



International Conference on Efficient & Sustainable Water Systems Management toward Worth Living Development, 2nd EWaS 2016

Water glass as a promising agent for the removal of Cr and P from drinking water

Tomáš Kučera^{a,*}, Renata Biela^a, Zdeněk Zelený^a

^a*Brno University of Technology, Faculty of Civil Engineering, Institute of Municipal Water Management, Žitkova 17, Brno, 602 00, Czech Republic*

Abstract

The paper deals with the possibilities of innovation in water treatment. Attention is focused on the possibilities of using water glass in removing heavy metals and nutrients in water treatment. The partial results are presented from the research, which deals with the removal of chromium and phosphorus from water. A conventional coagulant (aluminium sulfate) was used as a comparison. To verify the effectiveness of these chemicals a series of laboratory experiments was conducted in order to determine the appropriate dosage and working procedure to remove a selected group of pollutants. During the laboratory tests the overall efficiency of removing selected pollutants (chromium and phosphorus) and also turbidity were monitored using liquid aluminium sulfate and water glass.

The process of removing mentioned compounds from water was simulated under laboratory conditions. The laboratory experiments carried out on the model water which contained increased concentrations of chromium and phosphorus showed the capability of water glass to remove these pollutants from water. During the research, the dependence between pollutants removal and dose was investigated to achieve the best efficiency using innovative means.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of the EWaS2 International Conference on Efficient & Sustainable Water Systems Management toward Worth Living Development

Keywords: drinking water; water glass; removal of metals; water treatment

* Corresponding author. Tel.: +420-541-147-723 ; fax: +420-541-147-728.
E-mail address: kucera.t@fce.vutbr.cz

1. Introduction

The presented paper is focused on the treatment of the properties of surface water above all in the indicators that do not present such usual pollution. Nowadays, the treatment of water from surface water sources commonly incorporates physical and chemical processes involving coagulation and subsequent separation.

As is known, the coagulation and separating process includes the following equipment: dosage of chemicals (coagulant, agent for changing pH), homogenising element and flocculation basin, degree of separation (sedimentation tank, filters, etc.), sludge management and technology work. The coagulating agents used in present conditions are still to a great degree iron and aluminium salts, in the conditions of the Czech Republic but also elsewhere in the world (McNeill and Edwards 2003), most of all aluminium sulfate, iron(III) sulfate, iron(III) chloride and polyaluminium chloride. The coagulation process is part of conventional water treatment and is traditionally used to improve the removal of colloidal and finely suspended particles. Other pollution can also be removed under specific conditions.

The coagulation process is traditionally used to remove solid colloidal type of components from treated water. Coagulants make some soluble components (such as natural organic matter, hydrophobic synthetic organic components) insoluble and during coagulation produced by metal hydroxides due to the addition of iron or aluminium salts can absorb other pollutants [1,2].

In some cases, in some areas, it is necessary to use treatment processes resulting in the effective removal of specific substances. We often face a requirement for the elimination of metals such as arsenic, nickel, chromium, radioactive substances such as uranium or other substances such as phosphorus. Various pollutants occur in waters in different aggregation, valence and in different forms (organic versus inorganic, soluble versus insoluble, etc.). These substances are removed from water due to their toxicity, radioactivity, or because of their effect on the nutrient cycle in waters [3].

The Enhanced Surface Water Treatment Rule [4] requires water treatment tools to increase the removal of the amount of natural organic matter from the water. One of the possible approaches is to “increase” the performance of existing coagulation processes by increasing coagulant doses, change of the type of coagulant or reduction of pH coagulation. Some new U.S. EPA rules requiring change in water treatment can actually speed up degradation of the infrastructure. Concerns are also growing that these changes in treatment could cause the degradation of elements of the infrastructure facilities of water supply systems. A survey of the impacts of enhanced coagulation on 275 water treatment facilities in the US showed that in 24% of facilities some form of infrastructure degradation has been observed [5].

Hence it is considered necessary to devote attention to increasing the separating efficiency of treatment processes by using new agents. The described research focused on determining the efficiency of the removal of chromium and phosphorus from water during its treatment using processes with unconventional agents – water glass. Experiments using water glass are described in the following text.

The main goal of this research was to found the curve of effectiveness of removal of selected pollutants from water – chromium and phosphorus. As an innovative reagent, the water glass was used.

1.1. Water glass

Soluble silicates are the main group of synthetic chemicals. Only commodity acids and alkalis exceed them in the volume of production. They are known as water glass and represent a group of highly universal compounds. Given their many suitable properties they are used in many varied applications and in industry. Silicon from water glass transforms quickly into biologically active orthosilicic acid (soluble silicate). Important areas of application are household detergents, production of cellulose and paper, stabilisation of soil and various industrial sectors. It is estimated that about 88000 – 121000 tons of SiO₂ is produced annually. This amount represents only a small fraction (< 2%) of the expected total amount of soluble silicates transported by rivers into oceans. It is for this reason that significant negative effects are not expected on water ecosystems [6,7].

Water glass is a colourless, transparent, vitreous substance commercially available in the form of powder or as a transparent, viscous aqueous solution. In terms of chemistry this concerns sodium silicate, potassium silicate or a combination of both. The raw materials for the production of silicates are quartz sand (or other sources rich in silicon dioxide), alkali carbonates such as sodium carbonate (Na₂CO₃) or potassium carbonate (K₂CO₃) and alkali metal

hydroxides (NaOH, KOH, LiOH etc.). The greatest part of the produced volume representing approximately 90% of the total production of soluble silicates is contained as sodium silicate in the form of granules, aqueous solution, hydrothermal liquid, powder or crystals. The soluble (alkali) silicates are produced as sodium, potassium, lithium or in various combinations. This is a combination of silicon dioxide with alkali metals in differing ratio. Soluble silicates do not follow a definite stoichiometric formula and a specific chemical formula or molecular mass cannot be assigned to them [6].

Among the beneficial properties of detergents containing silicates is their low surface tension, good emulsification and suspension, supply of alkalinity for the neutralisation or saponification of soil materials and high buffering capacity. By incorporation into strongly acidic soil the buffering capacity is effectively used for preventing the dramatic fall of pH and subsequent soil remediation problems. Silicates stabilise the bleaching effect of complex metal ions and thereby prevent adverse effects on fabrics. Last but not least, silicates increase the efficiency of tensides and soaps by reducing surface tension. Based on their physical and chemical properties, and toxicological and ecological behaviour soluble silicates are generally considered safe, low-risk chemicals. The classification of the danger of silicates depends on the molar ratio of individual products. The higher the share of alkali metal oxide the more likelihood there is of skin and eye irritation and causticity. There are also respiratory problem if in powder form [6].

Released into the environment, pH and concentrations lead to dynamic polymerisation-depolymerisation balance with speciation and various mono-, oligo- and polymeric anions and amorphous silicon dioxide. All soluble silicates are moderately to highly soluble in water and virtually insoluble in organic solvents. This means that lipophilic decomposition is unlikely. As soon as soluble silicates get into the hydrosphere they dilute and quickly depolymerise. Subsequently these molecules cannot be distinguished from natural soluble silicon dioxide. It is interesting that silicates do not contribute to chemical or biological consumption of oxygen in a water course. Silicates are ever-present in the environment, in foods and drinking water, have been used in various applications for decades. No adverse system effects have ever been reported caused by their application. Acute, subacute and chronic toxicity is very low. Soluble silicates are not carcinogenic, mutagenic and do not produce reproductive toxins.

2. Methodology

The presented research was focused on the removal of chromium and phosphorus from water. The treatment processes were simulated in laboratory conditions during the series of standardized jar tests.

2.1. Jar test

The known methodical procedure for coagulation tests was also used during the described laboratory research for the purpose of verifying the efficiency of water glass in removing chromium and phosphorus from water.

Determining optimal coagulant doses, rate and time of quick and slow mixing takes place in the following steps [8]:

1. Optimisation of the dose of the destabilising agent under constant conditions of quick and slow mixing while respecting the assumed water treatment plant technology.
2. Optimisation of the agent dose for water pre-treatment when dosing the optimal dose of destabilising agent, see the previous optimisation point.
3. Optimisation of the course of quick mixing (rate and time) when dosing the optimal dose of the destabilising agent from point 1 and the optimum agent dose for pre-treatment from point 2.
4. Optimisation of the course of slow mixing (rate and time) when using optimised values, see above.
5. New optimisation of the dose of destabilising agent using parameters from points 1 – 4.
6. If an auxiliary aggregation agent is used then optimise its dose under optimised conditions. In this case no auxiliary aggregation agent was used.

The results are analysed using the values of residual concentrations of the basic component of the destabilising agent (Al/Fe) and/or other monitored criteria such as chemical oxygen demand COD, TOC, turbidity. The optimal dose achieves a maximum reduction in the contents of the monitored parameter (Al/Fe, DOC, turbidity etc.), leads to

the suppression of the energy barrier and to the effective destabilisation of polluting admixtures. The optimal area is the surrounding area of the optimal dose where the efficiency does not change that much [8].

In this research, the turbidity and concentration of the selected pollutants (chromium and phosphorus) were considered when analysing the optimality of conditions. The processes for the removal of pollutants were implemented in the form of jar tests with next steps:

1. Homogenization of raw water;
2. Preparing of samples of raw water;
3. Dosing of agents;
4. Rapid mixing;
5. Slow mixing;
6. Sedimentation;
7. Analyses of turbidity and concentrations.

For every test, six 1 L samples were prepared with controlled value of pH. The same mixing intensity was used for every jar tests. In the case of quick mixing, the rate of 150 revolutions per minute for 2 minutes was set. The slow mixing rate of 40 revolutions per minute was kept for 20 minutes. Then sedimentation took place for 60 minutes. Both, the turbidity and the concentration were checked once sedimentation ended. The conditions of mixing, both for rapid and slow, were set up according to result of jar test with aluminium sulfate. The mentioned rates and time interval were determined as optimal conditions with respect to the turbidity removal. For test with water glass, the same mixing conditions were kept because better comparison.

The marginal value of turbidity in drinking water caused by inorganic and organic colloidal and finely suspended particles, according to the decree valid in the Czech Republic, which sets the hygiene requirements for drinking and hot water and the frequency and scope of checking drinking water, is 5 NTU.

All experiments were carried out simultaneously with a dose of aluminium sulfate and water glass to compare and check results with respect to the efficiency in the reduction of turbidity.

2.2. Raw water

At first, the required volume of model water was prepared. The natural water was abstracted from surface water resource. As raw water, the water reached from the Brno water reservoir was used for the research tasks. The obtained water was continuously mixed until the water was used for the experiments.

Afterwards, this water was enriched with the specific concentration of the pollutants mentioned. For every pollutant was model water prepared separately. The chromium concentration was dosed into the model water so that its value would be approximately double the limit set by legislation for drinking water which is 50 µg/L in the Czech Republic. In case of the phosphorus no limit value has been set in the relevant decree. Therefore the applied value was taken from updated note to the decree. This note sets the value at 1-2 mg/L.

Finally, the trivalent chromium concentration value was set at 0.0994 mg/L and the phosphorus (meaning total) was set at 1.98 mg/L by the use of standard solution (see below). Both, the concentration of chromium and phosphorus were verified by the spectrophotometer analysis. The value of pH was kept at 7.5. Turbidity in the raw water varied between 4.3-5.8 (NTU) and average temperature of water during the research was about 20 °C.

2.3. Materials used

In the laboratory experiments chemicals were used as agents for treatment processes such as water glass (density 1420 kg/m³, Na₂O 10.24 %, SiO₂ 29.50%) and aluminium sulfate as well agents for pH treatment (calcium hydroxide, sulfuric acid).

For the simulation of water pollution, standard chromium trivalent and phosphorus (as PO₄³⁻) solutions were used. Concentration of chromium solution was 50 mg/L and phosphorus 1000 mg/L.

The process of removing chromium and phosphorus from the water was simulated under laboratory conditions using standard equipment – mixing columns.

3. Results

3.1. Aluminium sulfate

For the purpose of checking and possibility of comparing efficiency, experiments were conducted simultaneously also with the dosing of aluminium sulfate as a representative of traditional and the most commonly used coagulants. This inorganic agent based on aluminium salt is suitable for the treatment of drinking water, water for outdoor swimming pools and sewage water. The used liquid aluminium sulfate meets the requirements of standard EN 878 Chemicals used for treatment of water intended for human consumption – aluminium sulfate and the requirements of the national decree. Aluminium sulfate hydrolyses in reaction with water with the formation of positively charged polymers. It discharges negatively charged colloidal and suspended substances contained in water while individual particles can form deposits one on top of the other and create bigger separable flocs.

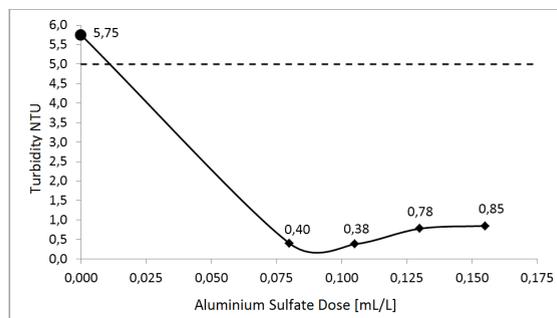


Fig. 1. Dependence of the reduction of turbidity on an optimised aluminium sulfate dose

Turbidity, temperature and pH were measured in the model water. Experiments were conducted according to known methodology for conducting jar tests. The primary coagulant dose which showed the highest removal of turbidity of 0.105 mL/L was subsequently optimised with regard to the mixing revolutions and pH value.

The jar test showed that the value of pH 7.5 appears as the optimal value for coagulation. It was also found that the best results are achieved during the intensity of quick mixing at 150 revolutions per minute and then slow mixing at 40 revolutions per minute. Figure 1 shows dependence of turbidity on the coagulant dose under optimal conditions. In figures 1 and 2 the dashed line marks the limit for turbidity at the level of 5 NTU, as the value required by legislation in the Czech Republic for drinking water.

In the case of liquid aluminium sulfate as a coagulant for removing turbidity from water coming from a surface water source – water reservoir, the optimal dose appears to be 0.105 mL of aluminium sulfate for 1 L of raw water at pH = 7.5. It was also found that the optimal rate of the quick mixing stage was 150 revolutions per minute and during which optimal homogenisation of the contents occurs. The best results were achieved during slow mixing equal to 40 revolutions per minute. After the coagulation parameters were optimised the level of turbidity was reduced from the initial value of 5.75 NTU to the value of 0.38 NTU, i.e. a reduction of 93.39%.

3.2. Water glass

The main objective of the paper was to show the effect of water glass on the removal of selected pollutants. Trivalent chromium, as a representative heavy metal, was selected as the monitored pollution and total phosphorus as a representative nutrient. The level of turbidity removal was also monitored and the results were compared with a conventional coagulant.

Seventeen different doses of sodium water glass were tested to obtain the necessary amount of data. The doses ranged from 0.030 mL to 0.500 mL of water glass to 1 L of prepared model water. The model water was always homogenised for about 2 minutes before the start of the tests.

The dependence of the reduction of turbidity on the water glass dose is shown in figure 2. We can see different progress of lines in the figures 1 and 2. The dependence of turbidity removal on dose of agent is completely different.

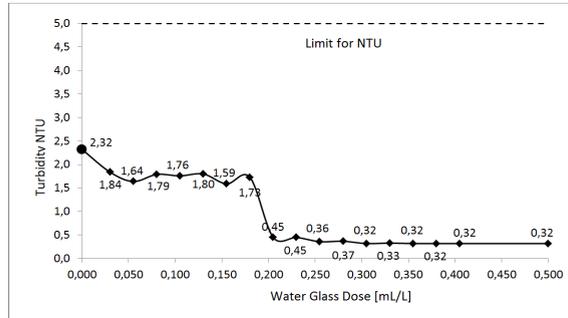


Fig.2. Dependence of turbidity on a water glass dose

Then the residual concentrations of trivalent chromium and total phosphorus were determined. The efficiency of removal can be deduced from the following figures 3 and 4. The efficiency of removal was then calculated from the residual concentrations of turbidity, chromium and phosphorus at various dosed amounts of sodium water glass.

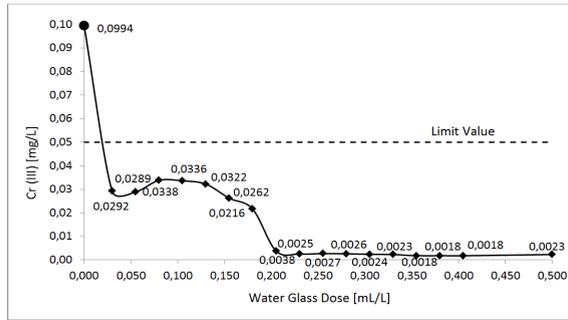


Fig. 3. Dependence of Cr (III) concentration on a water glass dose

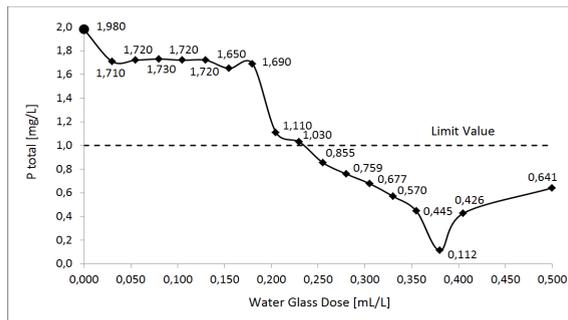


Fig. 4. Dependence of phosphorus concentration on a water glass dose

4. Conclusions

The laboratory experiments carried out on the model water which contained increased concentrations of chromium and phosphorus showed the capability of water glass to remove these pollutants from water. A significant value found during the experiments is a water glass dose of 0.205 mL/L of model water. At water glass doses below 0.200 mL the values of residual concentrations of Cr (III) were in lineal hundredths of mg/L, more precisely from 0.02 to 0.04 mg/L and the values of residual concentrations of phosphorus were about 1.70 mg/L.

At doses above 0.200 mL of water glass there was a lineal fall of the residual concentration of chromium and of the residual concentration of phosphorus an approximate lineal fall right down to a dose of 0.355 mL of water glass. The next dose of 0.380 mL of water glass brought the lowest measured residual concentration of phosphorus, at a further increase of the water glass dose the residual concentration of phosphorus increased again linearly.

The residual concentration of trivalent chromium at water glass doses above 0.200 mL/L of the model water was almost constant, therefore in terms of the removal of chromium from water containing about 0.100 mg/L of chromium the dosage of water glass in concentrations above 0.250 mL/L of treated water is uneconomical.

Pollution is reduced by being trapped in the form of beige coloured flocs with the application of sodium water glass. Individual flocs begin to appear during the slow mixing stage and their number and size are in proportion to the dosed amount of water glass. Before the cut-off the flocs appear in a low number and are very small, after crossing the cut-off concentration of water glass in the model water their number rises significantly and their size is about 2 mm in diameter. During the sedimentation stage of the laboratory tests, these formed flocs sedimented on the bottom of the used reaction vessel. At the end of the sedimentation stage flocs could be seen settled in heaps at the bottom of the reaction vessel and the model water was clear.

By applying the sodium water glass it was possible during the laboratory tests to achieve a maximum degree of the removal of turbidity of 86.21%. Using the trivalent chromium it was possible to achieve a reduction of residual concentration of 98.19%, which is almost complete removal of trivalent chromium from the model water. In the case of the phosphorus the maximum achieved degree of removal was 94.34% using a dose of 0.380 mL of sodium water glass in 1 litre of model water. The achieved results are significantly below the limit values required by valid legislation for drinking water therefore in view of the safety of the used water glass it is possible to recommend the use of this method of removing trivalent chromium and phosphorus from drinking water. Water glass is a very good alternative to the already established water treatment processes used to remove chromium and phosphorus.

Acknowledgements

This paper has been drawn up under Project No. LO1408 “AdMaS UP - Advanced Materials, Structures and Technologies”, supported by the Ministry of Education, Youth and Sports under the “National Sustainability Programme I” and under Project No. FAST-S-15-2701 “Efficiency monitoring of water treatment processes in microcontamination elimination” supported by Brno University of Technology.

References

- [1] J. Simms, F. Azizian, Pilot Plant Trials on the Removal of Arsenic from Potable Water Using Activated Alumina. Proceedings AWWA Water Quality Technology Conference, November 9-12, 1997.
- [2] D. Clifford, C.C. Lin, Ion Exchange, Activated Alumina, and Membrane Processes for Arsenic Removal from Groundwater. Proceedings of the 45th Annual Environmental Engineering Conference, University of Kansas, February 1995.
- [3] P. Pittel, *Hydrochemie*. 3. přeprac. vyd. Praha: Vydavatelství VŠCHT, 1999, 568 s. ISBN 8070803401.
- [4] U.S. EPA Surface Water Treatment Rules
- [5] L. McNeill, M. Edwards, Degradation of Drinking Water Treatment Plant Infrastructure from Enhanced Coagulation, *J. Infrastruct. Syst.* 9:4 (2003) 145-156, 10.1061/(ASCE)1076-0342(2003).
- [6] C.H. Baehr, W. Koehl, Soluble Silicates: -Highly Versatile and Safe. *International Journal for Applied Science*. (2007) Cefic - Centre Européen d'Etudes des Silicates [online]. 4, 88-94 [cit. 2013-07-02]. Dostupné z: <http://www.solublesilicates.eu/docs/BaehrandKoehl2007.pdf>
- [7] H.P. Van Dokkum, J.H.J. Hulskotte, K.J.M. Kramer, J. Wilmot, 2004. Emission, Fate and Effects of Soluble Silicates (Water glass) in the Aquatic Environment. *Environ. Sci. Technol.* [online] 38:2 (2004) 515-521. Available from: <http://pubs.acs.org/doi/abs/10.1021/es0264697>
- [8] M. Pivokonsky, *Tvorba suspenze při úpravě vody: teorie a praxe*. Vyd. 1. Libeznice: Medim, 2011, 218 s. ISBN 9788087140185.