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In Situ Hexavalent Chromium Reduction by Injection of Organic Substrates in the Aquifer

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ABSTRACT: Among the innovative technologies for in situ remediation of hexavalent chromium in groundwater, bio-induced reduction is under investigation. In this process the reduction of Cr(VI) is stimulated by a strongly reducing environment, created by the injection of organic substrates that are rapidly degraded by autochthonous heterotrophic microorganisms. Tests were performed at the laboratory scale to investigate the behavior of two different organic substrates from food industry (permeate from cheese whey ultrafiltration and a waste from the brewing process), in terms of dissolved Cr(VI) abatement and kinetics, also as a function of the initial Cr(VI) concentration (5000 or 10000 µg/L). The tests showed that, under proper conditions, very low Cr(VI) concentrations (1.3 µg/L) and removal efficiency up to about 100% can be obtained after 36 d incubation.

INTRODUCTION

Chromium can have several oxidation states, but the most common forms in the subsoil are Cr(III) and Cr(VI) (Figure 1). Cr(III) is rather insoluble in water under environmental conditions (pH 6-9); it tends to form oxides and hydroxides by reacting with iron and aluminum, and stable complexes with organic molecules (Fruchter, 2002; Dhal et al., 2013). Cr(VI) is generally present as hydrogen-chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-}), primarily according to the pH value and Cr concentration (USEPA, 2000). It is very soluble and mobile, and carcinogenic to humans. Cr(VI) can be reduced to the trivalent form by redox reactions involving organic substances in the soil (carbohydrates, proteins, and humic acids) or as part of metabolism of certain microbial species.

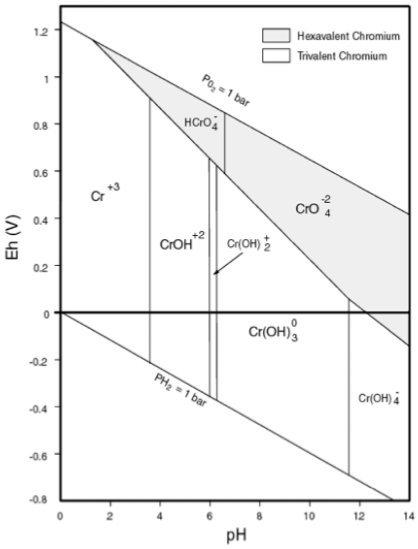


FIGURE 1. Pourbaix's diagram of Chromium (Palmer and Wittbrodt, 1991).

In compliance with the Italian legislation (Legislative Decree no. 152/06s), the threshold concentration (CSC) in groundwater is 5 µg/L for Cr(VI) and 50 µg/L for total chromium.

During the last decade, innovative in situ technologies have been considered to remediate Cr(VI)-contaminated groundwater, in replacement of the traditional pump-and-treat approach. Taking into consideration sustainability, the most interesting technologies are based on biological or chemical mechanisms, which often act together, aimed at reducing Cr(VI) to stable Cr(III) species. During bio-induced reduction, an organic substrate is injected into the aquifer to create a negative redox potential zone. The injected carbon substrate, in fact, is rapidly degraded by the heterotrophic microorganisms present in the aquifer, thus consuming the dissolved oxygen. After

oxygen, nitrates, manganese and iron oxides, sulphates and carbon dioxide are consumed. The resulting environmental conditions make Cr(VI) reduction possible (USEPA, 2013).

In this work, Cr(VI) bio-induced reduction was investigated at the laboratory scale. Two different soils, two different organic substrates from food industry, and two different Cr(VI) initial concentrations were investigated to assess the dissolved Cr(VI) abatement and the kinetics of the process.

MATERIALS AND METHODS

The soils used in the experiments ("Milano" soil and "Ticino" soil, see Table 1) were from two different areas in northern Italy.

TABLE 1. Soils used in the laboratory tests.

Parameter	"Ticino" soil	"Milano" soil	Analytical method
Particle size distribution	Sand	Slightly silty sand with gravel	ISO 11277 (2009)
Dry bulk density (kg/m^3)	1478±22	1606±63	ISO 11272 (1998)
Organic carbon (%)	0.27±0.02	0.59±0.03	UNI EN 15169 (2007)
pH (-)	8.5±0.1	8.52±0.01	Rayment and Higginson (1992)
Total heterotrophic bacteria (CFU/g d.w.)	10	10^4	Plate counting

The microcosms were prepared in batch mode, using tap water (see Table 2) similar in composition to groundwater, with a solid to liquid ratio of 50% on weight basis.

TABLE 2. Features of water used in the laboratory tests.

Parameters	Value	Method
Dissolved oxygen (mg/L)	6.5±0.5	Standard Methods 4500-O (2012)
Nitrate (mg/L)	34±3	EPA 300.1 – Rev. 1 (1997)
Iron (mg/L)	0.10±0.01	EPA 6020B (2014)
Manganese (mg/L)	0.30±0.03	EPA 6020B (2014)
Sulphate (mg/L)	66±7	EPA 300.1 (1997)
Carbon dioxide (mg/L)	15	Saturation concentration at 20°C
Alkalinity (mg $CaCO_3$/l)	280±28	Standard Methods 2320 (1997)
Calcium (mg/L)	99±10	UNI EN ISO 17294 (2007)
Phosphate (mg P/l)	0.40±0.06	EPA 300.1 (1997)
pH (-)	7.2±0.2	EPA 150.1 (1982)

Permeate from cheese whey ultrafiltration or a waste from the brewing process were used as the organic substrates (see Table 3). For permeate from cheese whey ultrafiltration, the dose necessary to consume the electron acceptors present in the microcosms at the beginning of the experiments was calculated according to the hydrogen theoretical production in case of incomplete oxidation of the reference molecule (lactose) and a safety factor of 1.25 (third method in Parsons [2010]), resulting in 5 mL of permeate per liter of aqueous phase. As for the waste from the brewing process, the dosage was set in order to have the same initial chemical oxygen demand (COD) as for the microcosms with permeate from cheese whey (300 mg COD/L of aqueous phase), resulting in 2.5 mL substrate per liter of aqueous phase.

TABLE 3. Organic substrates used in the experiments.

Parameters	Permeate from cheese whey ultrafiltration	Waste from brewing process
Reference molecule	Lactose ($C_{12}H_{22}O_{11}$)	-
COD (g/L)	60±12	122±24
Total heterotrophic bacteria (CFU/100 ml)	10^6	10^3

Cr(VI) contamination in the microcosms was carried out with a 0.2 N potassium dichromate solution, dosed to obtain a different initial Cr(VI) concentration (5000 and 10000 µg/L of water).

Tests were performed at 17±1°C for 36 d, using six replicates for each type of microcosm that were sacrificed at specific times to analyze the dissolved Cr(VI). During the tests, redox potential (ORP), dissolved oxygen (DO) and pH were also monitored.

RESULTS AND DISCUSSION

ORP, OD and dissolved Cr(VI) over time are shown in Figures 2, 3 and 4 respectively, for microcosms prepared with "Ticino soil " (a) and "Milano soil"(b).

With "Ticino soil", the ORP (Figure 2-a) decreased to values of about -500 mV in 4 d of incubation with the substrate from brewery and initial Cr(VI) concentration of 5 mg/L; this was the case with the higher ORP decreasing rate during the first week of treatment. In the other microcosms, values between -200 mV (permeate of cheese whey, 10 mg Cr(VI)/l) and -600 mV (permeate of cheese whey, 5 mg Cr(VI)/) were obtained after 10 d.

In the tests with "Milano" soil (Figure 2-b), ORP values of about -600 mV were obtained after 4-5 d incubation where the initial Cr(VI) concentration was 5 mg/L, with a very steep slope of the curve after 3 d of treatment. In microcosms with the initial concentration of 10 mg Cr(VI)/l, the ORP underwent minor decrease in 7 d treatment, reaching a slightly negative value (-50 mV), in case of the brewery substrate, or a positive value (130 mV), in case of permeate of cheese whey; at any rate, the ORP values decreased down to -300 mV and -550 mV, respectively, during 10 d incubation.

Dissolved oxygen could be measured only in the microcosms with 5 mg Cr(VI)/l as the initial concentration (Figures 3-a, and 3-b); OD values <0.5 mg/L were reached by 2 d of incubation, while the ORP values were still above 200 mV. Comparison between the two different soils shows that the electron acceptor consumption was quicker with "Milano soil", which has a total heterotrophic bacteria concentration three orders of magnitude higher than "Ticino soil".

In all microcosms, the initial pH value was in the range of 7.1 ÷ 7.5. After 36 d incubation, values in the range 6.7 ÷ 7.1 were measured with "Ticino soil" and 6.7 ÷ 6.9 with "Milano soil", resulting in insignificant variations during the treatment.

Referring to Cr(VI) concentration in water, Figure 4-a shows that with "Ticino soil" 11 d incubation were necessary to appreciate any pollutant abatement, resulting in residual values between 5 µg/L and 5500 µg/L at 36 d of treatment. In particular, when the initial Cr(VI) concentration was 10 mg/L, the final values were approximately 5.4 mg/L with both the permeate of whey cheese and the waste from brewing process, while final values of 394 µg/L (permeate of whey cheese) and 5 µg/L (waste from brewing process) were obtained starting from 5 mg Cr(VI)/l.

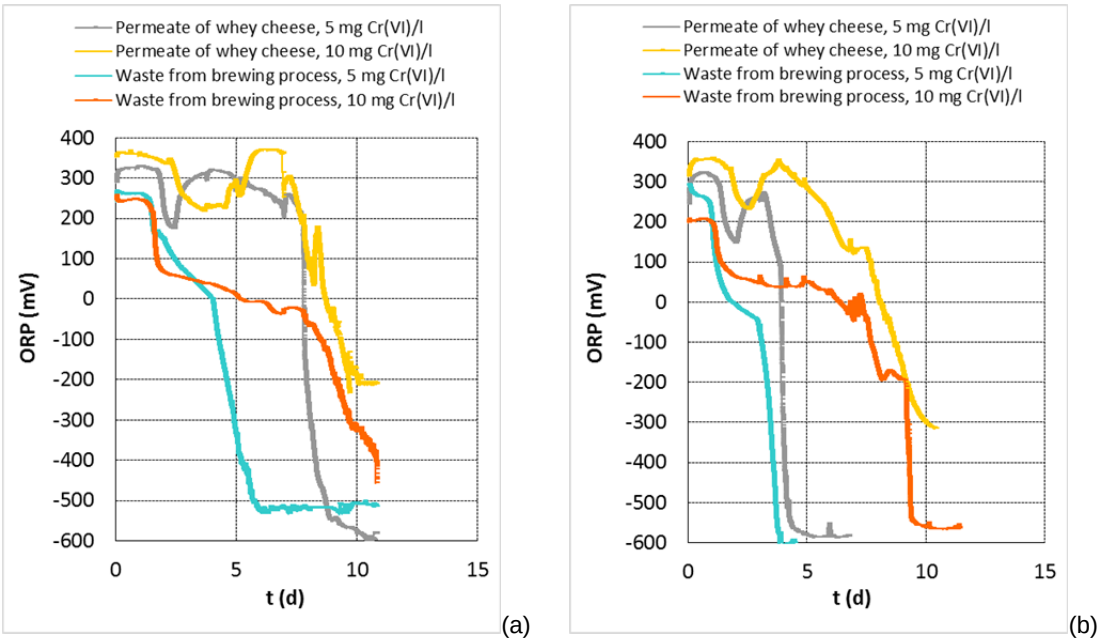


FIGURE 2. Redox potential over time t, in microcosms with "Ticino soil" (a) and "Milano soil" (b).

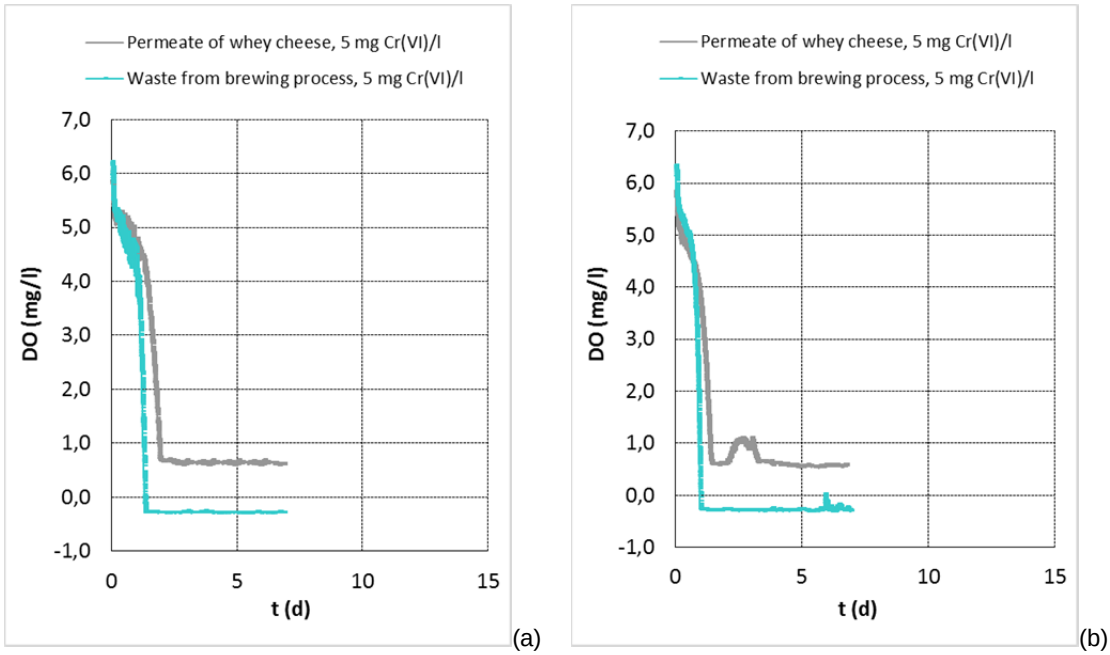
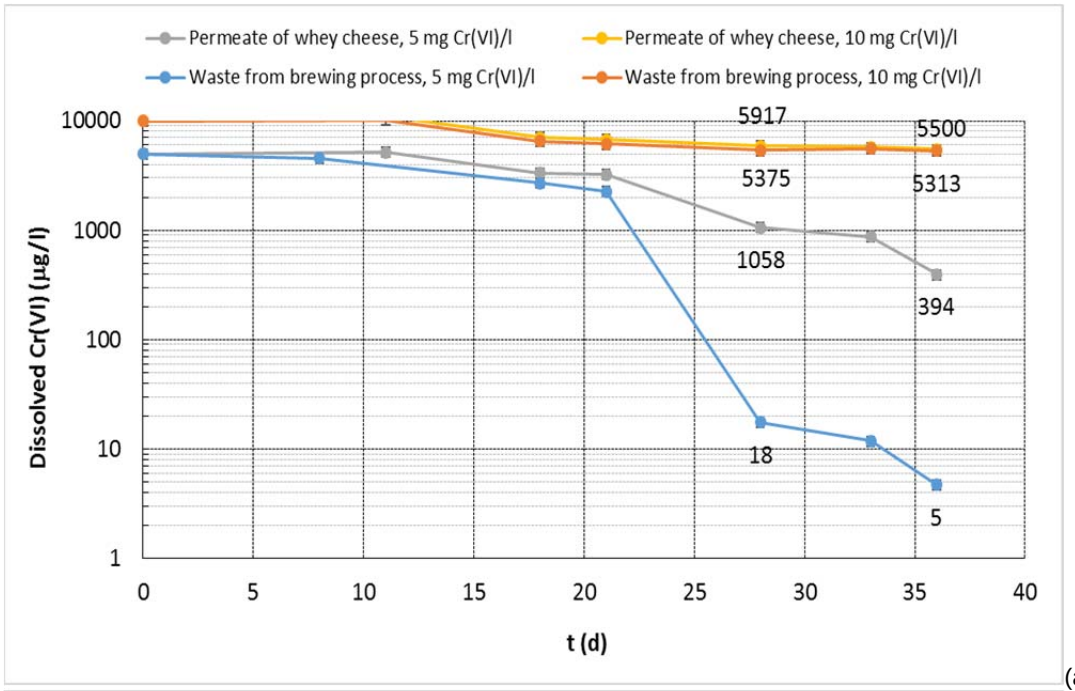
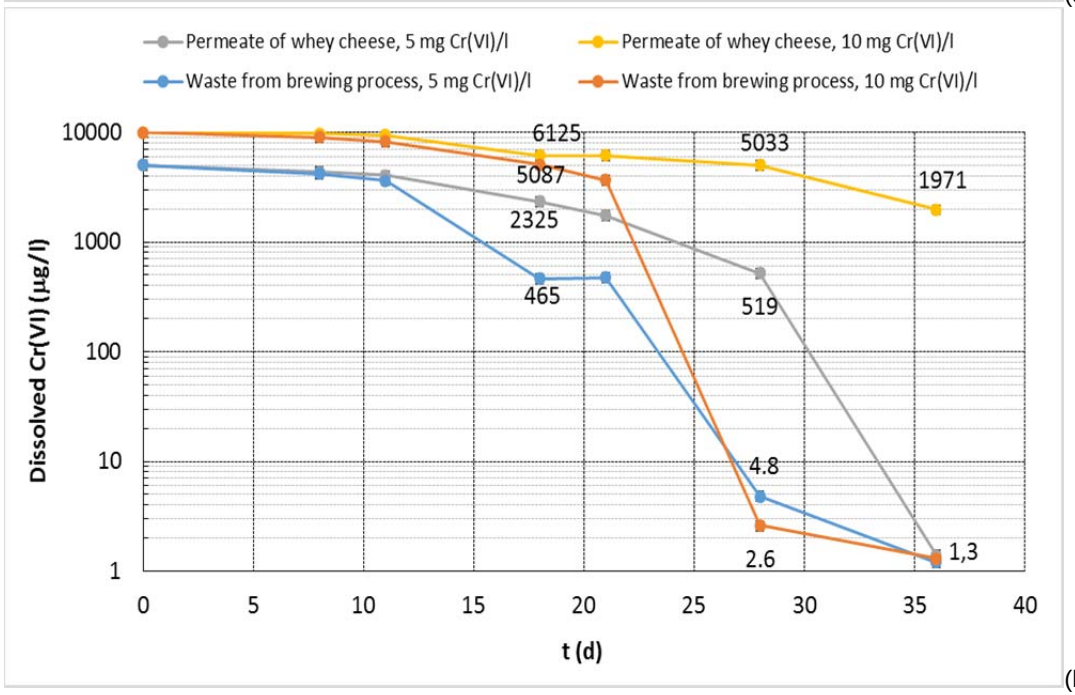


FIGURE 3. Dissolved oxygen over time t, in microcosms with "Ticino soil" (a) and "Milano soil" (b).

In the microcosms with "Milano soil" (Figure 4-b), Cr(VI) removal started after 8 d incubation, with residual values of about 1.3 µg/L after 36 d of incubation in all microcosms, except when whey cheese was used and the initial Cr(VI) concentration was 10 mg/L; in this case, the residual value was about 2 mg/L.



(a)



(b)

FIGURE 4. Dissolved Cr(VI) over time t, in microcosms with "Ticino soil" (a) and "Milano soil" (b).

Figure 5 shows the removal percentage of dissolved Cr(VI) after 11, 21 and 36 d in the different types of microcosms. Values above 30% were obtained only at 21 d incubation, after strongly reducing conditions had been kept for a few days. Comparing microcosms with "Milano soil" and “Ticino soil”, at a specific Cr(VI) initial concentration and organic substrate, a better performance was obtained with the first one.

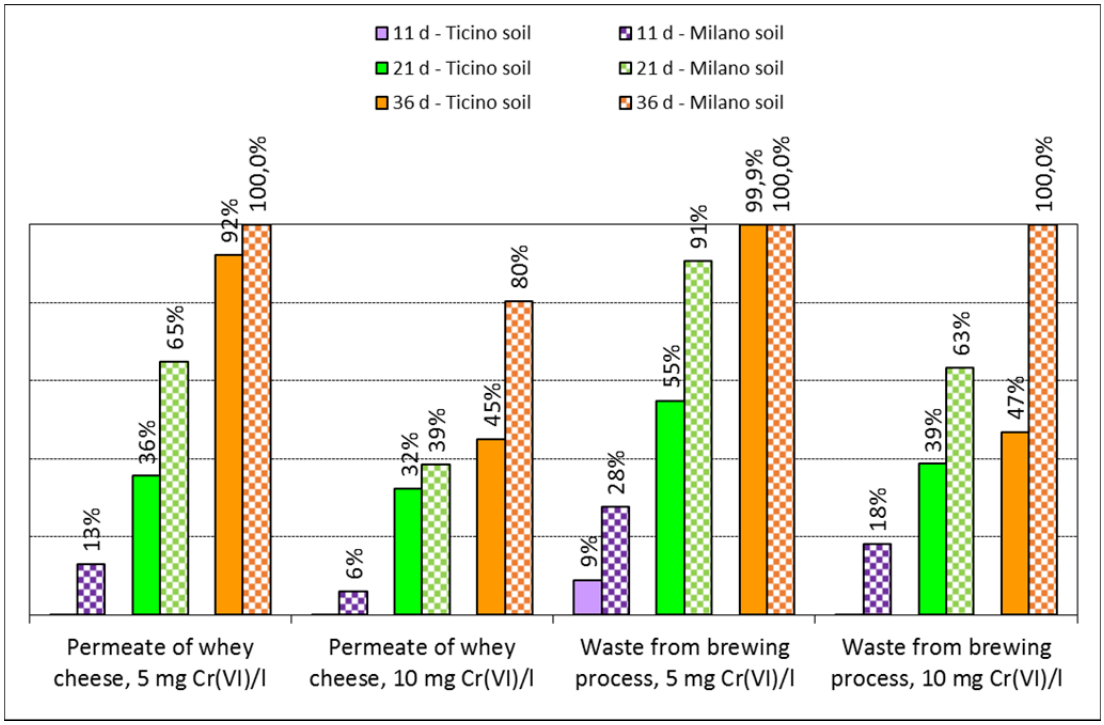


FIGURE 5. Cr(VI) abatement after 11, 21 and 36 d incubation in the different types of microcosms.

Iron has a fundamental role in Cr(III) coprecipitation; therefore, to investigate potential causes for the different results obtained with the two soils, Fe(II) release by the two solid matrices was assessed as a function of time after addition of permeate of whey cheese. Preliminary results revealed that the kinetics of Fe(II) release by "Ticino soil" was slower than from "Milano soil"; in fact, after 10 d in water, “Ticino soil” released very few iron (<100 μg Fe(II)/l), while "Milano soil" released more than 1 mg Fe(II)/l, as much as “Ticino soil” after 30 d incubation.

CONCLUSIONS

The theoretical Pourbaix diagram of Cr had to be properly adjusted to site-specific conditions, taking into account groundwater and soil composition. In fact, redox potentials below -200 mV were necessary in order to get Cr(VI) reduction.

Cr(VI) removals were high, resulting in values up to 100,0% after 36 d incubation and a final concentration lower than the Italian regulatory limit (5 µg Cr(VI)/l).

Different results were obtained with the two soils that still have to be investigated. Preliminary tests showed that the kinetics of Fe(II) release might have been a key factor in Cr(VI) reduction and Cr(III)-Fe(III) coprecitipitation.

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