

## REMOVAL OF IRON AND ORGANIC SUBSTANCES FROM GROUNDWATER IN AN ALKALINE MEDIUM

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**Abstract.** The article discusses the effectiveness of alkalisation with calcium hydroxide or sodium hydroxide in the treatment of groundwater from Quaternary formations with an increased content of total iron (up to  $6.82 \text{ mgFe/dm}^3$ ) and organic substances (TOC up to  $5.60 \text{ mgC/dm}^3$ ). The aim of the research was to determine the effectiveness of the groundwater treatment, in particular, the removal of iron and organic substances in the sorption process and co-precipitation with calcium carbonate and magnesium hydroxide. The correction of the reaction was carried out with aqueous solutions of calcium hydroxide and sodium hydroxide in the pH range from 8.5 to 10.5. As the pH of the water increased, the efficiency of its treatment increased. The treatment results depended on the type of alkalizing reagent, especially in the case of removal of organic substances, reduction of colour and organic substances fixed in iron-organic complexes. Higher suitability of calcium hydroxide than sodium hydroxide in alkalisation has been demonstrated. Calcium ions introduced into the treated water together with calcium hydroxide probably neutralized organic anions fixed in iron-organic complexes and determining colour and TOC, increasing their susceptibility to adsorption.

**Keywords:** groundwater, organic substances, iron, alkalisation, calcium hydroxide, sodium hydroxide, sorption, co-precipitation.

### Introduction

Treating groundwater usually involves the need to remove excessive amounts of various forms of iron, manganese, organic substances and aggressive carbon dioxide. The presence of organic substances in water taken for communal purposes, including mainly humic substances, is a major problem in many groundwater treatment stations. These high-molecular organic compounds, characteristic of boggy waters and deeply deposited waters from the Miocene lignite formation, can occur in all aquifers as a result of a hydrogeological bond between them and their improper exploitation. In underground waters characterized by an increased content of organic substances, iron compounds and increased turbidity and intensity of colour, iron compounds with organic substances, most often with humic substances, are formed (Khatri, Tyagi, & Rawtani, 2017; Knocke, Conley, & Van Benschoten, 1992). The use of a conventional groundwater treatment system in this case does not provide the required cleaning efficiency (Albrektiene, Rimeika, & Lubyte, 2011; Albrektiene, Rimeika, Zalieckiene, Saulys, & Zagorskis, 2012; Marsidi,

Hasan, & Abdullah, 2018). Well sedimenting iron(III) hydroxide agglomerates do not precipitate in the water aeration process, however, colloidal and water-soluble coloured organic iron compounds are formed, and the stability of these connections increases with the increasing concentration of organic ligands (Albrektiene, Rimeika, & Grazeniene, 2014; Albrektiene & Rimeika, 2017; Krupińska, Kowalczyk, & Szczepaniak, 2013; Krupińska, 2017a, 2017b). According to numerous researchers (A. Pandey, S. Pandey, & Mistra, 2000; Sharma, 2001), the binding ability of the humic acids is bigger in relation to  $\text{Fe}^{2+}$  ions whereas Schnitzer and Skinner (Schnitzer & Skinner, 1996) state that  $\text{Fe}^{3+}$  ions are bound more strongly than  $\text{Fe}^{2+}$ . Several researchers suggest various mechanisms of binding iron by the humic acids. As Gonczarow et al. (Gonczarow, Kołosow, & Kapli, 2003) as well as Pandey et al. (2000) point out formation of chelate complexes with the humic acids in natural waters occurs as a result of an exchange reaction between hydrogen ions of carboxyl and phenol groups of the humic acids and iron cations existing under such conditions mainly in a form of hydroxo-complexes  $[\text{Fe}(\text{OH})]^{2+}$ ,  $[\text{Fe}(\text{OH})_2]^+$ , such chelate iron

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complexes are regarded as the most stable. According to numerous researchers (Gonczarow et al., 2003; Sharma, 2001; Shiyan, Tropina, Machekhina, & Gryaznova, 2014; Khatri et al., 2017; Krupińska, 2017a), one of the reasons for iron stabilisation by organic substances in groundwater may also be formation of the so called protective colloids of hydrophilic character as a result of adsorption of organic substances on iron(III) hydroxide surface. Summing up, the conclusion may be clear that presence of organic substances, and especially humic substances in groundwater significantly impedes removal of iron. Various attempts are being made to intensify the removal of iron occurring in combinations with organic ligands. One of the recommended methods is to use coagulation with aluminium salts or lime (Eikerokk, 2000; Liao & Randtke, 1985, 1986; Lin, Couperthwaite, & Millar, 2017; Marsidi et al., 2018; Nowacka, Włodarczyk-Makuła, & Macherzyński, 2014; Nowacka & Włodarczyk-Makuła, 2014; Urbanowska & Kabsch-Korbutowicz, 2016). Before coagulation, oxidation of  $\text{Fe}^{2+}$  ions occurring in inorganic combinations is required, after which the sedimentation process is not required. The use of iron coagulant may result in the formation of coloured, difficult-to-remove combinations of  $\text{Fe}^{3+}$  ions with organic substances, especially humic acids (Duan & Gregory, 2003; Huang & Shiu, 1996; Krupińska, 2012, 2016; Myszograj, Płuciennik-Koropczuk, Jakubaszek, & Świętek, 2017; Płuciennik-Koropczuk et al., 2017; Xu et al., 2016). During coagulation, on the one hand, the possibility of neutralizing negatively charged combinations of iron with organic compounds by coagulation cations or their positively charged hydroxide complexes is used, on the other hand, the high adsorptive capacity of precipitated aluminium hydroxide or iron is also used (Cheng & Ghi, 2002; Davis & Edwards, 2014; Ghernaout, 2014; Ghernaout & Boucherit, 2015; Lin, Couperthwaite, Huang, Dempsey, & Hu, 2014; Nowacka & Włodarczyk-Makuła, 2014; Saxena, Brighu, & Choudhary, 2018; Silanpää, Ncibi, Matilainen, & Vepsäläinen, 2018; Wolska, 2011; Xu et al., 2018). During coagulation carried out in an alkaline medium, the degree of the removal of iron compounds as well as organic pollutants and their combinations with iron depends on the processes of adsorption and co-precipitation with calcium carbonate and magnesium hydroxide, as well as neutralization of iron and organic combinations with a negative charge by calcium cations (Ghernaout et al., 2018; Świdarska-Bróz, 1987; Wang, Wu, Shammass, & Vaccari, 2005). Due to the fact that during the coagulation with lime the destabilization of colloids has a smaller share in the total degree of removal of pollutants, it is not a typical coagulation. At  $\text{pH} = \text{ca.}9.3\text{--}9.5$ , the maximum precipitation of  $\text{CaCO}_3$  takes place, and at  $\text{pH} \geq 10.2$  precipitation of  $\text{Mg}(\text{OH})_2$ , which is a good adsorbent, and because of the positive electric charge it effectively binds organic anions (Brastad & He, 2013; Esmaeilirad, Carlson, & Ozbek, 2015; Mahasti, Shih, Vu, & Huang, 2017; Randtke, Thiel, Marcia, Liao, & Yamaya, 1982; Rescorla, Semmens, & Hozalski, 2017; Wang et al., 2005; Zotter & Licsko, 1992). For this

reason, coagulation in the alkaline environment is often referred to as coagulation-adsorption. Freshly precipitated calcium carbonate has a specific surface area of a dozen or so  $\text{m}^2/\text{g}$ , which decreases with the age of the sediment. Calcium carbonate has a crystalline structure, a negative electric charge and begins to precipitate from the solution at  $\text{pH ca.}9.3$ , while magnesium hydroxide precipitates at  $\text{pH} = 10.2$ .  $\text{pH} = 11.2\text{--}11.5$  is required to completely precipitate magnesium hydroxide. Magnesium hydroxide does not have crystalline structure and its particles are positively charged (Liao & Randtke, 1985; Moel, Verberk, & Van Dijk, 2007; Świdarska-Bróz, 1987; Wolska, 2015). The  $\text{pH}$  required for the precipitation of calcium carbonate and magnesium hydroxide can be reduced by increasing the concentration of  $\text{Mg}^{2+}$  ions in the solution. The precipitating calcium carbonate, as well as partially magnesium hydroxide, very effectively sorb pollutants by embedding them in their volume. Significant amounts of admixtures are also sorbed on the surface of precipitated sorbents, mainly magnesium hydroxide as a result of physical and chemical sorption. The sorbate binding force depends on its type, and its sorption changes the rate of volume growth and the shape of the precipitated particles of calcium carbonate and magnesium hydroxide. Among the organic pollutants, compounds containing oxygen functional groups, e.g.,  $-\text{COOH}$  and  $-\text{OH}$  are very efficiently sorbed, which confirms the high efficiency of the removal of humic substances obtained during lime coagulation. The susceptibility of organic pollutants to sorption increases with their molecular weight, and decreases with increasing solubility. It was shown that, along with the increase in the solubility of the fulvic acid fraction, the effectiveness of their sorption on  $\text{CaCO}_3$  molecules decreased from 31 to 13% (Świdarska-Bróz, 1987). Due to the importance of solubility, electrically neutral (sparingly soluble) metal hydroxides are well sorbed. Since both  $\text{CaCO}_3$  crystals as well as the majority of organic admixtures and other colloids present in the water have a negative electric charge, the presence of  $\text{Ca}^{2+}$  ions or other multivalent cations is necessary for the proper course of sorption in the solution being purified (Gao, Yan, & Korshin, 2015; Zhou, Yan, Liu, Wang, & Qu, 2017). They fulfil the role of factors that neutralize organic anions and bridge emerging agglomerates. In the presence of  $\text{Mg}(\text{OH})_2$ , a sorbent with a positive electric charge, the presence of cations also increases the efficiency of anion sorption, but is not so important. Interaction between  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  is also possible, which results in the formation of flocs with an electric charge depending on the quantity of reacting compounds and the presence of other cations and anions in water. The disadvantage of lime coagulation is the elimination of magnesium from water and the need to restore the carbonate-calcium balance in water after coagulation. It can be obtained using a recarbonisation process, i.e. saturating water with carbon dioxide (Ghernaout et al., 2018; Ayoub, Zayyat, & Al-Hindi, 2014a; Ayoub, BinAhmed, Al-Hindi, & Azizi, 2014b; Chen, Fan, An, Cheng, & Tan, 2016; Dowling, O' Dwyer,

& Adley, 2015; Liao & Randtke, 1986; Randtke et al., 1982; Yan, Lu, Gao, Benedetti, & Korshin, 2015). In water treatment for purposes of human consumption, lime is rarely used as a basic coagulant, more often it can be used to correct the alkalinity of water before coagulation, to bind aggressive carbon dioxide after coagulation or as a substance supporting the coagulation with iron salts, due to the pH value of their effective operation. The optimum pH of coagulation with aluminium salts is 5–6, while for iron salts it is 5–6 and above 9 (Krupińska, 2012, 2016; Wolska, 2013). According to many authors, the coagulation process carried out in an alkaline environment can be used to purify waters in which there is a significant amount of organic matter, because in this process not only suspended and colloidal contaminants are removed, but also dissolved organic substances. High degree of organic pollutants removal is ensured by alkanisation of water up to  $\text{pH} > 10$ , where there are conditions of sorption and co-precipitation of organic pollutants with calcium carbonate and magnesium hydroxide precipitating from water (Liao & Randtke, 1986; Randtke et al., 1982; Wang et al., 2005). The article presents and discusses the results of research on the removal of pollutants from groundwater, in particular the removal of iron and organic substances, in the sorption process and co-precipitation with calcium carbonate and magnesium hydroxide.

## 1. Materials and methods

The subject of the study was groundwater from Quaternary formations. The groundwater intake is located in the area of the Warsaw-Berlin Urstromtal, 3–4 km from the shoreline of the river, in the area of the Odra river oxbow. They are 22 wells, 19 to 30 meters deep, located near peat bogs. The ranges of values of selected indicators of the physical-chemical composition of raw water and water after aeration and 2-hour sedimentation are presented in Table 1. Aerating the water has ensured high efficiency of ca. 95% Fe(II) oxidation to Fe(III), increase in colour and turbidity. The Fe(III) compounds formed were characterized by a very high degree of dispersion, and thus, poor sedimentation properties. Aeration and 2h sedimentation made it possible to reduce the total iron concentration by ca.11%, organic substances by only 1% and, unfortunately, increased turbidity and colour intensity (Table 1). Presence of significant concentrations of Fe(III) iron to 5.74  $\text{mgFe/dm}^3$  in purified water, and at the same time high colour up to 60  $\text{mgPt/dm}^3$  and almost no removal of organic contaminants (only 1% TOC) suggest that part of the organic pollutants present in water formed with iron combinations dispersed to a large extent.

This was confirmed by the results of the groundwater filtration tests (after 15-minute aeration and 2 h sedimentation) through filters with different pore diameters (filter: soft, hard or with 0.45  $\mu\text{m}$  pore diameter) or through an “incorporated” sand filter bed covered with iron and manganese oxides at a speed of 5 m/h (Table 2).

The required efficiency of iron compounds removal ( $\leq 0.2 \text{ mgFe/dm}^3$ ) and decreasing turbidity ( $\leq 1 \text{ NTU}$ ), which were 0.12  $\text{mgFe/dm}^3$  and 0.07 NTU respectively, was ensured only by filtration through the filter with 0.45  $\mu\text{m}$  pore diameter. Comparison of the amounts of pollutants removed as a result of filtration through the “incorporated” sand bed ( $V_f = 5 \text{ m/h}$ ) and through a soft filter showed that the effects of removing iron compounds were comparable. However, in the case of elimination of

Table 1. Characteristics of groundwater quality before and after Fe(II) oxidation and sedimentation

Indicator	Unit	Raw water	Water after Fe(II) oxidation and sedimentation
Temperature	°C	9.2–12.1	10.8–18.4
pH	–	6.88–7.11	7.61–7.99
Dissolved oxygen	$\text{mgO}_2/\text{dm}^3$	0.54–1.22	9.94–11.37
Colour	$\text{mgPt/dm}^3$	21–30	29–60
Turbidity	NTU	15–25	32–35
Iron total	$\text{mgFe/dm}^3$	5.30–6.82	4.71–6.07
Iron (II)	$\text{mgFe/dm}^3$	3.09–4.26	0.22–0.33
Iron (III)	$\text{mgFe/dm}^3$	1.04–3.55	4.49–5.74
Iron fixed in metal-organic complexes	$\text{mg/dm}^3$	1.54–1.70	1.80–2.00
Calcium	$\text{mgCa/dm}^3$	97–122	97–122
Magnesium	$\text{mgMg/dm}^3$	11–20	11–20
Alkalinity	$\text{mval/dm}^3$	3.60	3.60
Manganese	$\text{mgMn/dm}^3$	0.34	0.34
TOC	$\text{mgC/dm}^3$	3.98–5.60	3.98–5.55
DOC	$\text{mgC/dm}^3$	3.00–4.30	3.00–4.30

Table 2. Influence of filtration on the effectiveness of removing pollutants from groundwater after aeration and 2-hour sedimentation

Indicator, Unit	Raw water	Water after aeration, sedimentation and filtration by:			
		Soft filter paper	Hard filter paper	Filter paper 0.45 $\mu\text{m}$	Filter bed covered with iron and manganese oxides ( $V = 5 \text{ m/h}$ )
Colour, $\text{mgPt/dm}^3$	27	37	15	5	36
Turbidity, NTU	19	10	4	0.07	13
Iron total, $\text{mgFe/dm}^3$	5.83	1.65	0.60	0.12	1.60
Iron (III), $\text{mgFe/dm}^3$	2.38	1.50	0.50	0.06	1.40
Iron (II), $\text{mgFe/dm}^3$	3.45	0.15	0.10	0.06	0.15
TOC, $\text{mgC/dm}^3$	4.30	4.26	4.00	3.05	3.70

organic compounds, better results were obtained as a result of filtration through the “incorporated” sand bed (Table 2). The results of the tests presented in Table 2 also showed that the dominant amount of organic pollutants (ca. 71%) remaining in the filtrate were dissolved fractions, and the iron compounds (mainly Fe(III)) in the aerated water occurred in the form of colloids and very hard sedimenting particles.

Therefore, in order to intensify the treatment of groundwater, the alkalisation process was included in the technological system. The aim of the research was to determine the effectiveness of the groundwater treatment, in particular, the removal of iron and organic substances in the sorption process and co-precipitation with calcium carbonate and magnesium hydroxide. Prior to the alkalisation process, in order to ensure the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  groundwater was aerated for 15 minutes. The correction of the reaction was carried out with aqueous solutions of calcium hydroxide and sodium hydroxide in the pH range from 8.5 to 10.5. The flocculation time was 25 minutes with the rotational speed of the stirrers 30 rpm, and the sedimentation time was two hours. After the sedimentation process, the water samples underwent filtration through a soft filter or filtration at a speed of 5 m/h through the sand “incorporated” filter bed covered with iron and manganese oxides (bed height 1 m and  $d_{10} = 0.85$  mm,  $d_{60} = 1.3$  mm). The studies also determined the effect of the flocculation time, varying from 15 to 60 minutes, on the efficiency of removing pollutants from groundwater during alkalisation with calcium hydroxide up to pH = 10. The physical-chemical composition of both the raw as well as treated water was determined according to the International Standard methods. A decrease in the values of the studied water quality indicators in relation to the values permissible in the water for human consumption was assumed as the required effectiveness of water treatment (Regulation of the Minister of Health dated December 7, 2017). The NOM concentration was monitored by measuring the TOC and DOC. The TOC and DOC were measured using the thermal method and a Shimadzu TOC analyzer. DOC was analyzed by the TOC analyzer after filtration through 0.45  $\mu\text{m}$  pore diameter membranes.

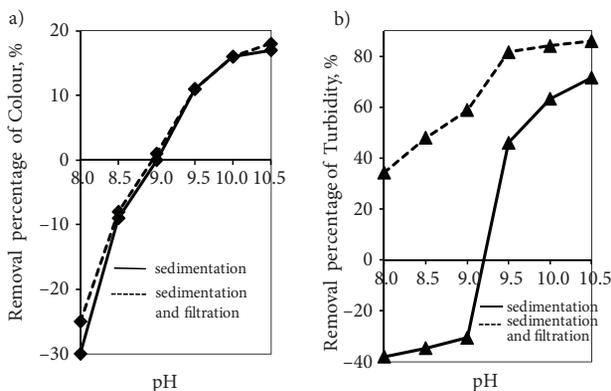


Figure 1. Influence of pH on the efficiency of reduction of colour (a) and turbidity (b) in the process of  $\text{Ca}(\text{OH})_2$  alkalisation and two-hour sedimentation

The colour (according to Pt scale), total iron, iron (II) concentrations were determined with the Agilent Cary 60 UV-VIS spectrophotometer. Iron (II) was measured using the 1.10 phenanthroline method. Total iron was measured using the same method. As a reducing agent of ferric ions to ferrous ions, hydroxylamine hydrochloride was used. Iron fixed with organic substances was determined as a difference between the iron concentration determined in the post-mineralization test and without mineralization, taking into account the amount of iron-inorganic bounds. The water samples were mineralized under reflux with nitric acid (V) and hydrochloric acid for 30 minutes, then sulfuric acid (VI) was dosed and the solution was evaporated until appearance of white fumes. Manganese, calcium and magnesium concentrations were determined with the atomic emission spectroscopy (ISP-OES, 5300DV, Perkin Elmer Company, US). The temperature and pH of the raw water and the purified water was determined with an WTW Multi Line P4 with a combination pH electrode with temperature corrections. The dissolved oxygen of the raw water and the purified water was determined with an WTW Multi 3410 SET 4 with an optical oxygen sensor FDO<sup>R</sup> 925 (Germany). Turbidity was measured using the Hach 2100N Turbidimeter. The alkalinity was determined with a titrimetric method against methyl orange using 0.1 M aqueous solutions of HCl.

## 2. Results and discussion

The tests determined effectiveness of removing pollutants from groundwater after aeration in the alkalisation process with calcium hydroxide or sodium hydroxide in the pH range from 8.5 to 10.5.

### 2.1. Alkalisation with calcium hydroxide

The effects of tests presented in Figure 1 and Figure 2 indicate that the effectiveness of water treatment as a result of alkalisation with calcium hydroxide increased with increasing concentration of  $\text{OH}^-$  ions. The maximum reduction in the concentration of total iron, TOC, DOC, colour intensity and turbidity was obtained at pH = 10.5 (Figure 1 and Figure 2), in which, in addition to

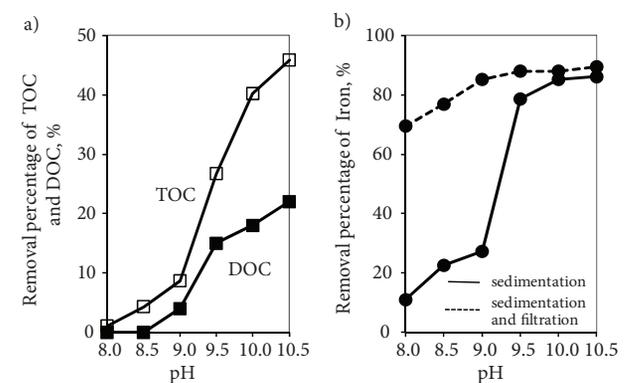
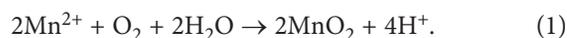


Figure 2. Influence of pH on the efficiency of reduction of TOC, DOC (a) and total iron (b) in the process of  $\text{Ca}(\text{OH})_2$  alkalisation and two-hour sedimentation

the precipitation of calcium carbonate, the precipitation of magnesium hydroxide with good adsorption properties also begins. Thus, the degree of water purification depended on both the processes of adsorption and coprecipitation of pollutants with  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  precipitating from water. However, the total iron concentration ( $\leq 0.2 \text{ mg/dm}^3$ ), colour intensity ( $\leq 15 \text{ mgPt/dm}^3$ ) and turbidity ( $\leq 1 \text{ NTU}$ ) required for water intended for human consumption were not obtained. The smallest concentrations of total iron, colour and turbidity in water after alkalisation to  $\text{pH} = 10.5$  and sedimentation were:  $0.95 \text{ mgFe/dm}^3$ ,  $13 \text{ mg Pt/dm}^3$  and  $7.04 \text{ NTU}$  respectively. In the opinion of Ghernaout, Świdarska-Bróz and Wang et al. (Ghernaout et al., 2018; Świdarska-Bróz, 1987; Wang et al., 2005) removal of organic substances increase with increasing pH, since they will dissociate to a greater extent and bind  $\text{Ca}^{2+}$  more strongly.

According to Liao and Randtke (Liao & Randtke, 1985) and Zhou et al. (2017) one of the best ways to improve removal of many contaminants especially organic contaminants is precipitate a significant amount of  $\text{Mg}(\text{OH})_2$  by adding enough lime to raise the pH to about 10.5–11.0 and adding magnesium salts if they are not already present in the raw water. The types of contaminants that are expected to adsorb onto and coprecipitate with  $\text{Mg}(\text{OH})_2$  are generally the same as those that adsorb onto  $\text{CaCO}_3$ , however removal of anionic species will be enhanced by the reinforcement of chemical forces by electrostatic forces and by the superior sorptive properties of the  $\text{Mg}(\text{OH})_2$ . Removal of cationic species by  $\text{Mg}(\text{OH})_2$  will be inhibited by electrostatic repulsion. Moel et al. (2007), Świdarska-Bróz (1987) and Teh Fu Yen (2007) found  $\text{Mg}(\text{OH})_2$  present as blossom-petal-like crystals in softening sludge it is possible that  $\text{Mg}(\text{OH})_2$  is initially precipitated in the form of gelatinous colloids that function as powerful adsorbents able to effectively remove contaminants. According to Zotter and Licsko (1992) in alkaline media the magnesium hydroxide is almost comparable in effectiveness to the aluminium or iron(III) hydroxide coagulants in neutral media. The application of filtration of water samples through a soft filter improved the effects of removing total iron, especially in the pH range up to 9.5, as well as reducing turbidity (Figure 1b and Figure 2b). The influence of filtration found and the changes in the amount of pollutants removed in the pH function testify to the positive role of the precipitating  $\text{CaCO}_3$  as a sorbent and a factor co-precipitating pollutants removed from water (Figure 1 and Figure 2). To adsorb onto on ionic solid like  $\text{CaCO}_3$ , a compound needs to be moderately hydrophilic. Compounds that are too hydrophilic will remain in the aqueous phase, but highly hydrophobic compounds cannot adsorb onto  $\text{CaCO}_3$  because they possess neither the electrical charge nor the calcium complexing functional groups necessary to effect adsorption (Liao & Randtke, 1986). In the corrected range of water pH, even as a result of the use of filtration, the required effectiveness of removing iron compounds and decreasing turbidity has not been obtained. The lowest concentration of total iron and

turbidity were  $0.72 \text{ mgFe/dm}^3$  and  $3.49 \text{ NTU}$  respectively after alkalizing the water to  $\text{pH} = 10.5$  and two hours of sedimentation. A sufficient reduction in colour intensity has already been provided by alkalisation with calcium hydroxide to  $\text{pH} = 10$ . The colour intensity in water after alkalisation to  $\text{pH} = 10$  and two-hour sedimentation was  $14 \text{ mgPt/dm}^3$ . The complete removal of manganese compounds from water was obtained by alkalisation with calcium hydroxide, dosed in an amount that ensures  $\text{pH} \geq 10$ , sedimentation and filtration through a soft filter. According to Teh Fu Yen (2007) and Moel et al. (2007), the normal oxidation-reduction potential ( $E_0$ ) of  $\text{Mn}^{2+}/\text{Mn}^{4+}$  system decreases with increasing the pH of the water, its value at  $\text{pH} = 7$  is ca.  $0.5 \text{ V}$  and at  $\text{pH}$  ca.9.5 is ca.  $0.25 \text{ V}$ . Effective oxidation of divalent manganese with oxygen at a rate that is useful for technological purposes only takes place at  $\text{pH} \geq 9.5$  according to reaction 1:



The required alkaline reaction of  $\text{Mn}^{2+}$  oxidation with oxygen dissolved in water explains the insufficient effects of demanganizing water at  $\text{pH} < 9.5$  obtained during alkalisation with calcium hydroxide (Figure 3).

The analysis of the obtained test results showed also that the effectiveness of removing organic pollutants as a result of alkalisation with calcium hydroxide increased with the amount of removed total iron (Figure 4), which suggests the joint removal of these pollutants.

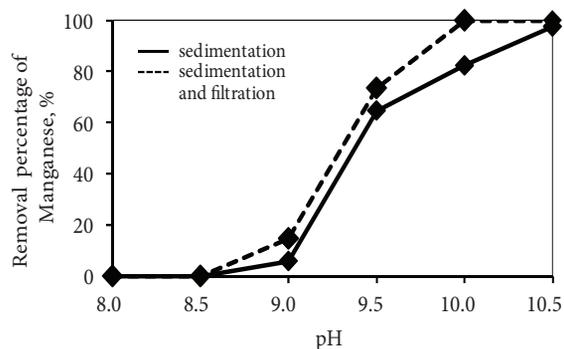


Figure 3. Influence of pH on the efficiency of reduction of manganese in the process of  $\text{Ca}(\text{OH})_2$  alkalisation and two-hour sedimentation

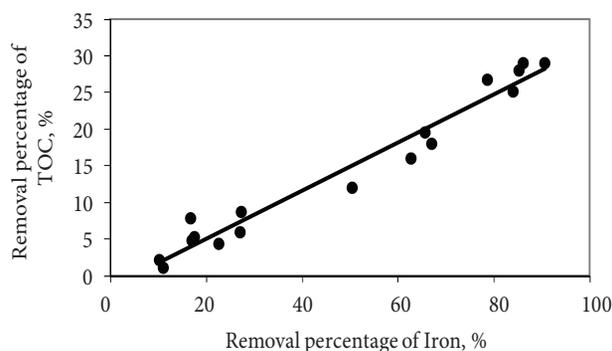


Figure 4. Dependence of the TOC reduction effectiveness on the effectiveness of removing total iron in water samples after the  $\text{Ca}(\text{OH})_2$  alkalisation in the range of  $\text{pH} = 8.5-10.5$  and two-hour sedimentation

Increasing the concentration of OH<sup>-</sup> ions (pH ≥ 9.0) shortened the Fe(II) oxidation time, as evidenced by the lack of turbidity and colour of the samples of water after sedimentation found for the majority of samples treated at natural pH (Table 1 and Figure 1). Despite the formation of iron (III) combinations that sediment better as a result of alkalisation with calcium hydroxide, in order to remove them from the water the filtration was necessary whose role in reducing turbidity and total iron concentration was lower in the pH range from 9.5 to 10.5 than in the case of treating water with an uncorrected pH value (Table 3).

Table 3. Effect of alkalisation with calcium hydroxide in the range of pH = 8.5÷10.5 on the filtration efficiency (Δη<sub>f</sub>, %) in reducing the concentration of total iron and turbidity

Filtration efficiency, %	pH					
	8.00 (without alkalisation)	8.50	9.00	9.50	10.00	10.50
Δη <sub>f</sub> Total Iron	58.50	54.25	57.90	9.00	2.80	1.40
Δη <sub>f</sub> Turbidity	73.00	83.00	90.00	36.00	21.00	14.00

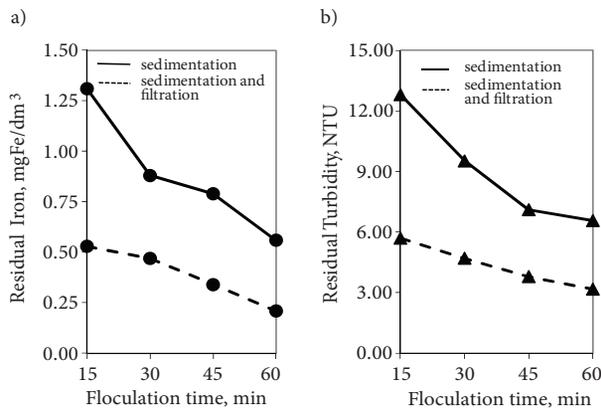


Figure 5. Influence of flocculation time on residual iron (a) and residual turbidity (b) in the water after the Ca(OH)<sub>2</sub> alkalisation to pH = 10

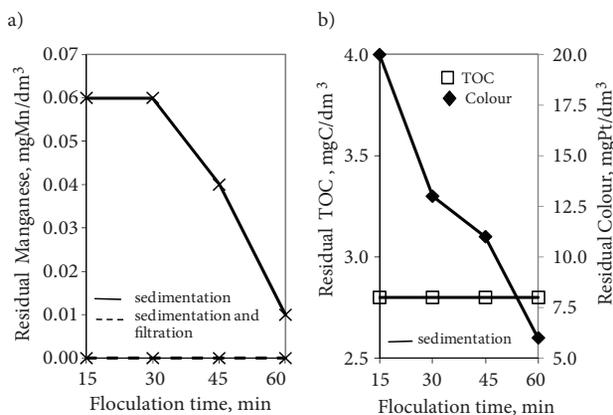


Figure 6. Influence of flocculation time on residual manganese (a) and residual TOC and residual colour (b) in the water after the Ca(OH)<sub>2</sub> alkalisation to pH = 10

The analysis of the dependences presented in Figure 5 and 6 showed that after water alkalisation with calcium hydroxide to pH 10 with increasing flocculation time from 15 to 60 min (which was supposed to improve the sedimentation properties of the precipitated agglomerates after alkalisation with calcium hydroxide), the level of contamination of water samples decreased, with the exception of removing organic substances. The effectiveness of removing organic substances did not depend on the time of flocculation changed in the range of 15–60 min and amounted to 33%. Filtration through a soft filter provided further removal of iron compounds and decreased turbidity (Figure 5). According to Kowal and Świdarska-Bróz (2007) the reaction of the purified water was a more important parameter in removing organic substances than flocculation time.

However, the use of the longest flocculation time of 60 minutes and the filtration of water samples through a soft filter did not provide the required values of the total iron concentration and turbidity, which amounted to 0.21 mgFe/dm<sup>3</sup> and 3.18 NTU respectively. Sufficient reduction of manganese concentration in water after 2h sedimentation (0.04 mgMn/dm<sup>3</sup>) was provided by 45 min flocculation, and the complete removal of manganese compounds from water was obtained using the shortest flocculation time of 15 min and additionally filtration through a soft filter.

### 2.2. Alkalisation with calcium hydroxide or sodium hydroxide

The effects of the treatment of aerated water as a result of alkalisation with calcium hydroxide or sodium hydroxide in the range of pH = 8.50–10.50 and two-hour sedimentation are shown in Figure 7–9. The concentration of OH<sup>-</sup> ions determined the effectiveness of removing total iron, organic substances (TOC and DOC), iron fixed in metal-organic complexes (Figure 7a and Figure 8a, 8b) and decreasing the turbidity and colour of water (Figure 7a, 7b).

The comparison of the amounts of pollutants removed from the water indicates the higher suitability of calcium

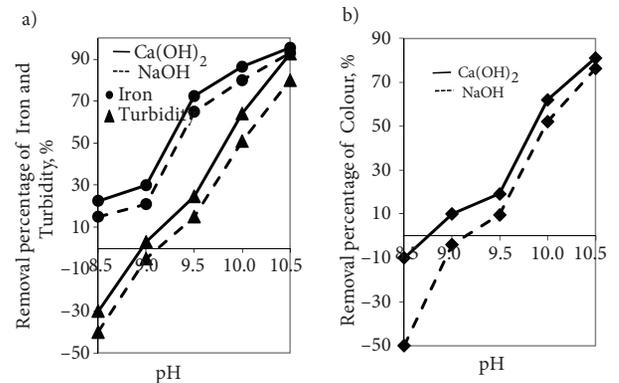


Figure 7. Effect of the type of alkalizing reagent: Ca(OH)<sub>2</sub> or NaOH on the amount of iron and turbidity (a) and colour (b) removed from the water in the sedimentation process

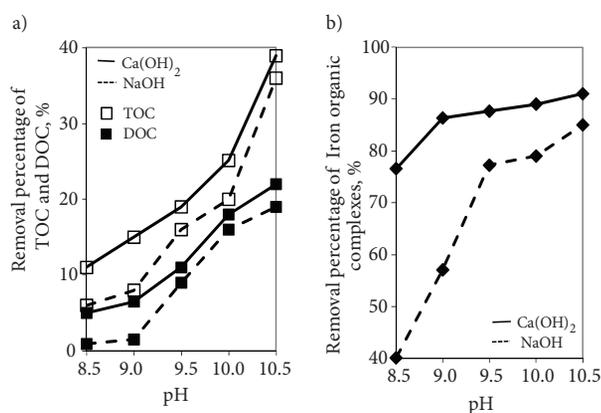


Figure 8. Effect of the type of alkalinizing reagent: Ca(OH)<sub>2</sub> or NaOH on the amount of TOC and DOC (a) and iron organic complexes (b) removed from the water in the sedimentation process

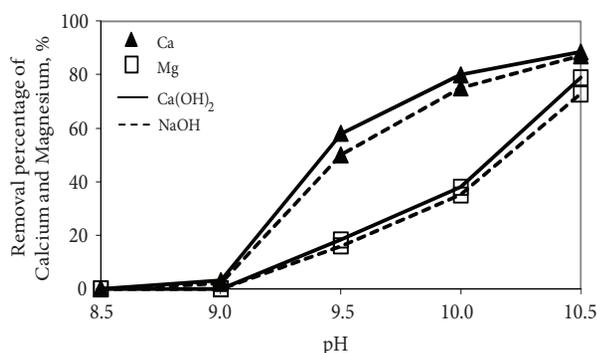


Figure 9. Effect of the type of alkalinizing reagent: Ca(OH)<sub>2</sub> or NaOH on the effectiveness of removing calcium and magnesium from the water in the sedimentation process

hydroxide for alkalisation, especially to pH = 9.5 corresponding to the minimum solubility of calcium carbonate.

This indicates that Ca<sup>2+</sup> cations introduced into the treated water during the alkalisation probably neutralized organic anions influencing the colour and TOC and fixed in iron-organic complexes, increasing their susceptibility to adsorption, and also fulfilled the role of cations bridging the agglomerates formed. Most organic contaminants in water are negatively charged and can adsorb onto CaCO<sub>3</sub> only if there are specific chemical forces strong enough to overcome electrostatic repulsion. Adsorption of anionic chemicals onto CaCO<sub>3</sub> can be enhanced by the presence of Ca<sup>2+</sup>, as demonstrated by Liao and Randtke using groundwater fulvic acid (Liao & Randtke, 1985). According to Świdarska-Bróz (1987) and Randtke et al. (1982) decrease in the colour and removal of organic substances depended on the pH of the treated solutions and the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions. For solutions without these cations (model solutions prepared on the basis of distilled water), according to Świdarska-Bróz (1987), in the pH range to 14, practically no organic pollutants were removed. The difference in the effectiveness of the precipitating factors tested, Ca(OH)<sub>2</sub> and NaOH decreased with increasing pH (Figure 7–9), and therefore, also the

amount of precipitated calcium carbonate, and mainly magnesium hydroxide characterized by good sorption properties and whose particles have a positive charge. According to the literature (Brastad & He, 2013; Ghernaout et al., 2018; Teh Fu Yen, 2007; Mahasti et al., 2017; Moel et al., 2007), calcium carbonate begins to precipitate from the solution at pH ca.9.3, while magnesium hydroxide precipitates at pH = 10.2. pH = 11.2–11.5 is required to completely precipitate magnesium hydroxide. In the tested pH range, no transition of Fe(OH)<sub>3</sub> to soluble Fe(OH)<sub>4</sub><sup>-</sup> anion was found, and the filtration through a sand bed at a filtration rate of 5 m/h improved the effects of removing iron, organic matter, colour and turbidity. According to the literature, the solubility of Fe(OH)<sub>3</sub> decreases with the increase in pH to ca. 8, and then increases. A significant increase in solubility at pH > 10 results from the transition of Fe(OH)<sub>3</sub> to soluble Fe(OH)<sub>4</sub><sup>-</sup> anion. The required total iron concentration and turbidity reduction, which amounted to 0.18 mgFe/dm<sup>3</sup> and 0.88 NTU respectively, were obtained only through alkalisation with calcium hydroxide to pH = 10.5 and additional filtration through an incorporated sand bed. Regardless of the type of alkalinizing agent used: calcium hydroxide or sodium hydroxide, a disadvantage of the alkalisation was the removal of calcium and magnesium ions from the water, as shown in Figure 9.

## Conclusions

Analysis of the results showed that:

1. With the increase of the pH of the water due to the alkalisation with calcium hydroxide or sodium hydroxide, the efficiency of its treatment increased, which proves the positive role of the co-precipitation of inorganic and organic pollutants with CaCO<sub>3</sub> molecules and, at a higher concentration of OH<sup>-</sup> ions, also with precipitating Mg(OH)<sub>2</sub> and MnO<sub>2</sub>.

2. The degree of removal of organic pollutants increased with the amount of removed total iron, which suggests the joint removal of these pollutants.

3. Alkalisation of water after aeration with calcium hydroxide to pH ≥ 10 and sedimentation and filtration through a soft filter paper ensured complete elimination of manganese, sufficient colour reduction, but no required turbidity and total iron concentration in which iron (III) predominated. The required total iron concentration and turbidity reduction, were obtained only through alkalisation with calcium hydroxide to pH = 10.5 and additional filtration through an incorporated sand bed covered with iron and manganese oxides.

4. Extending the flocculation time to 60 min, which was supposed to improve the sedimentation properties of the precipitated agglomerates after alkalisation with calcium hydroxide, also failed to provide acceptable turbidity and total iron concentration. The turbidity in treated water was 3.18 NTU, and the total iron concentration was 0.21 mgFe/dm<sup>3</sup>.

5. The comparison of the effects of water treatment obtained after the alkalisation process with lime and sodium hydroxide shows the importance of the precipitating  $\text{CaCO}_3$  and the presence of  $\text{Ca}^{2+}$  ions in neutralizing organic anions, organic anions fixed in iron-organic complexes as well as compounds that determine the colour of water.

6. The analysis of the obtained test results showed that in the case of groundwater treatment characterized by an increased content of organic substances, iron compounds and increased colour intensity, the removal of pollutants, in particular the removal of organic substances and lowering the colour intensity can be supported by the use of calcium hydroxide as alkalisng agent. The disadvantage of alkalisation is the removal from the treated water of calcium and magnesium ions, which are necessary for the proper functioning of the human body. The need to enrich water after alkalisation with calcium and magnesium ions should then be considered.

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