Geochemical modeling of chromium oxidation and treatment of polluted waters by RO/NF membrane processes

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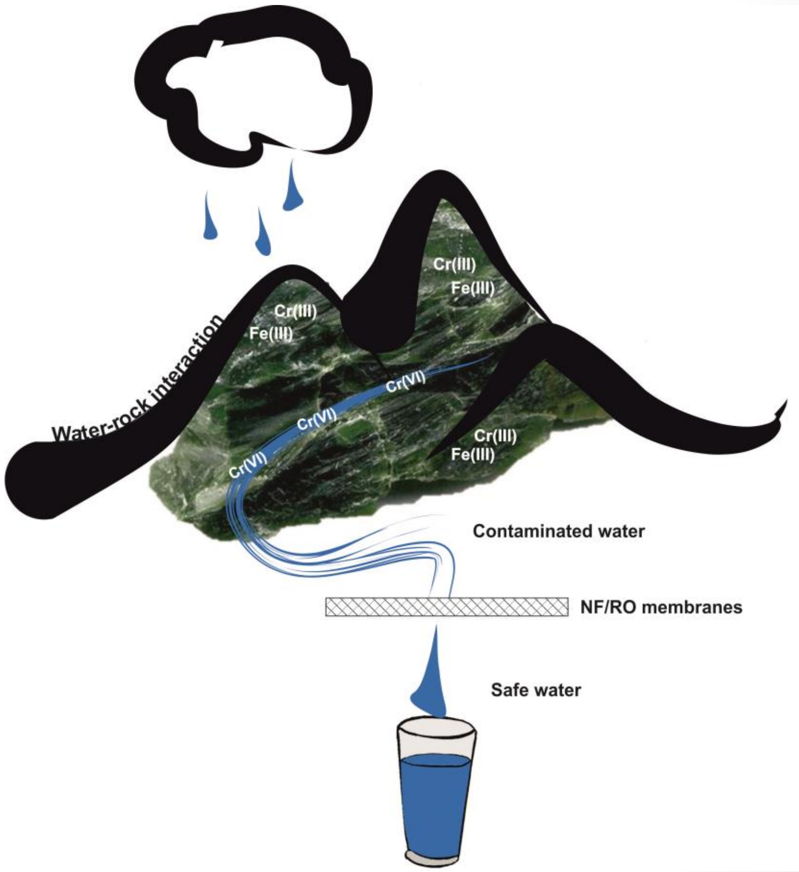
• INTRODUCTION

Geogenic Cr(VI) contamination is a worldwide environmental issue which mainly occurs in areas where ophiolitic rocks crop out. In these areas Cr (VI) can reach high concentrations into groundwaters becoming highly dangerous for human health. Indeed Cr(VI) is recognized as highly toxic element with high mobility and bioavailability. Due to these features, starting from July 2017, Italian government has lowered the Cr(VI) limit value for drinking water to 10 μg/L.

• AIM OF WORK

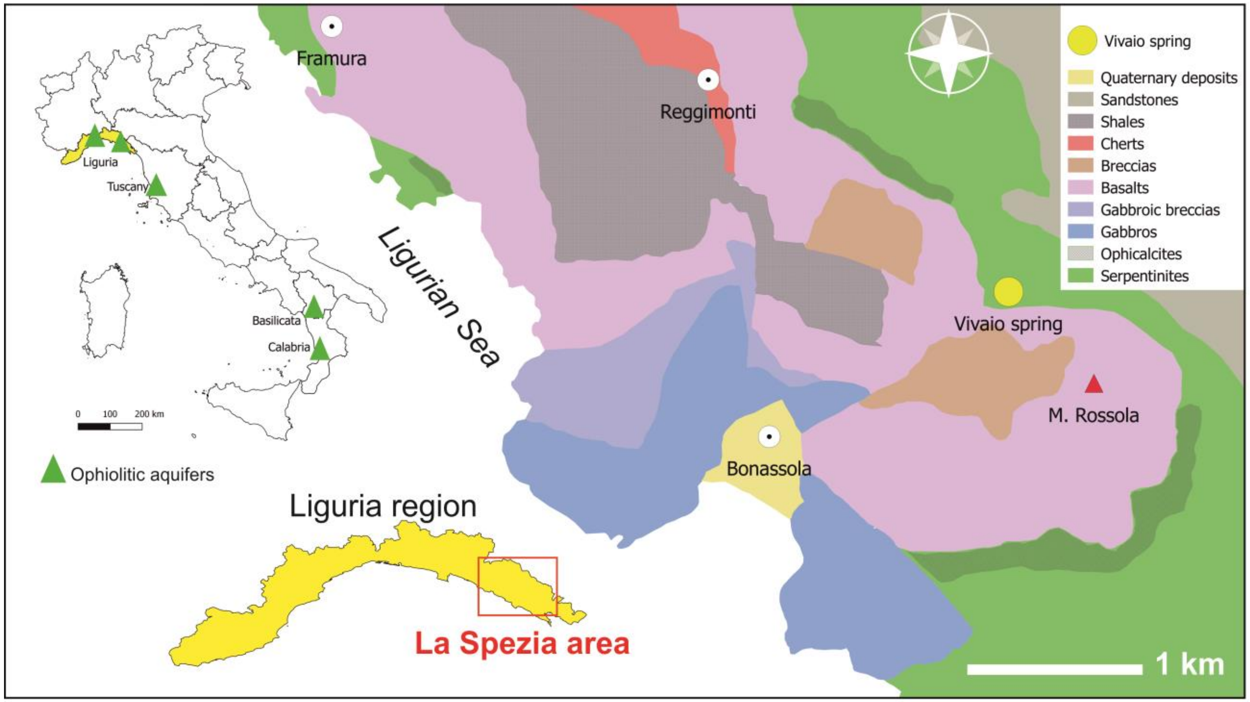
In this work, geochemical approach was used as strong-scientific tool for pre-selection of suitable remediation systems to treat Cr-contaminated groundwaters.

The geochemical characterization allowed to select Nanofiltration (NF) and Reverse Osmosis (RO) as suitable remediation processes, whereas through a new geochemical modeling, the evolution of water chemistry during the water-rock interaction was also studied



• GEOLOGICAL BACKGROUND

The considered water samples come from ophiolitic Italian areas.
These ophiolitic bodies exposed in both Alpine and Appeninic belts, represent the lithospheric relicts of the Ligurian–Piedmontese basin which occupied the Western and Northern Mediterranean region during Jurassic age (Piccardo et al., 2014; Vissers et al., 2013). These rocks are located in several Italian regions like Calabria, Basilicata, Liguria and Tuscany. The attention was focused in La Spezia area, in which the highest Cr content was detected in the Vivaio sping.



• MATERIALS AND METHODS

- **Sampling**

Sampling was carried out measuring in the field intrinsically unstable parameters (i.e. EC, Eh, T, pH, total alkalinity) by using portable instruments.

The water samples were collected using new polyethylene bottles after filtering through a 0.45 µm pore-size membrane filter. Moreover, higher volumes of the groundwater (about 50 L) were also collected for subsequent membrane treatments. Samples for the determination of major dissolved cations and Cr content were acidified by ultrapure acid (1% HNO_3).

- **Analysis**

Chemical analyses were performed using: (i) a Dionex ion chromatograph mod. ICS-2000 for determination of major anions and cations, fluorides, bromides and nitrogen species (ii) an ICP-OES PerkinElmer Optima 2000DV spectrophotometer equipped with ®Apex-E nebulization, heating and condensation system for measurement of trace metals and silica. The Cr(VI) content was evaluated by 1.5-diphenylcarbohydrazide colorimetric method.

• MATERIALS AND METHODS

➢ Geochemical Modeling

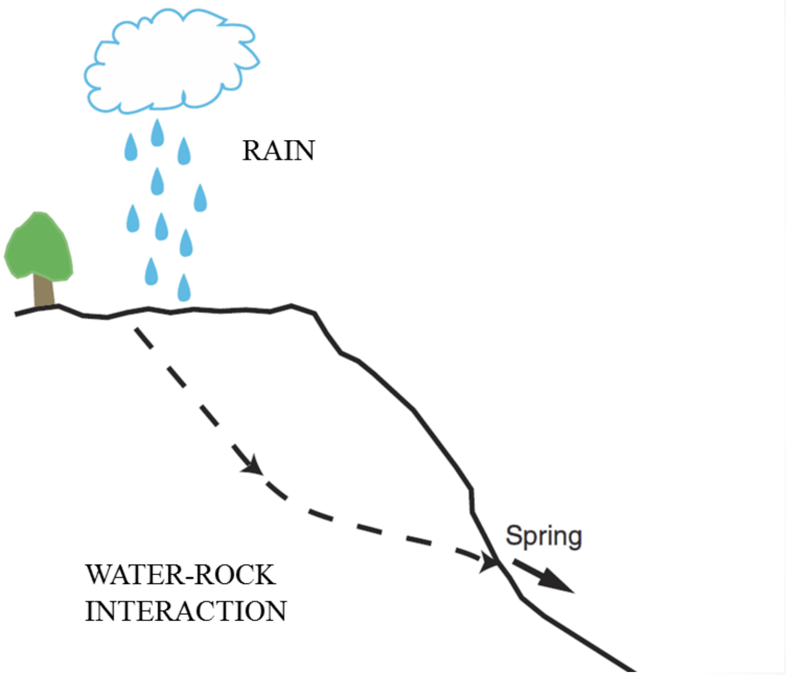
To model the Cr-release process from serpentinite rock, other 322 water samples coming from ophiolitic Italian areas were selected from literature data (Apollaro et al. 2019, Langone et al., 2013).

Softwares

EQ 3/6a and PHREEQC Interactive, v. 3.1.1.

Solid reactants:

Serpentine (~94%wt),
spinel rim (~15%wt)
spinel core (~0.08)
Clinoyroxene (~2.5%wt),
Cr-clinoclore (~10%wt)
magnetite (~3.5%wt)
calcite (~0.00025%wt).



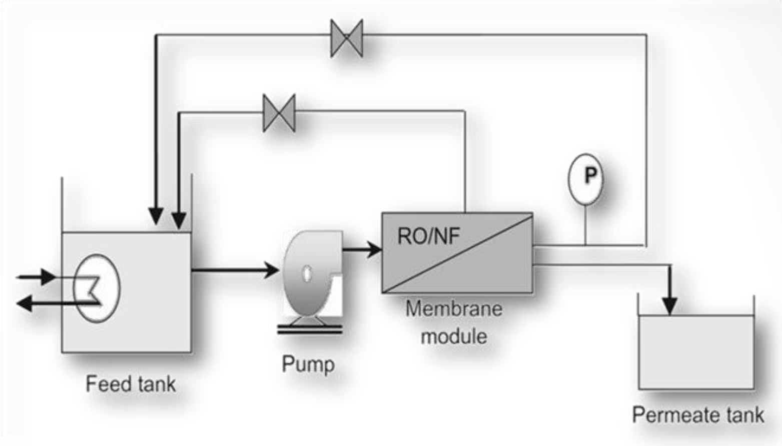
Geochemical modelling was performed varying Fe(III)/Fe_{TOT} weight ratios in serpentine minerals following the new approach proposed by Apollaro et al. 2019. via a careful data review on Fe redox state measurements in serpentine minerals obtained from several works, adopting the following Fe(III)/Fe_{TOT} weight ratios:

1.00, 0.95,0.90, 0.80, 0.70, 0.60

• MATERIALS AND METHODS

➢ **Experimental set-up for NF/RO tests**

Experiments were performed by using a laboratory pilot unit
One NF membrane named DK two RO membranes, named AD and CD 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). Experiments were performed at a temperature of 16 ± 2 °C and the operating flow rate was 9 L/min. At the end of each test, samples of feed and permeate were collected to evaluate the rejection
values after the treatment.



	DK[1]	AD[2]	CD[2]
Type	Nanofiltration	Reverse osmosis	Reverse osmosis
Materials	Polyamide	Polyamide	Cellulose
Supplier	Osmonics (Generalelectric)	Osmonics (Generalelectric)	Osmonics (Generalelectric)
Configuration	flat plate	flat plate	flat plate
MWCO	150-300 Da	-	-
MgSO4 (NF) and NaCl (RO) rejection (%)	96	99.75	98.5
pH operating range	2-10	4-11	5-6.5
Flux (GFD)/psi	22/100	7-11/800*	10-18/140-400*

* Data for spiral wound modules [1]www.nextdayscience.com

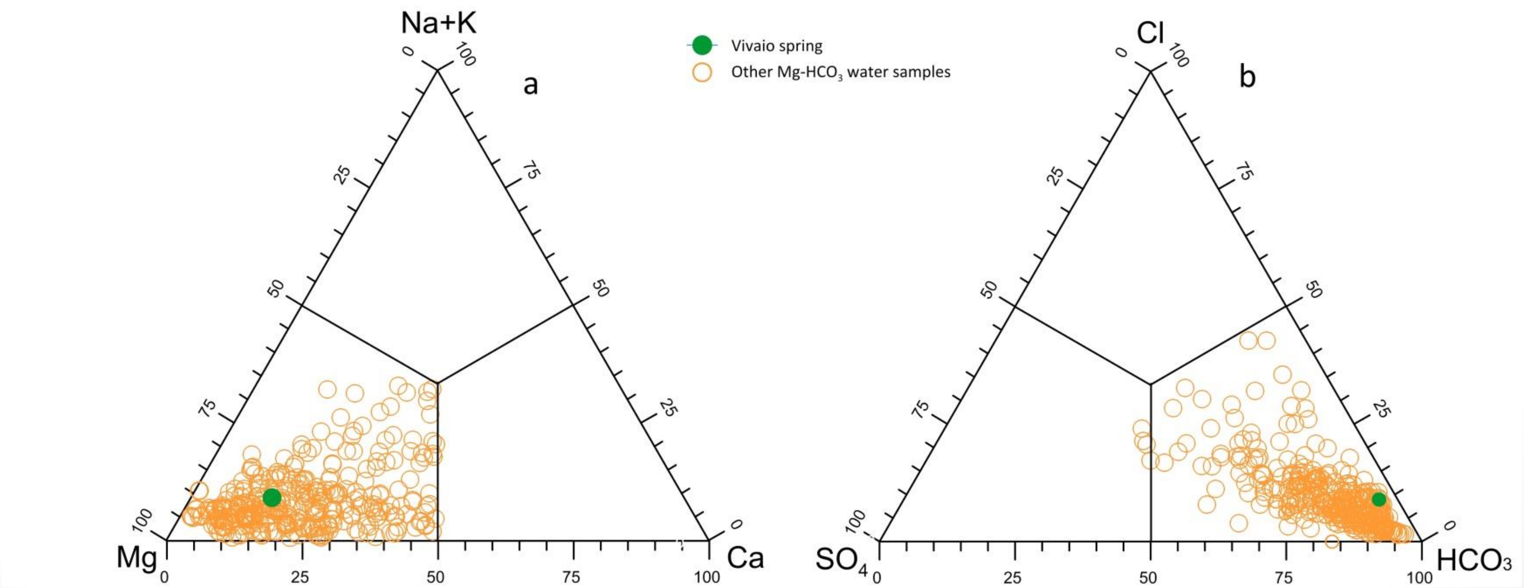
[2]https://www.lenntech.it/prodotti/membrane/osmonics-desal-.htm

• RESULTS AND DISCUSSIONS

➢ Geochemical characterization

The considered water samples, included the Vivaio spring, has interacted with serpentinite rocks, acquiring a Mg-HCO3 composition with variable amount of Cr. The Mg-HCO3 composition with low (0.16 µg/L) to high (75 µg/L) Cr content is typical in ophiolitic areas, confirming that the circulation of studied samples occurs mainly (or exclusively) into the serpentinitic reservoir. The main Cr(VI) aquous species in Vivaio spring are the following:

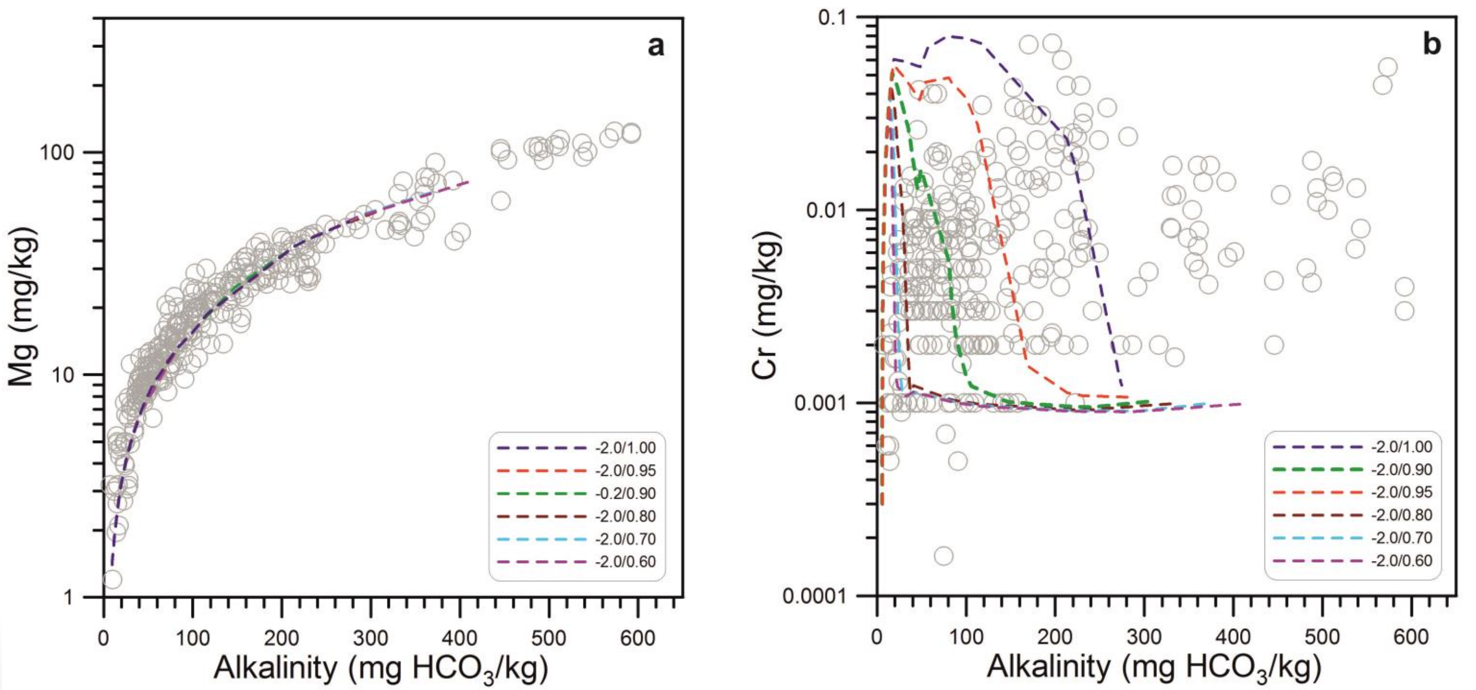
$$CrO_4^{2-} \gg MgCrO4° > HCrO_4^-$$



• RESULTS AND DISCUSSIONS

➢ Geochemical modelling

In the Mg vs. alkalinity plot the theoretical paths are superimposed and reproduced very well analytical data, whereas in the Cr vs. alkalinity plot they reproduce the wide range of analytical Cr concentrations With increasing of Fe(III)/Fe_{TOT} ratio in serpentine minerals, high Cr(VI) concentration hold into solution until high alkalinity values. It can be affirmed that the release of Cr(VI) depend on Fe(III) percentage into minerals of interest.



Although laboratory experiments showed that Mn oxides are able to oxidize Cr(III) during the water-rock interaction (e.g. Oze etal., 2007; Kim et al., 2002) the processes required the occurrences of particular natural events: (i) oxidation on surfaces of Mn oxides which are present as suspended particles; (ii) faster dissolution of Mn oxides rather than Cr-minerals which unlikely occur into natural environments as fractured ophiotic aquifers. Moreover, as shown by XRD and EMPA investigations on bulk rock and on single serpentine minerals the concentration of Mn is significantly lower than Fe. This difference is about two orders of magnitude. As highlighted by several authors Fe can be present in its trivalent form in serpentine minerals, contributing to oxidation process in this geological environment.

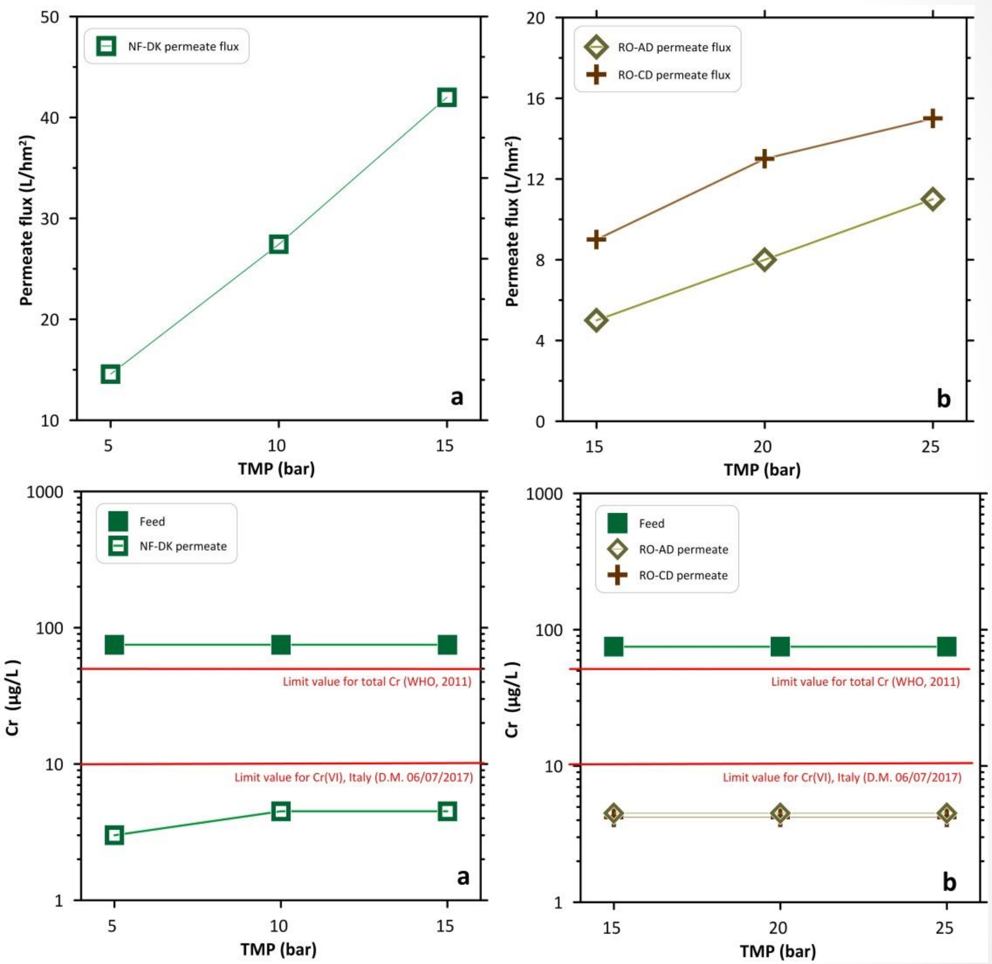
- The geochemical characterization, including information on Cr speciation, is the first essential step for a correct choice of the remediation technology. The chemistry features of La Spezia water showed a medium ionic load (Total Dissolved Ions (TDS) equals to 278 mg/L) and the presence of CrO_4^{2-} as main Cr chemical species. In these conditions, considering the need of lowering the Cr content down to the imposed limits, RO, which is usually used for desalination, and NF, characterized by a charging-effect on charged complexes during separation process, with a higher rejection for divalent ions, were identified as potential remediation technologies.

- Furthermore, the geochemical modelling explains the evolution of natural environment and what it should be expected. The robust data collection in this work, coupled with the results of reaction path modelling, give important information on this kind of geologic environment, like the maximum concentration of Cr(VI) which may occur if the natural geochemical conditions remain unchanged and no anthropogenic inputs interfere. Therefore, these data allow to assert if the chosen remediation technologies can be extended to all natural Cr-contaminated

• RESULTS AND DISCUSSIONS

➢ **NF/RO tests**

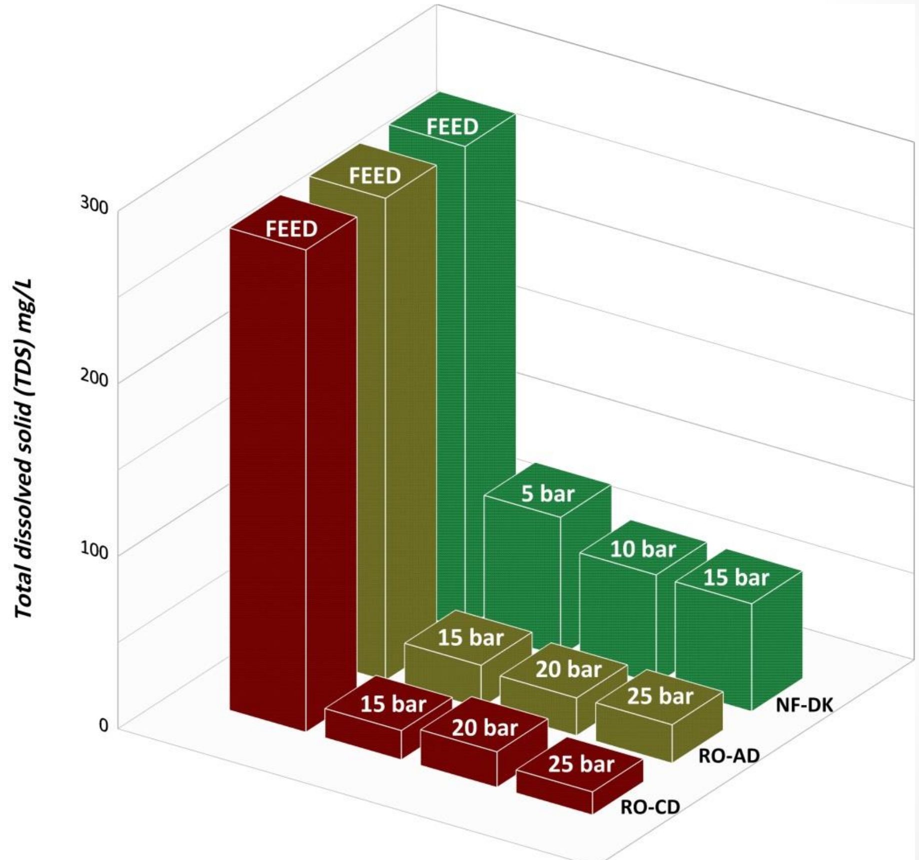
The highest flux was recorded for the DK membrane with values ranging between 15 and 42 L/hm2 at 5 and 15 bar, respectively. Despite the higher TMPs used, the RO membrane fluxes were lower (5–11 L/hm2 and 9–15 L/hm2 for AD and CD membranes, respectively).
The chromium content in the produced permeates was always lower than 10 µg/L, below the threshold defined hazardous for human health and it was independent on the TMP applied, with rejections around 95%



• RESULTS AND DISCUSSIONS

➢ **NF/RO tests**

The behavior of major ions was also studied during treatment tests considering the Total Dissolved Ionic (TDS). DK permeate showed to hold a higher ionic load after treatment than the permeates produced by the RO membrane types, for all considered pressures. This indicates that NF systems could be the preferable choice for water purification because they give back a decontaminated water which can be classified as low mineral water, suitable for drinking and agricultural purposes without need of other additional post-treatments.



• RESULTS AND DISCUSSION

The studies available in the literature are still limited to synthetic/model solutions and only few works deals on naturally Cr-contaminated groundwater. Here below a comparative table on treatment of Cr(VI)-contaminated groundwaters using RO/NF membrane processes is reported. In this framework, the results obtained with different membranes and water types are in line with literature data.

Membrane Type	Water Sample	Cr(VI) concentration befor treatment	Applied TMP	Flux	Cr(VI) Rejection	Cr(VI) concentration after treatment	Ionic Strength	Reference
		µg/L	bar	L/m^{2}h	%	µg/L	mM	
LFC-1 (RO-polyamide TFC)	LADWP Water	120	5.1	-	97*	3.6*	9.2*	Yoon et al., 2009
ENSA (NF-polyamide)	LADWP Water	120	3.7	-	45*	66*	9.2*	Yoon et al., 2009
MX07 (NF-polyamide)	LADWP Water	120	8.2	-	40*	72*	9.2*	Yoon et al., 2009
NF270 (NF-polyamide)	Turin Water site A	20.4	6.9	42*	71*	6	14.3	Giagnorio et al., 2018
	Turin Water site B	14.9	6.9	84*	90*	1.5	9.1	Giagnorio et al., 2018
	Turin Water site C	14.7	6.9	91*	93*	1	2.3	Giagnorio et al., 2018
NF90 (NF-polyamide)	Turin Water site A	20.4	6.9	47*	99*	0.3	14.3	Giagnorio et al., 2018
NF90 (NF-polyamide)	Birjand Water	100	4	-	94.3	5.7*	25.5*	Barikbin et al., 2011
AD (RO -polyamide)	La Spezia water	75	15-25	5-11	94	4.5	5.7	This work
CD (RO-Cellulose)	La Spezia water	75	15-25	9-15	94.4	4.2	5.7	This work
DK (NF-polyamide)	La Spezia water	75	5-15	15-42	96-94	3-4.5	5.7	This work

* Calculated value on the basis of available data in the reference work

• CONCLUSIONS

The new reaction path modelling was performed re-evaluating the role of Fe as main oxidant in the system and the analytic concentrations of relevant solutes, including Cr(VI), were reproduced. The spring with the highest Cr(VI) content was treated to lower its concentration below the threshold values. A laboratory-scale set-up was used to carry out both NF and RO experiments. The experiments were conducted on different commercial membranes varying the operating pressures. The results showed high Cr(VI) rejections (around 95%) for all tested membranes, leading to Cr(VI) concentrations below the threshold limits. The high flux, obtained already at lower operating pressures, combined with high selectivity towards Cr(VI) makes NF a favorable remediation option. The preliminary findings of this work are of interest to fill the current gap in knowledge on the treatment of natural Cr(VI)-contaminated groundwater, providing useful data for future scientific and application developments in similar geological settings worldwide. The installation of pilot-scale units can be a first step for future full-scale implementations for Cr(VI) remediation.

Further details:

Fuoco, I., Figoli, A., Criscuoli, A., Brozzo, G., De Rosa, R., Gabriele, B., & Apollaro, C. (2020). Geochemical modeling of chromium release in natural waters and treatment by RO/NF membrane processes. Chemosphere, 126696.

Thanks for the attention

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