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IMPROVEMENT OF ATYPICAL GROUND WATER CONDITIONING PROCESSES

Laboratory research into the treatment technology of ground water from the Huta Komorowska water intake was carried out. The water is drawn for drinking purposes.

The results of research were used in order to improve water conditioning technology for the existing water treatment plant. This new technology is based on two stages of filtration.

A water to be treated contains various forms of iron which forms chelates with humus compounds. They have to be removed in a contact coagulation process. In the first stage of filtration, raw water was passed through a triplex filter consisting of *aquacleanit* – support layer, *quartz sand* – proper layer and *anthracite* – surface layer. Coagulant SAX-18 (sodium aluminate) at the dose of 2 mg Al/dm³ proved to be most effective in reducing colour intensity, turbidity, iron content, oxygen demand and absorbance. It also increased pH, hence the water alkalinity, which made it less aggressive.

In the frame of the second filtration stage, the filter with chemical active mass (*Defeman*) was used. The water in the first and second stages was filtered at the rate of 7.5 m/h.

1. INTRODUCTION

Various forms of iron and manganese as well as nitrogen compounds belong to the impurities most often present in underground waters. Some underground waters contain also natural organic matter represented mainly by humus compounds. Water becomes enriched with humus substances in consequence of humus leaching from humus-rich soils and from brown-coal formations. Their content in natural waters depends on the type of soil, the time of contact of percolating water with the ground layer, on chemical composition and, first and foremost, on water pH. Underground waters containing natural organic matter are characterized by intense colour and high oxygen consumption [6], [10], [12].

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Until recently, humus substances were not believed to be harmful for humans. They were removed from water for drinking primarily because of esthetic reasons. Research of the recent years has shown that humus substances may be a source of undesirable smell and colour of water as well as may accumulate some toxic substances while forming complexes with heavy metals, compounds of phosphorus and ammonia, and adsorbing organic compounds (pesticides, phthalates, polycyclic aromatic hydrocarbons). Humus substances react with chlorine to form undesirable secondary halogen microimpurities [2], [9], [11].

One of the most popular technological processes applied in the removal of humus substances from water is their coagulation. However, in order to coagulate those impurities, the doses of coagulants should frequently be higher than those used for coagulation of particles which cause water turbidity, and strict observations of optimum process conditions, mainly pH, have to be made.

When the doses of ferric coagulants are too low or pH is not suitable, the coloured combinations (chelates) of humus acids with iron may be formed. In some cases, coagulation must be enhanced by chemical oxidation and/or polyelectrolytes [1], [3], [4], [7], [8].

Natural organic matter present in waters taken for communal needs poses a serious obstacle to many conditioning stations (SUWs), like that in Huta Komorowska.

The purpose of the present research was to analyse the underground water taken from four deep wells in Huta Komorowska. This allowed its conditioning, thus making it suitable for consumption. Based on the results obtained it was possible to create a good desing for improving technological process to be carried out in water conditioning station.

2. CHARACTERISTIC OF WATER DRAWN FROM WELL

The basic physicochemical parameters of the water drawn directly from well were determined in the laboratory of Water Purification and Protection Department of the Rzeszów University of Technology, in accordance with Polish standards. The results obtained were compared with the standards (table 1) given in the Regulation of the Ministry of Health of 29th March 2007 (*Official Gazette* Dz.U. No. 61, item 417).

Raw water from the well had substandard colour, turbidity, iron and manganese content as well as low pH. Intensive colour of water correlated with an increased oxygen demand and high UV absorbance testified to the presence of natural organic matter, which could form complexes with iron and manganese compounds.

Moreover, the water tested had low pH, which proved that it was aggressive. Physical and chemical composition of water allowed us to suspect that its treatment could be difficult.

Table 1

0.291

Parameters Permissible values Raw water рН 6.5 - 9.06.40 Total alkalinity (mval/dm³) 0.9 Oxygen demand (mg O₂/dm³) 5.0 4.85 Total hardness (mval/dm³) 1.2 - 10.01.76 (mg CaCO₃/dm³) 60 - 50088 Turbidity (NTU) 1.0 17.0 Colour (Hazen) 15 40 Manganese (mg/dm³) 0.05 0.40 Iron (mg/dm³) 0.20 2.75 Ammonium nitrogen 0.50 0.30 $(mg NH_4^+/dm^3)$

Physicochemical and chemical parameters of water sampled

3. EXISTING TECHNOLOGICAL SYSTEM OF WATER TREATMENT

UV absorbance (254 nm)

The raw water from well underwent three-stage filtration. In the first stage it was passed through 4 filters filled with quartz sand at the filtration rate approaching 5 m/h.

In the second-stage, the water was passed through 3 filters packed with an alkaline mass (containing mainly MgO), called *aquacleanit*, at the rate close to 7.5 m/h, while in the third stage, 3 filters, whose filtration rate was ca. 7.5 m/h, were filled with chemical active mass – *Defeman*.

Such a technological system does not ensure the water meeting permissible standards, hence the water treatment process has to be improved.

4. TECHNOLOGICAL STUDY FOR IMPROVING WATER CONDITIONING PROCESS

The purpose of the laboratory tests was to develop a process that meets the following conditions:

- water colour and turbidity as well as its oxygen demand are reduced to standard values.
- a standard pH as well as effective removal of iron and manganese from water are maintained.
- the equipment and facilities in operation should be used, which minimizes the cost of modernization.

The technological study was carried out in three stages. In the first stage, coagulant was selected and its optimal dose determined. The second stage made it possible to verify the coagulant dose in the process of contact coagulation, as well as to define the filtration parameters. The third stage involved the second stage of filtration and its main objective was to remove manganese from water.

The technological tests were performed once, but all the parameters of water are the averages of two analyses.

4.1. VOLUMETRIC COAGULATION PROCESS

Coagulation of colloidal particles in water was conducted in classical manner, based on 'jar test' and using a 6-stand laboratory coagulator equipped with a mechanical stirrer with a regulated r.p.m. [5]. The effectiveness of coagulants was assessed experimentally and their doses were determined.

The following coagulants, produced by Kemipol company, were tested:

- PAX-16 aqueous solution of polyaluminum chloride,
- PAX XL-61 aqueous solution of aluminum polychloride,
- PIX-111 aqueous solution of ferric chloride(III),
- SAX-18 sodium aluminate.

The first three compunds are pre-hydrolyzed coagulants, and the last coagulant is sodium aluminate. Customary coagulants were not used for the water of low alkalinity, because their activity depends on the presence of certain quantity of bicarbonates that are responsible for water alkalinity. These coagulants would cause the lowering of alkalinity.

 $$\operatorname{\texttt{Table}}\ 2$$ Selection of coagulant type and its optimum dose

Coagulants	Dose (mg/dm ³)	рН	Total alkalinity (mval/dm³)	Oxygen demand (mg/dm³)	Colour (Hazen)	Turbid- ity (NTU)	Iron (mg/dm³)	UV absorbance (254 nm)
PAX-16	1	6.9	1.0	2.9	73	6.5	0.8	0.294
	5	6.8	0.9	1.3	30	3.3	0.5	0.118
	10	6.8	0.9	1.4	36	4.2	0.6	0.106
PAX XL-61	1	6.9	0.8	2.8	63	5.3	1.1	0.300
	5	6.8	0.7	2.2	74	4.6	0.8	0.221
	10	6.7	0.6	1.2	28	2.4	0.7	0.135
PIX-111	1	6.9	1.0	3.0	62	4.4	2.0	0.344
	5	6.8	0.8	2.8	143	6.2	3.5	0.590
	10	6.8	0.6	2.7	112	8.8	4.5	0.540
SAX-18	1	6.9	1.0	0.6	45	4.6	0.9	0.280
	5	7.0	1.2	1.2	14	1.6	0.5	0.200
	10	7.2	1.6	1.8	15	1.1	0.1	0.215

Table 3

Prior to coagulation process water was aerated. The rapid mixing lasted 3 min, whereas the flocculation process (slow mixing) was run for 30 minutes. After coagulation completion, the samples were left for 30-minute sludge sedimentation. In decanted and percolated samples, the following determinations were carried out according to Polish Standards: pH, alkalinity, colour, turbidity, oxygen demand, iron content and UV absorbance. The coagulants selected and their optimum doses are presented in table 2.

As expected, the PIX-111 (ferric coagulant) appeared to be the least effective coagulant. With an increases in its dose the quality of water after coagulation became worse. Aluminum coagulants (PAX-16 and PAX XL-61) in the doses of 1 mg Al/dm³ caused the worsening of water quality. The doses of 5 and 10 mg Al/dm³ produced better effects but the colour, turbidity and iron content of the treated water still did not meet the quality standards. The best quality of water was obtained in the process of coagulation by sodium aluminate (SAX-18) and therefore optimizing the dose of that coagulant proved to be of a prime importance (table 3). As this coagulant rose pH, and according to professional literature [8] the most effective removal of humus compounds occurs at pH 5–6, the water was not aerated, which would rise pH.

Selection of coagulant dose (SAX-18)

Down or other	SAX-18 (mg Al/dm ³)						
Parameters	2	4	6	7	8	12	
рН	6.2	6.4	6.6	6.7	6.9	7.4	
Total alkalinity (mval/dm ³)	0.6	1.3	1.4	1.5	1.6	1.9	
Oxygen demand (mg/dm ³)	1.2	1.4	1.3	2.0	2.2	3.8	
Colour (Hazen)	43	22	28	19	24	48	
Turbidity (NTU)	3.7	1.3	1.8	1.4	1.4	3.0	
Iron (mg/dm ³)	0.26	0.16	0.13	0.1	0.05	0.03	
UV absorbance (254 nm)	0.235	0.178	0.119	0.220	0.200	0.240	

With increasing the dose of sodium aluminate the water pH and alkalinity increased and the iron content decreased.

The sodium aluminate hydrolysis in water is given by the following reaction:

$$Na_2 Al_2 O_4 + 2Ca(HCO_3)_2 + 2H_2O \leftrightarrow 2Al(OH)_3 + 2CaCO_3 + 3NaHCO_3$$
.

In acid and neutral environments, the aluminum hydroxide forms positively charged monomers, which react with negative colloidal particles of humic acids. The floccules produced by these processes easily undergo sedimentation and/or filtration.

The optimum dose of sodium aluminate should be within 2 and 4 mg Al/dm³. Although water turbidity and colour after volumetric coagulation exceeded slightly the

permissible values, it was assumed that contact coagulation with that dose may give better results.

4.2. CONTACT COAGULATION (THE FIRST STAGE OF FILTRATION)

Contact coagulation studies were conducted in two series.

4.2.1. SERIES I

Raw water with sodium aluminate (2 mg Al/dm³) was passed through a sand filter of sand grain distribution of 0.5–1.5 mm and the sand layer of the height of 0.7 m. The rate of filtration was 6.0 m/h. The results obtained are given in table 4.

Table 4
Results of contact coagulation

Parameter	Series I	Series II	
рН	6.75	8.60	
Total alkalinity (mval/dm ³)	0.9	Zf = 1.3, Zm = 3.4	
Oxygen demand (mg O ₂ /dm ³)	1.90	1.30	
Total hardness (mval/dm ³)	1.70	4.0	
(mg CaCO ₃ /dm ³)	85	200	
Colour (Hazen)	32	17	
Turbidity (NTU)	11	2.39	
Iron (mg/dm ³)	1.6	0.35	
Manganese (mg/dm ³)	0.14	0.15	
UV absorbance (254 nm)	0.225	0.117	

Since the results achieved, i.e. reduction of colour, turbidity and iron content, were insufficient, the second series of tests was carried out.

4.2.2. SERIES II

Raw water with sodium aluminate (2 mg Al/dm³) was passed through a sand filter consisting of the following layers:

- 10-cm thick supporting layer of aquacleanit material of grain size of 2–4 mm,
- 55-cm thick layer of quartz sand of grain size of 0.5–0.8 mm,
- 50-cm thick surface layer of *anthracite* of grain size of 0.6–1.5 mm.

The filtration rate was 7.5 m/h. The results of this series are summarized in table 4.

In the 2nd series, the water quality improved considerably. Its colour and iron content exceeded the permissible values only slightly. Still higher turbidity was caused by magnesium hydroxide and calcium carbonate penetrating into water. This fact was

confirmed by the rise in water alkalinity and hardness. The problem of both turbidity and excessive quantity of manganese, as well as a further reduction of iron content and coloration, was solved by applying the second stage of filtration.

4.3. THE SECOND STAGE OF FILTRATION

In the 2nd stage of filtration, the water was passed through the filter filled with *Defeman*, a chemically active substance, mixed with quartz sand in 1:1 ratio. The height of its proper layer was 100 cm, granulation of the mass ranged from 0.5 to 1.5 mm and that of sand from 0.5 to 0.8 mm. The rate of filtration was the same as that in water treatment plant, i.e. 7.5 m/h. The results obtained after the 2nd stage of filtration can be found in table 5. After two-stage filtration, the water parameters analyzed met sanitary requirements.

Table 5
Results obtained after the 2nd stage of filtration

Parameters of water after the 2nd stage of filtration			
рН	8.23		
Total alkalinity (mval/dm ³)	2.80		
Oxygen demand (mg O ₂ /dm ³)	0.70		
Total hardness (mval/dm³)	3.70		
(mg CaCO ₃ /dm ³)	185		
Colour (Hazen)	5.0		
Turbidity (NTU)	1.0		
Iron (mg/dm ³)	0.16		
Manganese (mg/dm ³)	0.02		
UV absorbance (254 nm)	0.101		

5. SUMMARY

Because of the complexes of iron and humus compounds present in the water taken it became necessary to implement coagulation process in the water conditioning station in Huta Komorowska. Sodium aluminate in the doses from 2 to 4 mg Al/dm³ appeared to be the most effective coagulant among those tested during volumetric coagulation. This coagulant was chosen not only because of its effectiveness in reducing water coloring, turbidity, iron content, oxygen demand and absorbance, but also because of its ability to rise water pH, thus alkalinity, which reduced its aggressiveness.

Classic (volumetric) coagulation carried out in an open system was replaced with contact coagulation conducted in a closed system, more economical and easier to automate. Because of the cost of coagulant and the quantity of sediments generated in

the contact coagulation, the lower dose of coagulant (2 mg Al/dm³) was used. The first stage of filtration (contact coagulation) should be conducted on a three-layer filter at the filtration rate of 7.5 m/h. A filter with chemically active mass (*Defemen* + sand) should be used within the 2nd stage of filtration. The filtration should proceed at the rate of 7.5 m/h.

As the beds reach adequate operation parameters (bed impregnation with coagulant in the first stage of filtration and formation of manganese dioxide envelopes on grains in the second one), the results obtained should become still better.

REFERENCES

- [1] DUAN J., WANG J., GRAHAM N., WILSON F., Coagulation of humic acid by aluminium sulphate in saline water conditions, Desalination, 2002, 150, 1–14.
- [2] DUAN J., WILSON F., GRAHAM N., TAY J., Adsorption of humic acid by powdered activated carbon in saline water condition, Desalination, 2002, 151, 53–66.
- [3] DUMAT C., STAUNTON S., Reduced adsorption of calcium on clay minerals caused by various humic substances, Journal of Environmental Radioactivity, 1999, 46, 187–200.
- [4] ELFARISSI F., PEFFERKORN E., *Kaolinite/humic acid interaction in the presence of aluminium ion*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2000, 168, 1–12.
- [5] Granops M., Kaleta J., Woda, uzdatnianie i odnowa, Wyd. SGGW, Warszawa, 2005.
- [6] KALETA J., Związki humusowe w środowisku wodnym, Rzeszów, Z.N. PRz., 2004, z. 38, 39-53.
- [7] KAM S.K., GREGORY J., The interaction of humic substances with cationic polyelectrolytes, Wat. Res., 2001, Vol. 35, No. 15, 3557–3566.
- [8] MELIA C., BECKER W., AU K., Removal of humic substances by coagulation, Wat. Sci. Tech., 1999, Vol. 40, No. 9, 47–54.
- [9] ODEGAARD H., EIKEBROKK B., STORHAUG R., Processes for the removal of humic substances from, water an overview based on Norwegian experiences, Wat. Sci. Tech., 1999, Vol. 40, No. 9, 37–46.
- [10] PERCHUĆ M., Żelazo i kwasy humusowe w barwnych wodach podziemnych, Gaz, Woda i Technika Sanitarna, 2003, 11, 394–397.
- [11] SMECK N.E., NOVAK J.M., Weathering of soil clays with dilute sulfuric acid as influenced by sorbed humic substances, Geoderma, 1994, 63, 63–76.
- [12] ŚWIDERSKA-BRÓŻ M., Przydatność koagulacji w usuwaniu mikrozanieczyszczeń i ich prekursorów, Międzynarodowa Konferencja Naukowo-Techniczna "Zaopatrzenie w wodę miast i wsi", Poznań, 1996, t. I, 319–333.