than the lower admissible limit equal to 6.5 pH. Moreover, water alkalinity decreased successively. Water hardness was not subject to significant changes.

Comparing the effectiveness of the coagulation process of model solution A and B by means of ferric(III)chloride, it can be stated that comparable effects were obtained. Better results were obtained for model solution A while applying smaller doses of coagulant. Greater doses of ferric(III)chloride led to the better effectiveness of colour removal from model solution B, and the comparable and slightly greater effectiveness of decreasing permanganate index (PI). The tests conducted by Swiderska and Anielak [2004] also demonstrated that HC are more effectively removed with an acidic pH which is conditioned by their structure and charge. This explains good results obtained in solution A which had the lowest pH value.

The best results were obtained during the coagulation process of solution C. The recommended colour was obtained at dose of $12 \text{ mgFe}/\text{dm}^3$, and the admissible value of permanganate index – at the dose of $10 \text{ mgFe}/\text{dm}^3$. At the largest dose of ferric(III)chloride, the decrease in colour reached the value of 94.9%, and permanganate index of 95.9%. At this dose, the pH value was above the lower permissible limit for potable water.

The effects obtained during coagulation by aluminium sulphate(IV) are presented in Figures 5 and 6.

During coagulation, the use of aluminium sulphate(IV) for model solution A, caused the decrease in colour within the range from 67.7% to 95.9%. At the dose of $15 \text{ mgAl}/\text{dm}^3$, the value of $12 \text{ mgPt}/\text{dm}^3$ (below the recommended value) was obtained. The admissible value of permanganate index was observed at the dose of $12 \text{ mgAl}/\text{dm}^3$. This parameter decreased from 51.2% to 85.1%. The water pH decreased along with the dose of coagulant and at two largest doses it was lower than the lower admissible limit.

Table 1. Control parameters of model solutions

Parameter	Unit	Limit value for drinking water	Average value		
			Solution A	Solution B	Solution C
Reaction	pH	6.5 – 9.5	7.34	7.79	7.78
General hardness	mval/dm ³	1.2 – 10.0	1.9	4.0	6.0
General hardness	mgCaCO ₃ /dm ³	60 – 500	95	200	300
Calcium hardness	mval/dm ³	-	1.8	3.4	3.6
Magnesium hardness	mval/dm ³	0.6 – 10.4	0.1	0.6	2.4
Magnesium hardness	mg/dm ³	7 – 125	1.2	7.2	28.8
Water alkalinity m	mval/dm ³	-	2.7	3.7	3.8
Water alkalinity f	mval/dm ³	-	-	-	-
Color	Hazen	Recommended 15	99	100	98
The permanganate index (PI)	mgO ₂ /dm ³	5.0	12.1	12.5	12.2

Table 2. Control parameters after coagulation process – model solution A

Doses, mg/dm ³	Reaction pH	General hardness, mval/dm ³	Calcium hardness, mval/dm ³	Water alkalinity m, mval/dm ³	Water alkalinity f, mval/dm ³	Color, Hazen	The permanganate index mgO ₂ /dm ³
Calcium hydroxide, mg Ca/dm ³							
40	8.72	3.32	3.04	2.0	0.5	91	8.3
50	8.91	3.02	2.89	1.9	0.5	89	8.3
60	9.12	2.80	1.60	1.8	0.4	88	8.2
70	9.47	2.20	1.40	1.8	0.4	85	8.1
80	9.81	1.80	1.20	1.8	0.4	79	8.1
90	9.98	1.70	1.20	1.8	0.4	71	8.0
Ferric(III)chloride, mg Fe/dm ³							
10	7.12	2.00	1.89	2.5	-	85	11.1
12	7.01	1.91	1.90	2.4	-	72	7.8
15	6.91	1.99	1.96	2.2	-	63	6.1
18	6.73	1.97	1.95	2.0	-	51	4.9
21	6.49	1.95	1.92	1.8	-	42	4.1
24	6.41	2.00	1.96	1.6	-	28	4.0
Aluminum sulphate(VI), mgAl/dm ³							
10	7.10	1.92	1.87	2.5	-	32	5.9
12	6.75	1.91	1.83	2.4	-	21	3.4
15	6.61	1.99	1.96	2,2	-	12	2.5
18	6.59	2.00	1.95	2.0	-	11	2.2
21	6.42	2.00	1.97	1.8	-	8	2.0
24	6.31	1.97	1.96	1.6	-	4	1.8

Table 3. Control parameters after coagulation process – model solution B

Doses, mg/dm ³	Reaction pH	General hardness, mval/dm ³	Calcium hardness, mval/dm ³	Water alkalinity m, mval/dm ³	Water alkalinity f, mval/dm ³	Color, Hazen	The permanganate index, mgO ₂ /dm ³
Calcium hydroxide, mg Ca/dm ³							
40	9.40	3.32	3.04	3.0	0,9	75	7.8
50	9.52	3.02	2.89	2.8	0,7	72	7.8
60	9.64	2.80	1.60	2.5	0,6	70	7.8
70	9.93	2.20	1.40	2.0	0,6	67	7.6
80	10.35	1.80	1.20	2.0	0,6	62	7.4
90	10.85	1.70	1.20	2.0	0,6	60	7.4
Ferric(III)chloride, mg Fe/dm ³							
10	7.28	4.01	3.42	3.7	-	92	12.0
12	7.21	4.00	3.46	3.5	-	76	8.5
15	7.09	3.98	3.41	3.3	-	59	6.6
18	6.88	4.00	3.42	3.4	-	31	5.0
21	6.63	4.00	3.43	3.0	-	25	4.8
24	6.58	3.99	3.42	2.7	-	19	4.6
Aluminum sulphate(VI), mgAl/dm ³							
10	7.10	4.01	3.42	3.6	-	20	6.4
12	6.95	4.00	3.41	3.3	-	13	3.7
15	6.83	3.99	3.43	3.0	-	9	3.2
18	6.69	4.00	3.41	2.6	-	7	2.8
21	6.62	4.00	3.42	2.5	-	6	2.5
24	6.56	3.99	3.42	2.4	-	5	2.1

Table 4. Control parameters after coagulation process – model solution C

Doses, mg/dm ³	Reaction pH	General hardness, mval/dm ³	Calcium hardness, mval/dm ³	Water alkalinity m, mval/dm ³	Water alkalinity f, mval/dm ³	Color, Hazen	The permanganate index, mgO ₂ /dm ³
Calcium hydroxide, mg Ca/dm ³							
40	9.34	4.84	2.28	3,5	0.7	24	4.2
50	9.48	4.36	1.96	2,9	0.4	20	4.0
60	9.67	3.92	1.52	2,2	0.3	18	3.7
70	9.73	3.80	1.48	2,0	0.5	17	3.6
80	10.14	3.20	1.16	1,5	0.5	15	3.5
90	10.34	3.14	1.15	1,4	0.4	11	3.4
Ferric(III)chloride, mg Fe/dm ³							
10	7.33	5.40	3.0	2,8	-	16	2.2
12	7.21	5.30	3.0	2,7	-	15	2.0
15	7.10	5.28	2.8	2,5	-	9	1.6
18	7.06	5.31	3.1	2,3	-	7	1.2
21	6.88	5.20	2.8	2,0	-	6	0.8
24	6.78	5.29	2.8	1,9	-	5	0.5
Aluminum sulphate(VI), mgAl/dm ³							
10	7.26	5.40	3.0	2,8	-	20	3.5
12	7.16	5.40	3.0	2,7	-	16	2.9
15	7.15	5.40	3.0	2,4	-	5	2.2
18	7.01	5.40	3.0	2,3	-	3	1.8
21	6.98	5.40	3.0	2,2	-	2	1.1
24	6.76	5.40	3.0	2,0	-	1	0.8

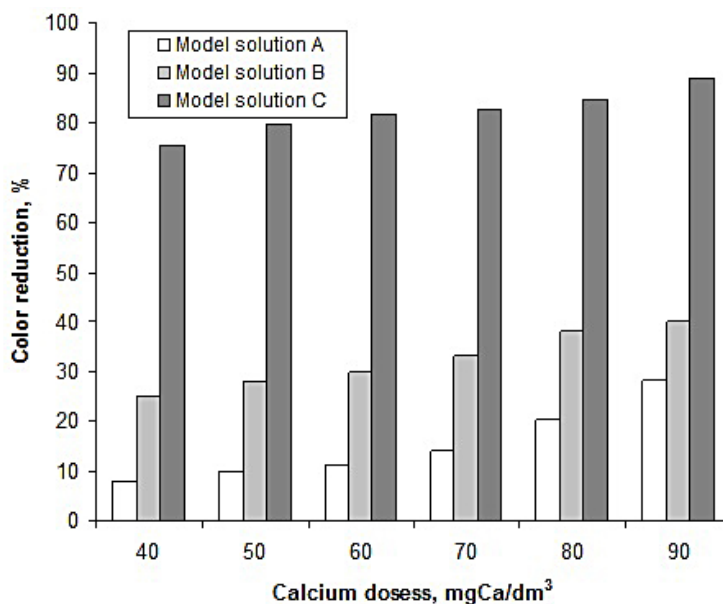


Fig. 1. Reduction of color after calcium coagulation

In the case of model solution B, better results in colour removal, but slightly worse at decreasing permanganate index (PI) were obtained than during coagulation of solution A. Water pH, similarly as in the case of solution A, decreased, but it remained within the permissible limits.

By conducting the coagulation process by aluminium sulphate(VI) for solution C, comparable results were obtained as with the use of ferric(III)chloride. At the largest dose, colour decreased by 99.0%, and turbidity by 93.4%.

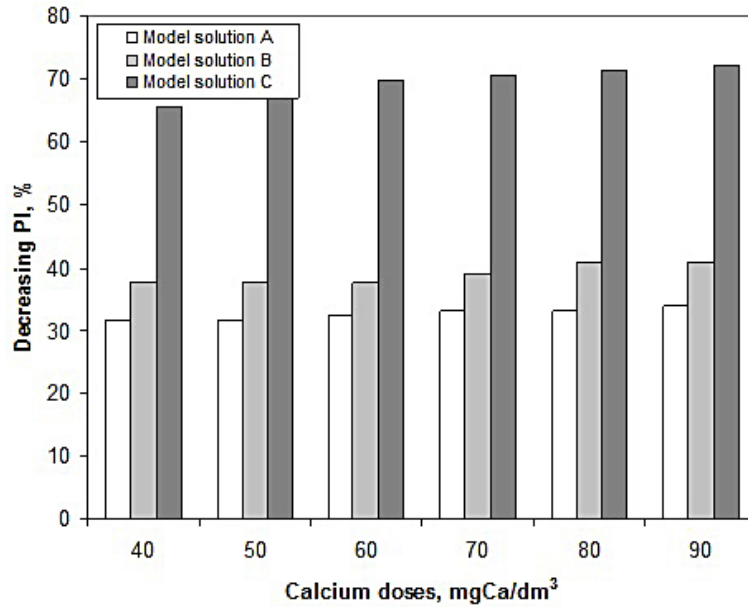


Fig. 2. Decreasing of the permanganate index (PI) after calcium coagulation

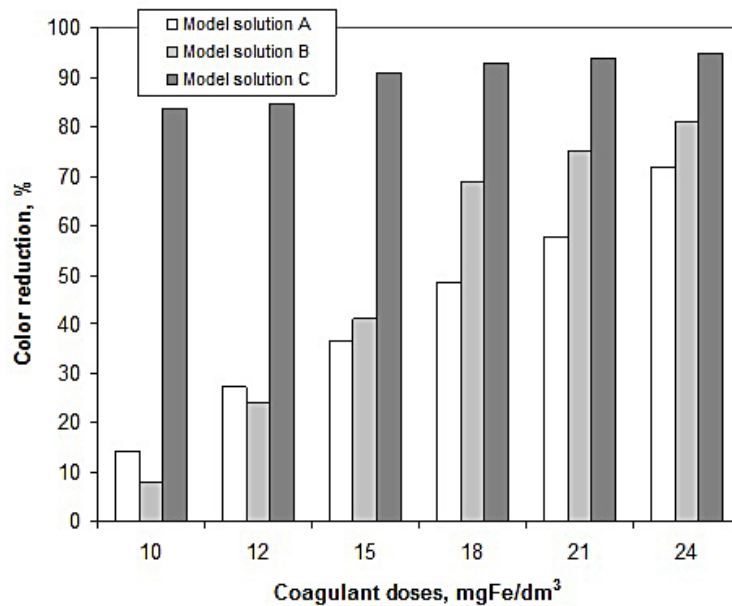


Fig. 3. Reduction of color after coagulation with ferric(III)chloride

Yang et al. [2010] and Stepniak [2017] also demonstrated that along the effectiveness of HS removal increases with an water hardness.

Along with an increase in doses of traditional coagulants, water pH decreased and at two largest doses in model solution A, it was below 6.5 pH, while in model solutions B and C, it was close to the lower normative value for potable water. Additionally, water alkalinity was subject to decrease. This was caused by hydrolysis of coagulants and neutralisation of formed mineral acids HCl

(H_2SO_4) by acidic carbonates (the main component of alkalinity).

While comparing traditional coagulants, it can be stated that the coagulation process conducted in solutions A and B was more effective with the use of aluminium sulphate(VI) than with ferric(III)chloride both in removal of compounds causing the colour and permanganate index. In the case of the solution with the highest hardness (solution C), the effectiveness of the coagulation process was comparable for both coagulants.

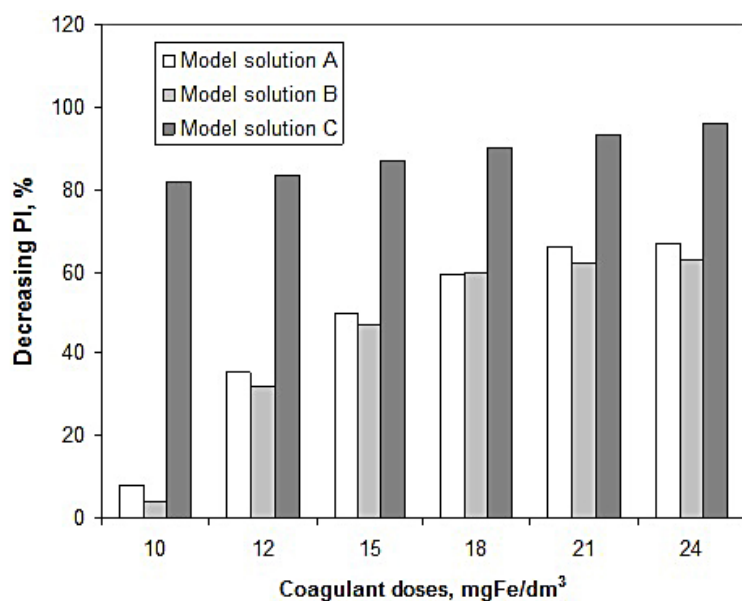


Fig. 4. Decreasing of permanganate index (PI) after coagulation with ferric(III)chloride

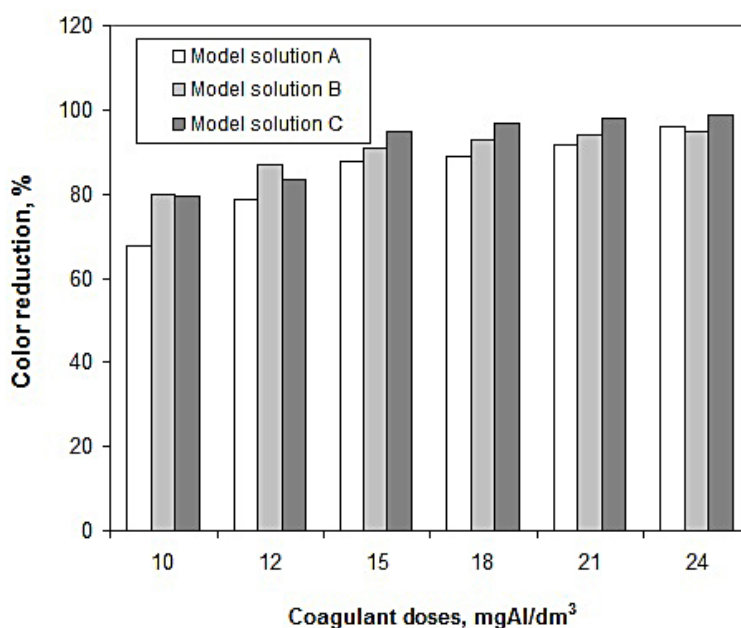


Fig. 5. Reduction of color after the coagulation process with aluminum sulphate (VI)

CONCLUSIONS

1. The increase in water hardness, particularly magnesium hardness, positively influenced the removal of humic substances in the coagulation process using calcium. The effectiveness of HC removal from solution C (semi-hard water) at the largest dose of calcium was greater by 48.8% for colour and greater by 31.3% for permanganate index than in the case of model solution A (very soft water).

2. The effectiveness of HC removal by means of calcium was determined by its dose. Along with its increase, water pH and the presence of calcium ions increased. In model solution C with the highest magnesium hardness, magnesium ions appeared additionally. At the value of pH > 9.0, the process of precipitation of CaCO₃ and Mg(OH)₂ occurred. These sediments played the role of a sorbent and HC co-precipitation factor. The effectiveness of the coagulation process for solution

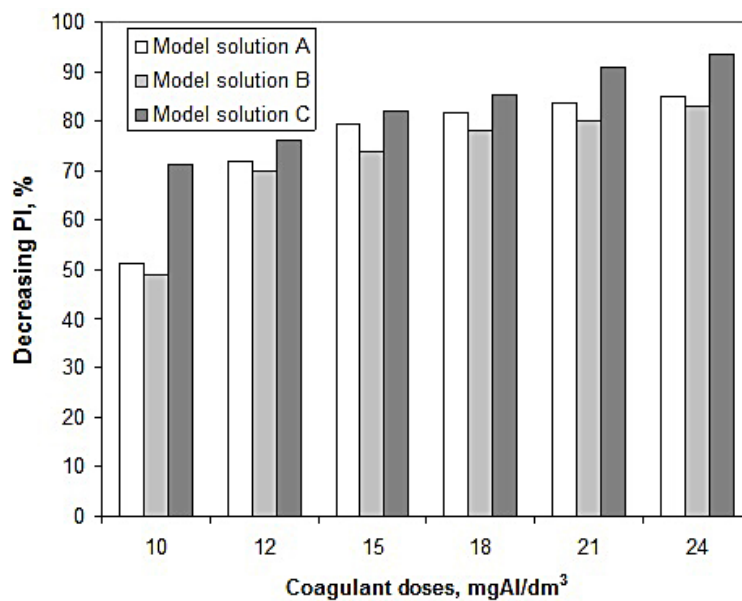


Fig. 6. Decreasing of the permanganate index (PI) after the coagulation process with aluminum sulphate (VI)

C reached 88.8% for colour, and 72.1% for permanganate index.

3. After the calcium dosing process, water does not meet the requirements for the quality of potable water due to high pH ($\text{pH} > 9.5$). After this process, water must be brought in the carbonate – calcium balance by means of dosing carbon dioxide (the recarbonisation process).
4. During the coagulation process conducted by means of ferric(III)chloride, no significant differences were observed in the removal of HC from very soft water (solution A) and soft water (solution B). At smaller doses of this coagulant, the process occurred better in very soft water, while at larger doses – in soft water. Significantly better results were obtained in solution C (semi-hard water), where the process effectiveness reached 95%.
5. Aluminium sulphate(VI) removed humic compounds from very soft water A and soft water B more effectively than ferric (III) chloride. The effectiveness of coagulation of semi-hard water C was comparable with the one obtained using ferric(III)chloride and was equal to 99% for colour and 93% for permanganate index.
6. The disadvantage of traditional coagulants is the reduction of water pH and alkalinity which can increase aggressive and corrosive water properties. Additionally, at large doses of coagulants, there is a danger of excessive concentration of iron ($> 0.2 \text{ mgFe/dm}^3$) or

aluminium ($> 0.2 \text{ mgAl/dm}^3$) in water after the coagulation process.

7. The economic balance, taking the costs of reagents, the amount of formed sediments and quality of water after the coagulation process into account, should in each case decide which coagulants should be applied to particular purified water.

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