

Preliminary study on Cr-rich groundwater treatment by membrane processes

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Abstract

The aim of this work is to treat chromium (Cr)-rich groundwaters through membrane processes as alternative to conventional methods. Commonly, the highest Cr (VI) concentrations into groundwater are detected in ophiolitic areas due to water-serpentinite interaction processes. In this work, the water sample treated comes from Bonassola serpentinitic aquifer (La Spezia, Liguria, Italy), in which a Cr(VI) concentration of 84 µg/l was detected. To lower down this value under the threshold established by law, NF/RO laboratory-scale system with membranes named DK (NF polyamide membrane, GE Osmonics) and AD (RO polyamide membrane, GE Osmonics) and CD (RO cellulose membrane, GE Osmonics) were used. The experiments were conducted at different operating pressures. Membrane process treatment was able to lower the Cr concentration within the threshold values, and rejections around 95% were registered for each used membrane. These preliminary results are quite promising for future developments on Cr removal from contaminated groundwaters.

Keywords: Chromium, groundwater, ophiolitic rocks, membrane processes

1. Introduction

Chromium (Cr) is a dangerous pollutant that has a strong impact on environment and ecosystem when it is released into natural water bodies. Although anthropogenic Cr-sources are widespread due to the common use of chromium in a large spectrum of industries, natural Cr pollution is the environmental issue of worldwide ophiolitic areas (Apollaro et al., 2019). Indeed, these rocks contain high amount of Cr(III) which, if mobilized during the weathering processes, can be oxidated to Cr(VI) form which is more dangerous and toxic for human health. Naturally occurring Cr(VI) in groundwater has been increasingly reported at concentrations exceeding the World Health Organization's threshold for total Cr in drinking water, which is set to 50µg/L (WHO, 2011), whereas some countries as Italy, have lowered the limit value of

Cr(VI) fixing it to 10 µg/L. The improving of living standards is becoming an urgent challenge and in this context, suitable and efficient remediation plays a crucial role. The techniques commonly used can be recognizable in precipitation, adsorption, solvent extraction with amines, ion-exchange, activated carbon adsorption, electro deposition, biological processes and membrane technologies (Di Natale et al., 2015 and reference therein). The latter can be viewed as innovative methods which fall within the Best Available Technologies (BAT) considered the high performance, in terms of costs and advantages, for instance environment protection, reduction of energy consumption by improving productivity and/or production quality (Figoli et al., 2017). In this work, the high performance of RO/NF membrane processes were tested to treat Cr-rich groundwater with the purpose of lowering the concentrations below the law limit.

2. Geological Setting

The analysed water sample is coming from La Spezia province (Liguria, Italy) where the high-Cr content of natural water is due to the extensive weathering process affecting the ultramafic rocks outcropping in the area (Fantoni et al., 2012). Ultramafic-gabbroic basement is mainly represented by its ultramafic portion, consisting of serpentinites, whereas gabbros are a subordinate portion. From these rocks emerges the Vivaio spring (Bonassola - La Spezia) and the water circulation in the serpentinitic rocks occurs in fractures originating in the superficial portion of the rock mass.

3. Methods and Materials

Sampling was carried out measuring in the field intrinsically unstable parameters (i.e., temperature, pH, Eh, and alkalinity) by means of portable equipment and collecting consistent volume of water for later treatment tests. NF experiments were performed by using a laboratory pilot unit with a SEPA membrane CELL equipped with a feed and permeate container, a pressurization pump, two pressure gauges, a thermometer for temperature measurement in the feed tank, a tap water heat exchanger for temperature control and a flow meter on the permeate exit pipe. One NF membrane module named DK (polyamide) and two RO membrane modules named AD (polyamide) and CD (cellulose) respectively, all commercialized by GE Osmonics, were used. During the experiments, the permeate flux was evaluated at different operating pressures (5 bar, 10 bar, 15 bar and 15 bar, 20 bar and 25 bar for NF and RO membrane types, respectively). For each one, a sample of permeate was collected to evaluate the Cr rejection after the treatment. Cr and Cr(VI) were evaluated by AAS and by 1,5-diphenylcarbohydrazide colorimetric method, respectively.

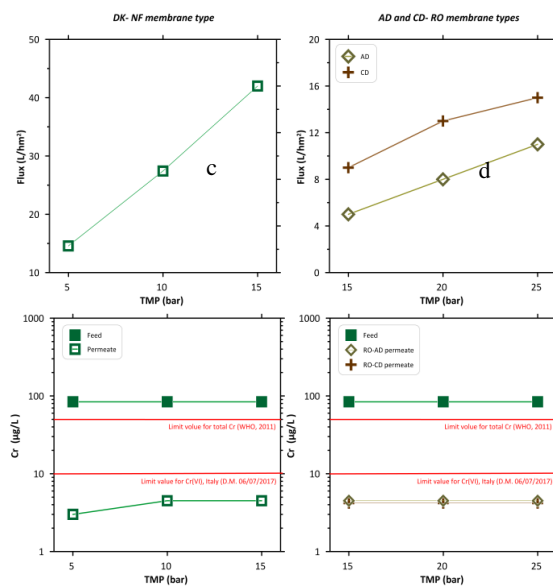
4. Results

In the analysed water sample, the total Cr detected was 84 ppb (feed). Analysis highlighted that the highest level of dissolved Cr was present as Cr(VI). Figure 1a and 1b illustrate a linear increase of permeate flux at increasing of operating trans-membrane pressures (TMP) whereas figure 1c and 1d illustrate the concentration of Cr before and after the membrane treatment for NF and RO membrane types, respectively. The highest flux was recorded for DK membrane type with values ranging between 15 and 42 L/hm². The results show rejection of Cr above 95% for all the operating conditions investigated and for each used membrane. The Cr concentration in the permeate was always lower than 10 µg/L, so below the threshold defined hazardous for human health.

5. Discussion and Conclusion

In this work, three membrane modules (DK- NF membrane type, AD- and CD-RO membrane types) were used to treat Cr-polluted groundwater named Vivaio spring coming from Bonassola serpentinitic aquifer (La Spezia, Liguria, Italy). The level of chromium detected in the Vivaio spring is above the maximum permissible threshold, limiting the use of natural source in the studied area. The Cr(VI)-rich groundwater is the result of water-ophiolitic rock interaction processes. The experiments performed show that NF is a valid method to remove Cr from

contaminated groundwater preserving an acceptable dissolved load in the purified water compared to RO ones. After the NF treatment, the Cr concentration



detected in the permeate sample for each operating pressure was below the limits established by the law. Despite the similar results obtained with AD and CD membranes, the operating pressures are higher and the flux are much lower than DK ones. On the basis of these results, it can be asserted that the DK-NF membrane is the most performant one to decontaminate Cr(VI)-rich waters. The results obtained in this work are much promising for future developments on the treatment of polluted natural water, allowing drinking use in the contaminated area.

References

- Apollaro, C., Fuoco, I., Brozzo, G., & De Rosa, R. (2019). Release and fate of Cr (VI) in the ophiolitic aquifers of Italy: the role of Fe (III) as a potential oxidant of Cr (III) supported by reaction path modelling. *Science of the Total Environment*, **660**, 1459–1471.
- Di Natale, F., Erto, A., Lancia, A., & Musmarra, D. (2015). Equilibrium and dynamic study on hexavalent chromium adsorption onto activated carbon. *Journal of hazardous materials*, **281**, 47-55.
- Fantoni, D., Brozzo, G., Canepa, M., Cipolli, F., Marini, L., Ottonello, G., et al. (2002). Natural hexavalent chromium in groundwater interacting with ophiolitic rocks. *Environmental Geology*, **42**, 871–882.
- Figoli, A., Criscuoli, A. (2017). Sustainable Membrane Technology for Water and Wastewater Treatment, in the Series “Green Chemistry and Sustainable Technology” Springer (Singapore); ISBN:9789811056215.
- WHO, 2011. Guidelines for Drinking-Water Quality, fourth ed.

Figure 1. a-b) Transmembrane flux at different TMP for NF and RO membrane type, respectively; c-d) Cr concentration at different TMP before and after the treatment for NF and RO membrane type, respectively.