higher Freundlich constant and enhancing the dechlorination rate, whereas the initial adsorption saturation on the non-reaction site increased the adsorption probability of P-CE and T-CE by benzene. In addition, for toluene, the initial adsorption saturation of toluene on the non-reaction site increased the adsorption possibility of P-CE and T-CE on the reaction active site of ZVI. However, organic compounds can transfer electrons and increase the speed of chlorine by ZVI (Ruey and Yen, 2005). This result was achieved owing to the higher polarity of benzene (3) compared with toluene (2.4) from the ZVI surface to P-CE and T-CE. A previous study showed the influence of benzene and toluene on the chlorine removal of single P-CE and T-CE. They found that benzene enhanced the P-CE chlorine removal rate by 14 %, although toluene decreased the dechlorination rate by 14.2 %. It was concluded that there were different influences on T-CE chlorine removal with or without P-CE compared to the chlorine removal of mixed P-CE and T-CE.

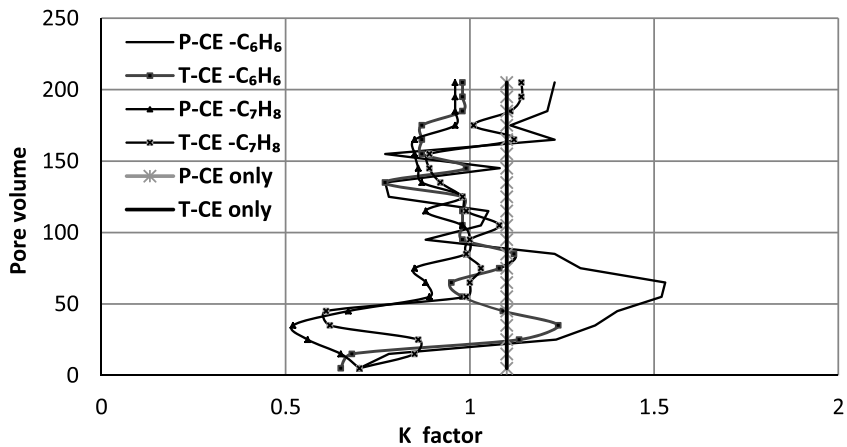


Figure 4. Kinetics reaction factor (K factor) in packed column.

SECONDARY PRODUCTS

In this study, secondary compounds were products in the columns at a PV of 40, including ethane (C_2H_6), ethylene (C_2H_4), 1,2-dichloroethylene (1,2 DCE), and vinyl chloride (C_2H_3Cl) as shown in Figure 5. This indicates that the pathways of chlorine removal transformed P-CE to T-CE, T-CE to 1,2 DCE, and the last one to vinyl chloride. Vinyl chloride was transformed to ethylene via a hydrogenolysis reaction. Thus, dechlorination processes led to a change in all ethylene to ethane through a hydrogenation reaction. The carbon mass balance in the columns at a PV of 80 was also calculated (Figure 6) to be between 67.1 % and 90 % on average. It decreased along the column from 90.3 to 72.3 using benzene and to 67 when using C_7H_8. This decrease may be due to the adsorption and volatilization of some secondary compounds, and some secondary products were not quantified in this study.

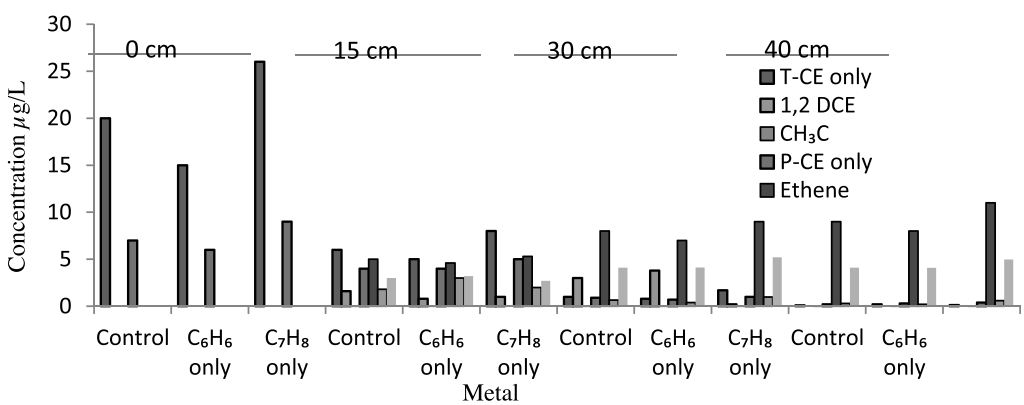


Figure 5. Secondary compounds of P-CE and T-CE.

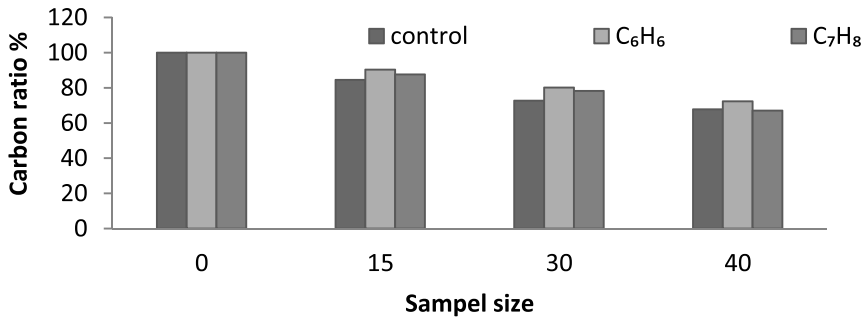


Figure 6. Column compounds carbon ratio at different sizes.

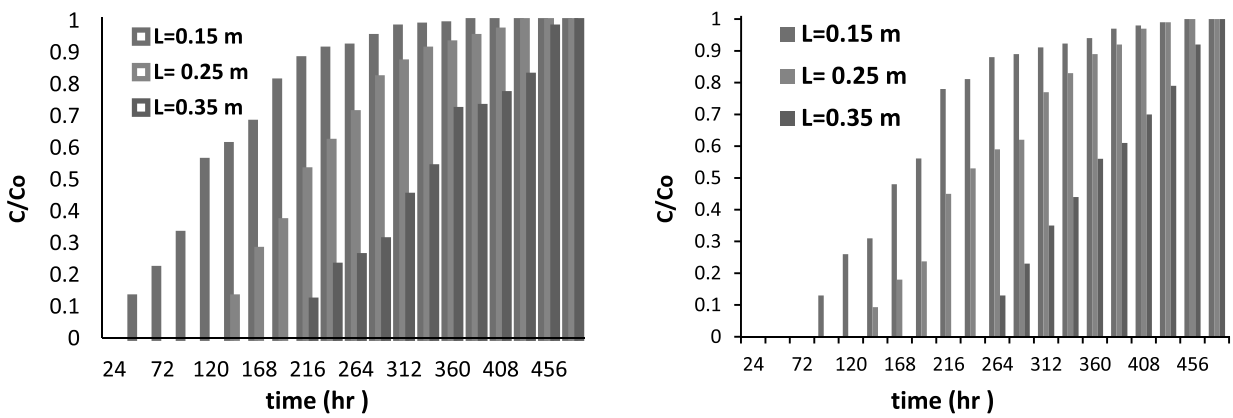
PACKED COLUMN STUDY

Bed height and flow rate were evaluated to investigate the breakthrough profile.

1. Effect of bed height

The effects of bed height on the chlorine removal of P-CE and T-CE in columns filled with ZVI were investigated at flow rates of 0.0277 cm/min. Different depths of 0.15, 0.25, and 0.35 m were selected. Figure 7 shows that the saturation points increased when the depth height increased from 0.15 to 0.35 m.

The breakthrough time required was 144 h at 0.15 m, increasing to 216 h at 0.35 m. As a result, the number of adsorption sites increased as bed height increased, which increased the adsorption capacity and delayed the saturation state of the breakthrough curve.



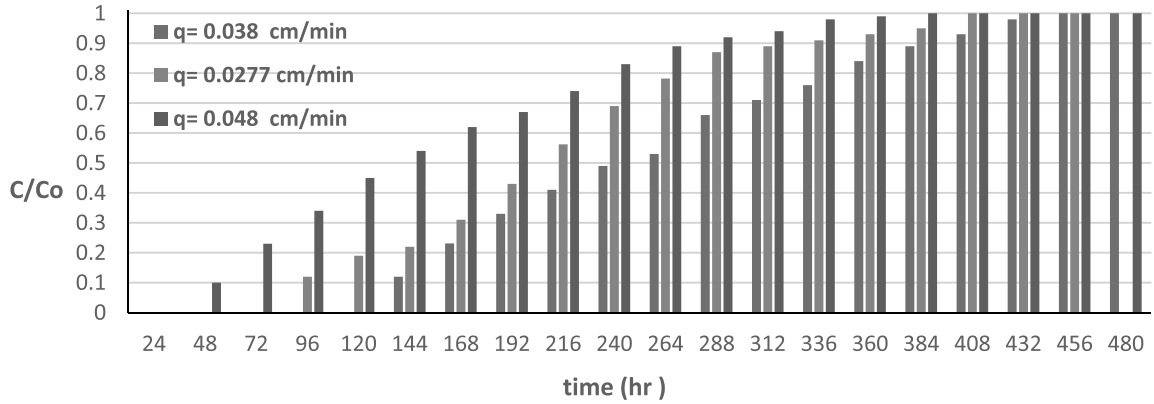
(a) Benzene (b) Toluene

Figure 7. Breakthrough curves of P-CE and T-CE chlorine removal at different depths.

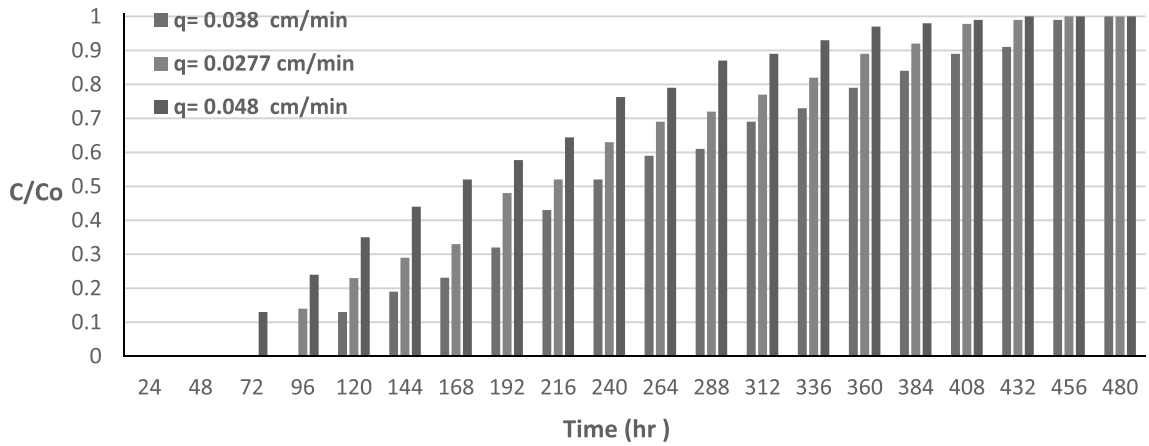
2. Effect of column rates

The effect of column rates on the adsorption of benzene and toluene was examined at different rates (0.038, 0.0277, and 0.048 cm/min) with a constant depth of 0.25 m. Figure 8 shows that the breakthrough times are influenced greatly by the column rate. It was noted that a long break time is needed with a low rate of 0.038 cm/min, while the saturation point was achieved at 432 h. As a result, both breakpoint and saturation time decreased by approximately 38–50 % as column rate increased for a given depth height owing to the packed time applied. When the column rate was low (0.038 cm/min), benzene and toluene had more time to saturate with packing, leading to an increase

in pollutant concentrations. At the maximum flow of 0.048 cm/min, low pollutant removal was observed owing to the insufficient contact between pollutants and the packed material. This reduced the number of active sites, thus decreasing the solution size.



(a) Benzene



(b) Toluene

Figure 8. Breakthrough curves of chlorine removal of P-CE and T-CE at different column rates.

CONCLUSION

Basra city has the largest proportion of oil wealth in Iraq. Currently, it houses more than 14 fields. Thus, numerous refineries from these fields and a huge network of oil pipelines pollute groundwater and influence the chlorine removal of P-CE and T-CE. The influence of benzene or toluene on the chlorine removal of mixture P-CE and T-CE was investigated using a column packed with ZVI. This work simulated the biodegradation of benzene or toluene in a ZVI permeable reactive barrier, which could reduce trichlorethylene. Enhancive and inhibitive effects of benzene and toluene, respectively, on P-CE and T-CE decrease were noted at PVs of 20–90 in the columns.

It was observed that increasing the PV from 20 to 200 led to a decrease in the kinetics of P-CE and T-CE by at least 45 %. A clear influence of benzene and an inhibitory effect of toluene on P-CE and T-CE decrease were observed at 20–100 PV, but these disparate effects disappeared when PV increased to 220. Furthermore, the chlorine removal advantage of P-CE by ZVI changed due to the different dechlorination locations of P-CE on ZVI, and it decreased with the accumulation of dechlorination by secondary components (ethylene, 1,2 DCE, vinyl chloride, and T-CE), with

T-CE exhibiting the strongest result. Continuous column experiments results demonstrated that the breakthrough point and removal efficiency increased as bed height increased from 0.15 to 0.35 m and reduced the feed flow rate.

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REFERENCES

Amy, P. & Makram, S. 2004. Effect of benzene, toluene, ethylbenzene, and p-xylene (BTEX) mixture on biodegradation of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) by pure culture UC1. Biodegradation, **41**(15): 213-227.

Aniefiok, E.I., Usenobong, F.U., Margaret, U.I., Idongesit, O.I. & Udo, J.I. 2016. Petroleum Industry in Nigeria: Environmental Issues, National Environmental Legislation and Implementation of International Environmental Law. American Journal of Environmental, **4**(1): 21-37.

A**PAT. 2006.** Manual for Environmental Investigations at Sites Contaminated, Section 5150. Rome: APAT, Manuals and Guidelines 43.

Chenju L., Chiu F.H., Nihar M., Chih J.L. & Rama M.K. 2007. Hydroxypropyl-β-yclodextrin-Mediated Iron-Activated Persulfate Oxidation of Trichloroethylene and Tetrachloroethylene. Industrial & Engineering Chemistry Research, **46**(20): 6466-6479.

Cynthia, R.E. & David, A.D. 1997. Remediation of Metals-Contaminated Soils and Groundwater. Technology Evaluation Report Ground. Water Remediation Technologies Analysis Center P:1-61.

David, R.B., Richelle, M.A., Valipuram, S.M., Timothy, J.C., Gregory, A.L. & Baolin, D. 1998. Chlorinated ethene reduction by cast iron: sorption and mass transfer. Journal of Environmental Engineering, **124**(10): 1012-1019.

Eykholt, G.R. & Sivavec, T.M. 1995. Contaminant transport issues for reactive-permeable barriers. New York: ASCE.

Fei, L., Roya, G., Cheryl, E., Yunchen, G. & Laura, A.H. 2014. Metatranscriptome of an Anaerobic Benzene-Degrading, Nitrate-Reducing Enrichment Culture Reveals Involvement of Carboxylation in Benzene Ring Activation, Applied Environmental Microbiology, **80** (14):4095-4107.

Gautham, P.J. & Prabhakar, T.C. 2012. A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. Journal of Contaminant Hydrology, **130**(15): 46-53.

Gillham, R.W.O. & Hannesin, S.F. 1994. Enhanced Degradation of Halogenated Aliphatics by Zero - Valent Iron. Ground Water **32**(6): 958-967.

Hafiz, N.A., Hafiz, M.R., Zahir, A.Z., Muhammad, Y,K., Muhammad, J.A., Muhammad, N. & Muhammad, S. 2016. Petroleum Hydrocarbons-Contaminated Soils: Remediation Approaches. Soil Science: Agricultural and Environmental Prospective. Springer International publishing chemical P.105-129.

J**an, D., Leen, B., Dirk, S., Spiros, N.A. & Ludo, D. 2004.** Competition for sorption and degradation of chlorinated ethenes in batch zero-valent iron systems. Environmental Science Technology, **38**(10): 2879-2884.

Kevin, F., Doug, M., Nick, D. & Murray E. 2008. Effect of ethanol on microbial community structure and function during natural attenuation of benzene, toluene, and o-xylene in a sulfate-reducing aquifer. Environmental Science Technology, **42**(7): 2289-94.

Lucy,. A,. Juliet, C.S. & Michael, J.C. 2011. The World's Water: The Biennial Report on Freshwater Resources. Fossil Fuels and Water Quality. Washington, DC: Island Press/Center for Resource Economics P.73-96.

Robledo, J.R., Ramírez, D.E., Pérez, A.A., Gómezc, C., González, O., Ramos, J. & González, R. 2011. Benzene, toluene, and o-xylene degradation by free and immobilized P. putida F1 of postconsumer agave-fiber/polymer foamed composites. International Biodeterioration & Biodegradation, **65**(3): 539-546.

Ruey, A.D. & Yen, J.L. 2005. Dechlorination of tetrachloroethylene by palletized iron in the presence of humic acid. Water Research, **39**(11): 2309-2318.

Scott, W.O. & Robert, W.G. 1995. Dechlorination of trichloroethylene. Environmental Science Technology, **30**(1): 66-71.

Syful, I., Yanlai, H. & Weile,Y. 2020. Reactions of chlorinated ethenes with surface-sulfidated iron materials: reactivity enhancement and inhibition effects. Environmental Science Process and impacts, **22**(3): 759-770.

Truex, M.J., Macbeth, T.W. & Vermeul, V.R. 2011. Demonstration of Combined Zero-Valent Iron and Electrical Resistance Heating for In Situ Trichloroethene Remediation. Environmental Science Technology, **45**(12): 5346-5351.

Vidic, R.D. & Pohland, F.G. 1996. Treatment walls, Pittsburgh, PA.Ground Water Remediation Technologies Analysis Center.

William, A.A. & Lynn, R. 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. Environmental Science Technology, **34**(9): 1794-1805.

Xiaohong, G., Yuankui, S., Hejie, Q., Jinxiang, L. & Irene, M. 2014. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: The development in zero-valent iron technology in the last two decades. Water Research, **100**: 277-295.