

RESIDUAL ALUMINIUM IN WATER INTENDED FOR HUMAN CONSUMPTION

Izabela KRUPIŃSKA^{1*}, Ewelina PŁUCIENNIK-KOROPCZUK¹,
Sylwia GAĞAŁA²
University of Zielona Góra, Zielona Góra, Poland

Abstract

Aluminium is one of the environmental factors that may have an impact on Alzheimer's and Parkinson's disease. Some epidemiological studies show a relationship between the concentration of aluminium in drinking water and the incidence of Alzheimer's disease. The article presents and discusses the results of research on the effect of the type and dose of non-prehydrolyzed aluminium coagulants on the concentration of residual aluminium in water intended for human consumption. Aluminium sulphate (VI) and sodium aluminate were tested as coagulants. Analysis of the obtained test results showed that lower concentrations of residual aluminium were found after coagulation with aluminium sulphate (VI), which is hydrolyzed acidally, lowering the pH of the water in the range of 7.47 to 7.12 providing good conditions for the formation of $\text{Al}(\text{OH})_3$. A less useful coagulant due to the concentration of residual aluminium was sodium aluminate, which undergoes basic hydrolysis creating conditions for the transition of $\text{Al}(\text{OH})_3$ into soluble $\text{Al}(\text{OH})_4^-$.

Keywords: residual aluminium, coagulation, non-prehydrolysed aluminium coagulants

^{1*} Corresponding author: University of Zielona Góra, Institute of Environmental Engineering, Szafrana st 15, 65-246 Zielona Góra, Poland, e-mail: i.krupinska@iis.uz.zgora.pl, tel. +48683282560

² Student of the University of Zielona Góra, Poland

1. INTRODUCTION

Coagulation is a commonly used process for treating most surface and infiltration water. In order to carry out the coagulation process, coagulants are dosed to water, which are usually aluminium salts. Analysis of literature information indicates greater usefulness in purifying water intended for human consumption of pre-hydrolyzed aluminium coagulants than non-prehydrolyzed aluminium such as: aluminium sulphate (VI) or sodium aluminate. The coagulant most commonly used at water treatment plants in Poland is non-prehydrolysed aluminium sulphate (VI). During coagulation with aluminium coagulants, the problem of residual aluminium in water may arise. Improper coagulation of hydrolysing aluminium coagulants ensures low efficiency of removing impurities and at the same time causes oversized concentration of residual aluminium in purified water [3-17, 21-24]. Aluminium is a chemical element with an atomic mass of 26.98 u and atomic number 13. Along with boron, gallium, indium and thallium, it belongs to the 13th group of the periodic table. Both aluminium oxide and hydroxide have amphoteric properties, which means that they can react with acids and bases. As a result of these reactions, aluminates and aluminium salts may be formed. Until recently, aluminium-containing compounds were thought not to be harmful to health, hence their use in the production of many food storage products such as cans, pots and aluminium foil. Alkaline aluminium compounds are also an essential component of drugs used in peptic ulcer disease. Individual forms of aluminium may have different properties. Some may be necessary for the proper functioning of living organisms, while others may have toxic properties. Aluminium aquacomplexes can be ranked according to increasing toxicity according to the following series [26]: $[\text{Al}(\text{OH})_2^+] < [\text{Al}(\text{OH})_2^{2+}] < [\text{Al}(\text{H}_2\text{O})_6]^{3+}$. The effect of aluminium on the human body can clearly be described as toxic. Already in the eighties it was found that aluminium ions from water can diffuse into the blood plasma causing damage to the nervous system, and the penetration of ions across the blood-brain barrier depends on the degree of compound ionization, lipid solubility and particle size. Subsequent studies showed the great importance of the dynamics of aluminium penetration into the brain and kidneys. Amyotrophic lateral sclerosis, parkinsonism associated with senile dementia are other disease entities that are largely thought to be aluminium. A common feature of these diseases is neuronal atrophy, neurofibril degeneration, lymphopenia, and T-cell dysfunction. According to epidemiological studies, there is some relationship between aluminium and Alzheimer's disease [19, 20], which shows an increased occurrence rate in areas with high aluminium content. Mc Lachlan [13] defined cases of Alzheimer's disease on the basis of clear neuropathological criteria and specific amounts of aluminium consumed in drinking water. The results of the study showed that the risk of disease was associated with increased levels

of aluminium in water. Magnetic resonance imaging studies indicate aluminium accumulation within the hippocampus. Histological studies of the brain of people who died as a result of neurodegenerative processes show higher levels of aluminium in places affected by degenerative changes. According to numerous studies, the concentration of Al^{3+} in the brain tissue of people who died of Alzheimer's disease was 1.0-11.5 mg/kg of dry matter, while in people who died for other reasons only 0.23-2.7 mg/kg of dry matter. It is likely that aluminium is also an etiological factor of classical Parkinson's disease. The interactions between aluminium and fluorides in water are unclear. Some reports point to the intensification, in the presence of fluoride, of the absorption of aluminium from the gastrointestinal tract, others to the protective role of fluoride in the development of dementia [2, 13, 26]. Despite the low acute toxicity, aluminium's effects on the body, especially after prolonged exposure, lead to many disorders, including in the blood, digestive and skeletal systems. Aluminium causes changes in red blood cell parameters manifested by a decrease in the number of erythrocytes, haemoglobin level and hematocrit value as well as an increase in reticulocyte content. The reported changes indicate that aluminium interferes with the erythropoiesis process. Monitoring studies have shown that aluminium is found in all natural and tap water. It can exist in dissolved and undissolved forms, in organic compounds and inorganic compounds. Aluminium compounds show low solubility in the range of $\text{pH} = 6-8$, therefore in surface waters aluminium concentrations are low and are in the range of 60-300 $\mu\text{g}/\text{dm}^3$. In the $\text{pH} 5.1-5.5$ range, monomeric toxic $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ hydroxocomplexes predominate [20]. Aluminium due to the low density of 2.7 g/cm^3 , small ion beam (0.50 pm) and high charge (3+) and high reactivity (standard redox potential for Al^{3+} $E_0 = -1.662$ V) occurs only in the bound state [1]. An important factor that affects the form of aluminium is the pH value [26]. Cationic and anionic forms of aluminium for $\text{pH} < 4.7$ and $\text{pH} > 8$ show good solubility. In an environment with a pH of 6-8 aluminium occurs in the form of sparingly soluble compounds. The widespread occurrence and a large variety of aluminium compounds and chemical forms, but first of all its toxic effect on living organisms obliges to conduct research aimed at controlling and possible elimination of aluminium [13, 19, 25]. The article discusses the impact of the type and dose of non-prehydrolyzed aluminium coagulants on the concentration of residual aluminium in purified water.

2. MATERIALS AND METHODS

The subject of the study was water being a mixture of groundwater from quaternary formations and surface water from the Obrzyca River taken at the water treatment plant in Zawada near Zielona Góra. Increased concentrations

of organic substances were found in raw water: TOC varied from 7.00 to 8.00 mgC/dm³ and DOC from 6.30 to 6.90 mgC/dm³. Aluminium and iron were found in water, the concentration of which was 0.020 mgAl/dm³ and from 1.00 to 2.00 mgFe/dm³ respectively. The pH of raw water ranged from 7.60 to 7.84, and the basicity from 3.60 to 3.80 mval/dm³. The aim of the study was to determine the effect of the type and dose of non-prehydrolyzed aluminium coagulant on the concentration of residual aluminium in water after the coagulation process. The coagulants used were classical hydrolyzing coagulants: aluminium sulphate (VI) and sodium aluminate. Jar tests were carried out by using a 1 dm³ six-place paddle stirrer. Coagulation was carried out in water samples of 1 dm³ through 1 min. fast mixing at a speed of 250 rpm and 25 min. flocculation with an intensity of mixing of 30 rpm. The doses of coagulants were expressed in mgAl/dm³ and varied from 1 to 5 mgAl/dm³. After coagulation the samples were subject to sedimentation process for 1 h. The physical-chemical composition of both the raw as well as treated water was determined according to the International Standard Methods.

3. RESULTS AND DISCUSSION

The effect of the hydrolysis of aluminium coagulants are monomers: Al³⁺, Al(OH)²⁺, Al(OH)₂⁺, Al(OH)₃, Al(OH)₄⁻ and various nonionic, anionic and cationic polymers with the general formula Me_n(OH)_y^{3n-y}. **THE QUANTITY OF** individual hydrolysis products, apart from the conditions under which hydrolysis takes place, is largely determined by the type of coagulant.

3.1. Effect of aluminium sulphate (VI) and sodium aluminate dose on the concentration of residual aluminium in water

Analysis of the obtained test results showed that among the tested coagulants only aluminium sulphate (VI) caused a decrease in the natural alkalinity and pH of the purified water. Sodium aluminate, which undergoes alkaline hydrolysis in water, increased the alkalinity and pH of purified water, which increased with the increase of the coagulant dose: alkalinity in the range from 3.7 to 4.2 mval/dm³, while the pH in the range from 8.06 to 8.55. After aluminium sulphate (VI) coagulation, which undergoes acid hydrolysis, along with the increase of the coagulant dose from 1 to 5 mgAl/dm³, the pH and alkalinity of the tested water decreased in the range from 7.47 to 7.12 and from 3.7 to 3.1 mval/dm³, respectively. Analysis of the relationships presented in Figure 1 showed that both aluminium sulphate (VI) and sodium aluminate caused an increase in the concentration of aluminium in the water after the coagulation process.

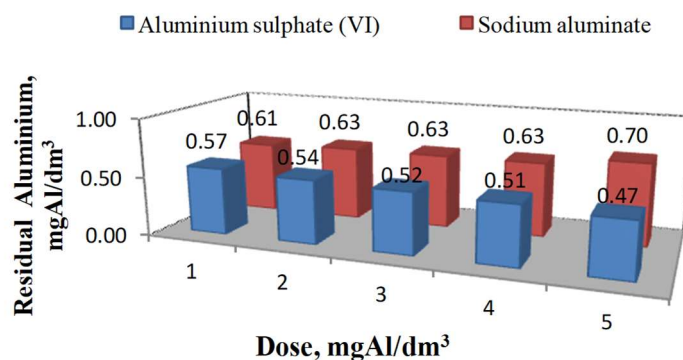


Fig. 1. Influence of the type and dose of coagulants on the concentration of residual aluminium in purified water

Higher concentrations of residual aluminium (Fig. 1) and aluminium present in dissolved form (Fig. 2) were found after the coagulation process with sodium aluminate, which undergoes alkaline hydrolysis and increased the pH of purified water in the range from 8.10 to 8.55 creating conditions for the formation of soluble aluminates $\text{Al}(\text{OH})_4^-$ [16, 23, 24]. The concentration of residual aluminium after coagulation with sodium aluminate ranged from 0.61 to 0.70 mg Al/dm³ and increased with the coagulant dose, and thus the pH increase in water after the coagulation process. The concentration of residual aluminium in water after coagulation with sodium aluminate more than three times exceeded the permissible concentration of aluminium determined for water intended for human consumption [18]. The concentration of aluminium in water after coagulation with the aluminium sulphate (VI) was lower and varied in the range of 0.57 to 0.47 mgAl/dm³ and conversely than in the case of sodium aluminate, it decreased with increasing coagulant dose (Fig. 1), and thus lowering the pH in water after the coagulation process. The residual aluminium in the water after the coagulation process with the tested coagulants was in colloidal and dissolved form (Fig.2 and Fig. 3). Due to the pH during the coagulation process in the range from 8.10 to 8.55 resulting from alkaline hydrolysis, almost the entire amount of residual aluminium in water after coagulation with sodium aluminate was in dissolved form and constituted from 98 to 100% aluminium in purified water.

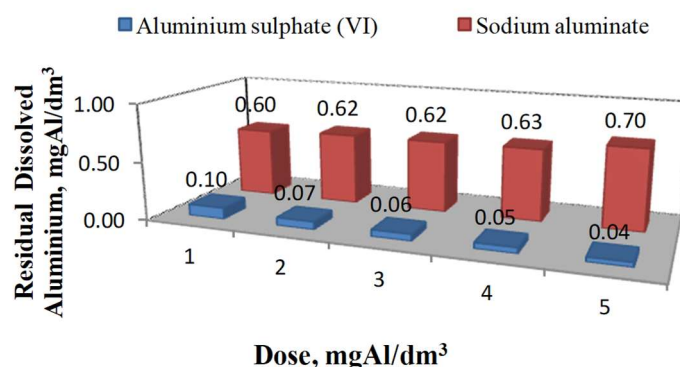


Fig. 2. Influence of the type and dose of coagulants on the concentration of aluminium in water in dissolved form

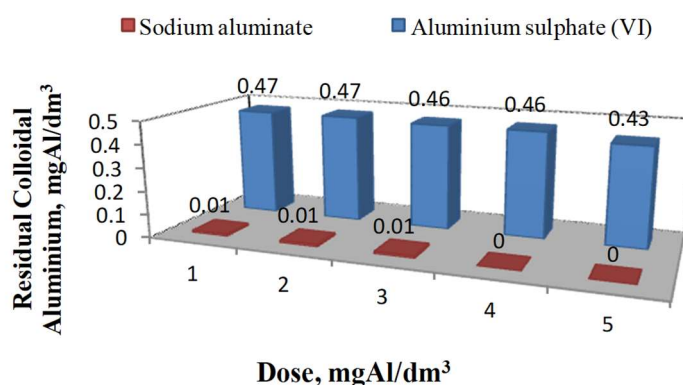


Fig. 3. Influence of the type and dose of coagulants on the concentration of aluminium in water in colloidal form

Much higher concentrations of aluminium in colloidal form compared to sodium aluminate was found in water after coagulation with aluminium sulphate (VI) (Fig. 3), which undergoes acid hydrolysis and therefore lowered the pH of purified water in the range from 7.47 to 7.12 creating good conditions for rapid precipitation of $\text{Al}(\text{OH})_3$. According to Dempsey and others [3], the optimal pH range for aluminium sulphate (VI) coagulation is from 5.5 to 7.0. The formed aluminium hydroxide flocs, however, were characterized by poor sedimentation properties. The lowest concentration of residual aluminium in water after aluminium sulphate (VI) coagulation exceeded, however, more than twice the permissible concentration for water intended for consumption (0.2 mgAl/dm^3) was found for the highest tested dose of 5 mgAl/dm^3 .

4. CONCLUSIONS

The analysis of the obtained test results showed that the concentration of residual aluminium in water after the coagulation process was determined by the type and dose of the tested aluminium coagulant, but above all the type of hydrolysis which the tested coagulant underwent in water. Unfavourable due to the very large amounts of residual aluminium was the use of sodium aluminate, which undergoes basic hydrolysis creating conditions for the transition of $\text{Al}(\text{OH})_3$ into soluble $\text{Al}(\text{OH})_4^-$ as evidenced by a very large percentage of aluminium dissolved in residual aluminium, which is easily absorbed by the human body. Aluminium sulphate (VI), which undergoes acid hydrolysis, lowered the pH of purified water, providing good conditions for rapid precipitation of $\text{Al}(\text{OH})_3$ as evidenced by the large amount of residual aluminium present in colloidal form. The resulting post-coagulation sediments after using aluminium sulphate (VI), however, were characterized by poor sedimentation properties. For none of the tested coagulants, the concentration of residual aluminium acceptable for water intended for human consumption was obtained. In further technological research, it is planned to conduct jar tests using pre-hydrolyzed coagulants less sensitive to changes in pH and temperature of purified water, whose post-coagulative sediments are also characterized by better sedimentation properties than post-coagulant non-prehydrolyzed aluminium coagulants such as aluminium sulphate (VI) or sodium aluminate. The type of aluminium sulphate (VI) and sodium aluminate hydrolysis products is highly dependent on the reaction. On the other hand, the fact of the initial hydrolysis of polyaluminium chlorides ensures the introduction into the water of polymeric aluminium forms produced during the production of these coagulants, regardless of the reaction of the treated water.

REFERENCES

1. Bachir, M, Brakchi, S and Azzouz, A 2016. Risk of residual aluminum in treated waters with aluminum sulphate. *Advances in Research* **6**, 1-8.
2. Campbell, A 2002. The potential role of aluminium in Alzheimer's disease. *Nephrology Dialysis Transplantation* **17**, 17-20.
3. Dempsey, BA, Ganho, RM and O'Melia, CR 1984. The coagulation of humic substances by means of aluminum salts. *Journal American Water Works Association* **76**, 141-151.
4. Gumińska, J 2011. Effect of Changes in Al Speciation on the Efficiency of Water Treatment with Pre-hydrolyzed Coagulants. *Ochrona Środowiska* **33**, 17-21.

5. Jakubaszek, A and Mossetty, J 2019. Changes to water quality in the water supply network of Zielona Góra. *Civil and Environmental Engineering Reports* **29**, 92–101.
6. Kimura, M, Motsui, Y, Kendo, K and Ishikawa, TB 2013. Minimizing residual aluminum concentration in treated water by tailoring properties of polyaluminum coagulants. *Water Research* **47**, 2075-2084.
7. Krupińska, I 2012. Suitability of coagulation for treatment of groundwater. *Rocznik Ochrona Środowiska* **14**, 491-501.
8. Krupińska, I 2015. Effect of temperature and pH on the effectiveness of pollutant removal from groundwater in the process of coagulation. *Ochrona Środowiska* **37**, 35-42.
9. Krupińska, I 2016. The impact of the oxidising agent type and coagulant type on the effectiveness of coagulation in the removal of pollutants from underground water with an increased content of organic substances. *Journal of Environmental Engineering and Landscape Management* **24**, 70-78.
10. Krupińska, I 2016. The Influence of Aeration and Type of Coagulant on Effectiveness in Removing Pollutants from Groundwater in the Process of Coagulation. *Chemical And Biochemical Engineering Quarterly* **30**, 465-475.
11. Krupińska, I 2018. Removal of natural organic matter from groundwater by coagulation using prehydrolysed and non - prehydrolysed coagulants. *Desalination and Water Treatment* **132**, 244-252.
12. Matsui, Y and Yuasa, A, 1998. Dynamic analysis of coagulation with alum and PACl. *Journal Americ Water Works Association* **90**, 96-108.
13. McLachlan, DR, Kruck, TP, Lukiw, WJ and Krishnan, SS 1991. Would decreased aluminium ingestion reduce the incidence of Alzheimer's disease. *Can Med Assoc J* **145**, 793-804.
14. Nilsson, R 1990. Residual aluminium concentration in drinking water after treatment with aluminium or iron salts. *Chemical Water and Wastewater Treatment* Springer Verlag, 399-410.
15. Nowacka, A, Włodarczyk Makuła, M and Macherzyński, B 2014. Comparison of effectiveness of coagulation with aluminum sulfate and prehydrolyzed aluminum coagulants. *Desalination and Water Treatment* **52**, 3843-3851.
16. Packham, RF 2007. The coagulation process. II. Effect of pH on the precipitation of aluminium hydroxide. *Journal of Applied Chemistry* **12**, 564-568.
17. Płuciennik-Koropczuk, E and Kumanowska, P 2018. Chemical stability of water in the water supply network - preliminary research. *Civil and Environmental Engineering Reports* **28**, 79–89.

18. Regulation of the Minister of Health dated December 7, 2017 amending the regulation on the quality of drinking water mean for human consumption.
19. Rondeau, V, Commenges, D, Jacqmin-Gadda, H and Dartiques JF 2000. Relation between aluminium concentration in drinking water and Alzheimer's disease: An 8 year foliow-up study. *Am J Epidemiol* **152**, 59-66.
20. Sieliechi, JM, Kayem, GJ and Sandu, I 2010. Effect of water treatment residuals (aluminium and iron ions) on human health and drinking water distribution systems. *International Journal of Conservation Science* **1**, 175-182.
21. Sigel, S 1998. Aluminium and its Role in Biology. New York 1988.
22. Yan, M, Wang, D, Yu, J, Ni, J, Edwards, M and Qu, J 2008. Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation. *Chemosphere* **71**, 1665-1673.
23. Yang, Z, Gao, B, Wang, Y, Wang, Q, Yue, Q 2011. Aluminum fractions in surface water from reservoirs by coagulation treatment with polyaluminum chloride (PAC): Influence of initial pH and OH⁻/Al³⁺ ratio. *Chemical Engineering Journal* **170**, 107-113.
24. Yang, Z, L, Gao, B,Y, Yue, Q,Y, Wang, Y 2010. Effect of pH on the coagulation performance of Al-based coagulants and residual aluminum speciation during the treatment of humic acid-kaolin synthetic water. *Journal of Hazardous Materials* **178**, 596-603.
25. Yue, Z, Baoyou, S, Yuanyuan, Z, Mingquan, Y, Darren, A, L, Dongsheng, W 2016. Deposition behavior of residual aluminum in drinking water distribution system: Effect of aluminum speciation. *Journal of Environmental Sciences* **42**, 142-151.
26. Zuziak, J and Jakubowska, M 2016. Glin w otoczeniu i jego wpływ na organizmy żywe. *Analit* **2**, 110-120.

Editor received the manuscript: 06.11.2019