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Rome, 16/09/2020

Evaluation/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.

Justification of the dissertation topic

The remediation of groundwater bodies contaminated by chlorinated solvents, and specifically by TCE, is a very relevant issue at both European and global scale. The use of these solvents in the past decades has produced hotspots of contamination, with concentration of TCE in the order of 1000 or more ug/l but also long plumes of contamination, often resulting in background TCE concentrations exceeding the GW screening values for wide areas. This requires the implementation of innovative approaches for dealing with these contaminants. The PRBs, which are the subject of this thesis, fall perfectly within the portfolio of suitable and innovative technologies, especially at European scale where the application of this technology has been so far quite limited, differently from the US. One of the reasons can probably be found in the installation costs, mostly linked to the cost of the reactive materials used, but also in the somehow complex hydrogeology with respect to the US. Therefore, any effort towards using innovative materials and for developing proper approaches for a correct and effective design of the PRB, properly accounting for the hydrogeological

conditions, represents a substantial innovation needed for increasing the penetration of PRBs in the remediation market.

Characteristic and overall evaluation of the dissertation

The structure of the thesis is clearly outlined in Chapter 1 (General Introduction) and specifically in Figure 1.2. Chapter 2 reports the literature review on the topic of the thesis (permeable reactive barriers) with information on PRB technology, reactive materials and considerations for PRB design. The core of the thesis (chapters 3 to 6) reports on the application of a PRB for the treatment of a GW plume contaminated by TCE (Nowa Deba site), describing the different steps which led to the design and cost estimate of the full scale PRB, i.e. the feasibility study of PRB for the Nowa Deba site (Chapter 3), the lab-scale batch and column-scale tests (Chapter 4), the pilot scale field test (Chapter 5) and the modelling of the intervention (Chapter 6). Chapter 7 summarizes and comments the main findings of the thesis and provides recommendation for further research in the field.

Chapter 2 reports a very detailed and quite up-to-date review of the scientific literature on PRBs. The chapter discusses in detail the experience gained so far on the main design issues of PRBs. A comprehensive discussion is carried out on the different treatment mechanisms adopted and the most interesting reactive materials used, accounting for the type of contaminants and geochemical conditions at the site. Pro and cons of the different materials and reaction pathways are discussed in detail and some information on configuration, construction methods and long term performance are also reported.

Chapter 3 reports on the location of the contaminated site, provides some information on the extent of TCE contamination and on the extension of the plume which already reached nearby waterworks providing drinking water to around 20.000 citizens. The Conceptual Site Model is developed and discussed and the PRB potential applicability is also discussed with respect to other options. The content of chapter 3 is based on a book chapter published by the Royal Society of Chemistry and on a paper published in the proceedings of an international conference, both in 2013.

Chapter 4 summarizes the results of the batch and column-scale experiments aimed at selecting the most suitable materials to be used in the PRB instead of the more traditional (and expensive!) Zero Valent Iron (ZVI). The approach used in the

dissertation was stepwise: namely, a number of potential candidates were tested through batch tests, allowing to select three materials (brown coal, compost, brown-coal/compost mixture) as best candidates for the second phase of the study, consisting in column tests. From these tests, the longer breakthrough time was achieved using the brown coal/compost mixture, which was chosen for the pilot scale field test. The issue of the mechanism underlying the TCE removal is discussed in the dissertation, pointing out that, differently from ZVI which reacts with TCE by beta-elimination or hydrogenolysis, the brown coal/compost mixture mostly acts through a sorption mechanism, as only 1% of TCE removal could be attributed to biodegradation by comparing batch tests carried out spiked or not with an inhibitor of microorganism growth (NaN3). Chapter 4 was published in a peer-review international journal in 2016.
Chapter 5 reports on the pilot-scale application of PRB using a mixture of brown coal and compost at different ratios (1:1, 1:3 and 1:5) which were installed in boxes positioned outdoor and fed with the groundwater pumped from the site in the vicinity of the waterworks. The results of a 198 days long test showed very good performance in terms of TCE removal (up to 99%) until around 50 to 60 days, followed by a decrease of TCE removal, which was more evident for the test carried out at 1:5 brown coal/compost ratio. This is attributed to desorption from the reactive material matrix. The presence of DCE as reaction intermediate product shows on the one hand that biodegradation occurs effectively (induced by compost fermentation), but also that the reaction did not go to the final (harmless) products using the experimental residence times. Chapter 5 was based on a paper published in an international peer-review journal in 2019.
Chapter 6 reports on the numerical modelling of different full-scale PRB configurations (continuos wall, funnel and gate, different width/thickness) for the Nowa Deba site, carried out in the MODFLOW environment, using the MT3DMS code for contaminant transport. The results allowed to select the most effective configuration in terms of capacity of capturing the contaminated plume and cost. Chapter 6 was based on a paper published in a volume published in Poland and on a paper in press in an international peer-review journal.
Overall, the dissertation is clearly written and organized, the review of the literature fairly complete, the experimental procedures used in lab and pilot-scale experiments robust, most of the results reported are innovative and the data interpretation is sound and correct.

Evaluation of the results and most important achievements of the dissertation

The dissertation provides a relevant advance in the field of remediation of TCE-contaminated sites and specifically on the application of PRBs for the containment of the contamination plume. Namely:

- It adds substantial information on the feasibility of using materials alternative to the traditional and expensive Zero-Valent-Iron, providing new data on the performance of these materials. In particular the combination of compost and brown coal is innovative as it allows to couple the readily available source of organic carbon (the former one) and the long-term source of organic carbon (the latter one).
- It propose an interesting stepwise approach, combining batch and column-scale experiments, for selecting the most suitable material within a number of potentially suitable candidates;
- It provides insight into the mechanisms underlying TCE removal in PRBs using alternative materials;
- It provides an integrated approach (tests + modelling) to design the full-scale PRB and to assess the sensitivity of its performance with respect to the design parameters, such as width, thickness and configuration (continuous or funnel and gate).

The quality of the dissertation and the high level of innovation of the work is confirmed by the fact that most of the chapters were taken (completely or partially) from papers published in international peer-review journals or books.

Critical comments

I have no major remarks. A few minor comments follow:

- In case the batch tests were carried out in duplicate /triplicate error bars should be preferably added
- Some data/information could be updated using more recent references, although the timeframe from the preliminary work (2013) to its conclusion (2020) motivates fully the references used in the thesis. For instance, the number of PRB installed(Page 71) makes reference to 2012 reference.
- In the description of the pilot scale test, it would be interesting to show how inlet

and outlet concentration changed with time, before showing the results already converted in terms of TCE removal, as fluctuations of inlet TCE concentration could be expected.

- More information on sorption and biodegradation parameters used in the modelling of PRB (Page 84) could be usefully included.

***C*onclusion**

The dissertation is very well organized, very clear to read and complete and it is perfectly fit for evaluation. It deals with a topic, which is of great interest both from a fundamental and from an application point of view. The issue of TCE contamination has a dramatic impact on groundwater quality and may affect, as in the case study discussed in the dissertation, the waterworks providing water to tens of thousands of people. There are many cases of contamination worldwide similar to the one considered in this work. Therefore, the importance and actuality of the problem fully justify the adoption of the topic as the research and utility problem of the dissertation.
The dissertation is clearly written and organized, the goals of the dissertation clearly stated, the experimental procedures used in lab and pilot-scale experiments robust, the results reported are innovative and are adequately described and interpreted and fully support the conclusions of the dissertation. The research goal was fully reached and research hypotheses proven. Besides, the PhD candidate presents excellent skills to perform independently scientific experiments, but also presents skills to organize the huge number of experimental data and modelling results in a very clear and concise way.
The dissertation of Mrs Sandra Johana Grajales-Mesa entitled: **'Remediation TCE contaminated groundwater using Permeable Reactive Barriers',** fully fulfills the requirements of PhD dissertations, because of its high scientific and application values in the area of Earth and environmental sciences. Therefore, I recommmend it to be the subject of the public defense.