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Review of the PhD dissertation of Mrs Sandra Johana Grajales-Mesa, MSc, entitled: "Remediation of TCE contaminated groundwater using Permeable Reactive Barriers"

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This review was prepared based on the decision of the Earth and Environmental Sciences Council of the AGH University of Science and Technology Stanislaw Staszic in Krakow of 29 June 2020 (letter no. WGGiOŚ–dz.0154-125/2020 of 8 July 2020) and the Assignment Contract from 27 July 2020".

Dissertation topic

Groundwater in Europe and worldwide is contaminated with many different substances such as pesticides, hydrocarbons and chlorinated solvents. The latter are of great concern due to their persistence and frequent occurrence in groundwater. Furthermore, chlorinated solvents like trichloroethylene (TCE) and tetrachloroethylene (PCE) are of health concern and have been widely used in many industrial and commercial applications mostly as degreasing solvents and dry-cleaning agents. Today, their use is restricted due to environmental concerns leading to more rigorous regulations but due to the legacy there are thousands of contaminated sites within Europe and worldwide that need to be cleaned up.

The main topic of the dissertation was to demonstrate that the use of unconventional low-cost reactive materials such as compost and brown coal waste may be an effective alternative to treat TCE contaminated groundwater to overcome the problems that zero valent (ZVI), the most often used remedial material, possesses. The main goal was achieve a good chemical status of the groundwater and to meet the drinking water standards of the water withdrawn by the waterworks at a case study site. The specific objectives included: a) selecting the most effective material for the removal of TCE from groundwater through laboratory batch and column tests, b) testing the effectiveness of selected reactive materials under field conditions to determine permeable reactive barrier (PRB) design parameters such as residence time, removal efficiency and hydraulic performance and c) applying numerical groundwater transport modelling to select the PRB configuration and location as well as to predict the long-term behaviour of the reactive materials used in the barrier by simulating the reduction in hydraulic conductivity over time. Thus, it can be stated that the dissertation topic is very important, timely and of high relevance in the context of its scientific and application significance on the European scale and globally.

Overall evaluation of the dissertation

The PhD thesis of Sandra Johana Grajales-Mesa contains overall seven chapters written on 133 pages with 22 tables and 30 figures plus an appendix. The large number of references to literature shows that the candidate has an excellent overview of the international state of the art in the subject.

In Chapter 1 Sandra Johana Grajales-Mesa presents the general introduction that includes the background information, objectives and the hypothesis. In Chapter 2 she gives an overview to the PRB technology for remediation of chlorinated solvents in groundwater. Details are given on advances in the PRB technologies and advantages as well as limitations of the techniques are presented. Furthermore, the used reactive materials to remove chlorinated solvents are described and considerations for PRB designs are discussed.

Chapter 3 presents the feasibility study on the removal of TCE from contaminated groundwater at the selected case study field site Nowa Deba using the PRB technology. This chapter includes the site description (geology, hydrogeology and present contaminants), the conceptual site model and the potential of the PRB technology at the site.

In Chapter 4 Mrs. Grajales-Mesa describes the laboratory batch and column studies which she performed to select the appropriate reactive materials for the PRB. She performed the batch tests in several stages. First, she evaluated TCE removal for pre-selected materials (four individual materials and four mixtures). Secondly, one reactive mixture (compost and brown coal) was chosen from the first experiments and tested for removal efficiency using

three different mixing ratios. Thirdly, the removal mechanisms were evaluated. After these different stages of batch tests, column tests were performed. She tested compost, brown coal and their mixture to estimate the removal efficiency of TCE.

Chapter 5 presents the results of the pilot-scale test performed at the contaminated field site. Contaminant removal under field conditions for selected reactive materials was investigated. Thereby the occurrence of TCE degradation by-products was checked. Furthermore, an assessment of implications of the field-test performance to the full-scale PRB design was undertaken.

Chapter 6 contains the numerical modelling being performed for the final design of the PRB. Here groundwater flow under different barrier configurations was evaluated to determine the optimal barrier location. In addition, the long-term behaviour of the materials was simulated by reducing its hydraulic conductivity over time. In the end, an overall cost estimation was done for the PRB installation at the site.

In Chapter 7, Sandra Johana Grajales-Mesa presents the general discussion and gives a summary of the overall work. This is followed by specific and general conclusions and she gives recommendations for future work in terms of scientific and application questions.

Results and most important achievements of the dissertation

Remediation of groundwater contaminated with TCE using PRBs with alternative reactive materials is not fully recognized and its comprehensive solution requires the development of a methodical approach. This dissertation aimed to demonstrate that low-cost reactive materials, such as compost and brown coal waste may be an effective alternative to treat groundwater contaminated with TCE to overcome the problems that ZVI possesses. It is anticipated that the PRB with compost and brown coal waste mixture at the selected field site in the vicinity of Nowa Deba will allow to meet both groundwater and drinking water guideline values. The feasibility study proved that the site conditions are favourable for the installation of the PRB to reduce TCE concentrations to target values.

Through an extensive review of the international literature, example materials were identified that included brown coal waste, compost, diatomaceous earth as waste from a brewery, mulch and zeolite. They were selected based on availability, low costs and suspected or proven ability to remove TCE through biotic or abiotic processes. Laboratory batch and column tests were conducted to select effective reactive materials to be placed instead of ZVI in a PRB to treat TCE contaminated groundwater. Results of batch tests indicate that brown coal was the most effective with a removal efficiency of 97%, followed by compost (86%) and the brown coal compost mixture (86%). Although the addition of

compost to brown coal did not result in higher removal efficiency, it increased the hydraulic conductivity and showed the potential to simultaneously reduce the TCE concentration in groundwater by two processes: sorption and biodegradation. It was found that biodegradation needs to be further investigated to ensure the complete dechlorination of TCE to ethane to avoid the accumulation of its daughter products. Considering the results of column experiments, breakthrough curves showed that brown coal was the most efficient in removing TCE from groundwater followed by the brown coal-compost mixture.

The selected brown coal-compost mixture was further tested in a pilot-scale installation to evaluate under field conditions the efficiency of a proposed PRB to remove TCE at startin concentrations of 109 µg/L from contaminated groundwater. During the almost 200-day experimental period TCE concentrations in groundwater decreased to about 1 µg/L. This means that both groundwater and drinking water standards were achieved.

A three-dimensional groundwater flow and transport model was developed for the selected field site and applied to help the design of the PRB with brown-coal and the compost mixture to treat TCE contaminated groundwater. The modelling results allowed to: a) estimate the groundwater flow changes as influenced by diverse PRB designs such as a continuous wall and a funnel and gate system, here an optimum PRB system was found; b) the evaluation of the effect of decreasing hydraulic conductivity of the reactive materials over time and its impact on key design parameters like capture zone, residence time and discharge rates; c) the selection of the optimal locations of downgradient piezometers to assess the PRB performance. Simulation results suggested that the most effective barrier configuration comprises a funnel and one gate.

The costs of different PRB installations for the studied site were also investigated. Comparing the costs for different PRB configurations, it was found that the barrier with one gate is the least expensive alternative. This work all together contains a wide range of laboratory, field and modelling tasks. Overall, it can be stated that these are very comprehensive results and important achievements of this dissertation.

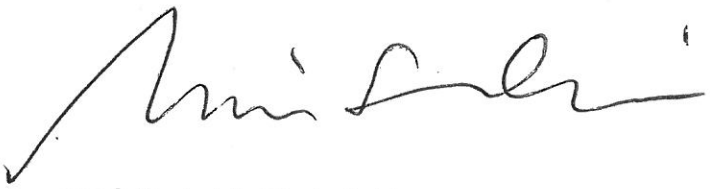
Critical comments

A very minor point is that I would have liked the dissertation to be printed double-sided to safe resources.

Conclusion

The dissertation of Sandra Johana Grajales-Mesa is sufficient for its evaluation. It is clear that the importance and actuality of the problem fully justify the adoption of the topic as the research and utility problem of the dissertation. The presented results are complete and are adequately described and interpreted. The results fully support the conclusions of the dissertation. The research goals were fully reached and the research hypotheses were proven. The PhD candidate presents very good skills to perform independently scientific research.

In summary of my above evaluation, I state without any hesitation that the dissertation of Mrs. Sandra Johana Grajales-Mesa entitled: "Remediation TCE contaminated groundwater using Permeable Reactive Barriers" fulfills the requirements of a PhD dissertations. It is of high scientific and application values in the area of Earth and Environmental Sciences. I, therefore, recommend it to be the subject of the public defence.



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