Chromate reduction
Selective catalytic hydrogenation

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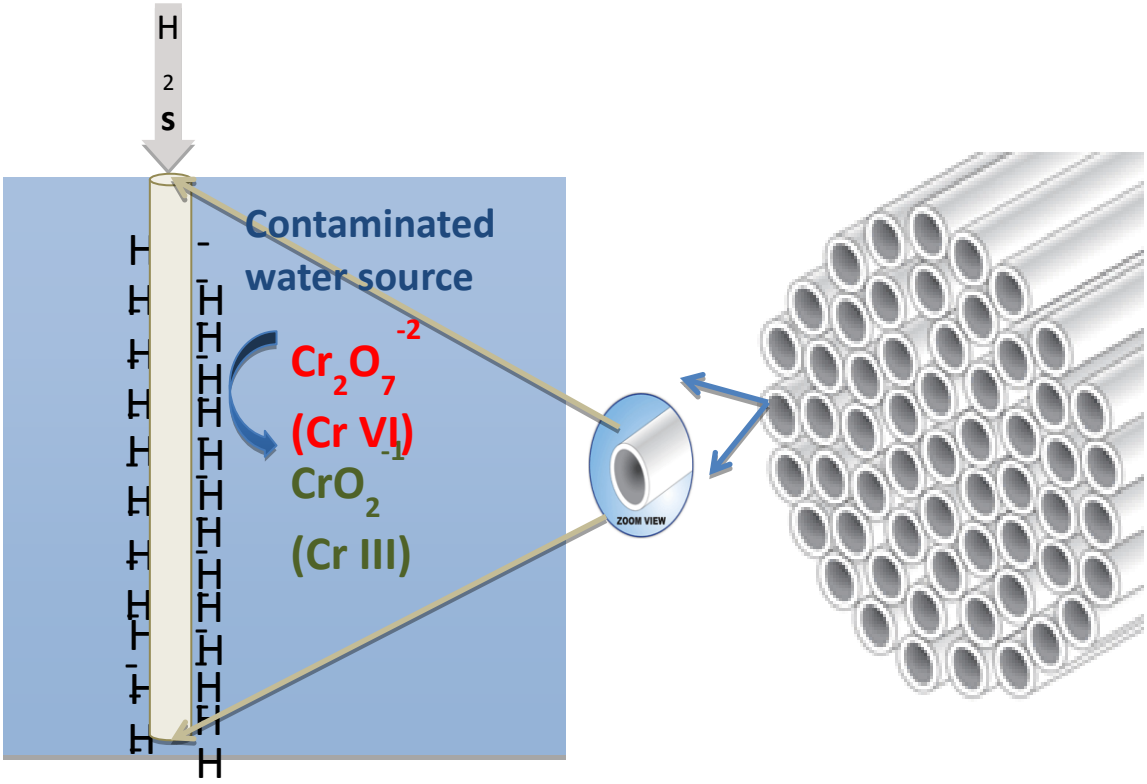
Lab report

Introduction

The technology deals with the reduction of dichromate anions (hexavalent chrome) presented in water sources at ppm levels. The final dichromate concentration in the treated water is below the detection limit, 16 ppb.

The novel approach combines the use of membrane and the catalysis. Schematic depiction of the process is presented in the below figure.



The reducing agent used in the process is hydrogen so except the dichromate reduction no chemical changes occur or additional species remain in the treated water.

Process description

In the fabrication of the membrane reactors are used commercial ceramic membranes for ultra /nano filtration. The catalytic phase is deposited on the external surface of those commercial membranes by conventional methods. Controlled amount of hydrogen is continuously supplied into the inner channels of the membrane module. The porous membrane structure allows hydrogen to reach the external membrane layer in homogeneously distributed manner. When in contact with the catalytic phase the hydrogen is activated. The reduction potential of the activated hydrogen is high enough in order to reduce the dichromate anions to the more innocuous Cr III species.

The hydrogen supply is thoroughly controlled by mass flow valve. Therefore no excessive overdose of hydrogen is needed. Indeed, the hydrogen consumption can be adjusted near stoichiometric amount. In fact the catalytic membrane reactor operates as contactor.

Due the hydrophilic nature of the ceramic material the hydrogen side pressure is between 1 and 2 bars in order to overcome the capillarity pressure exerted by the water in the porous media.

$$Cr_2O_7^{2-} + 5H_2 \rightarrow 2CrO_2^{1-} + 5H_2O$$

$$CrO_4^{2-} + 2H_2 \rightarrow CrO_2^{1-} + 2\,H_2O$$

Dichromate reduction results

In the following Figures are presented some results of the dichromate reduction using tap water. The water is polluted by addition of dichromate salt and the pH is adjusted to 3, 5 by hydrochloric acid.

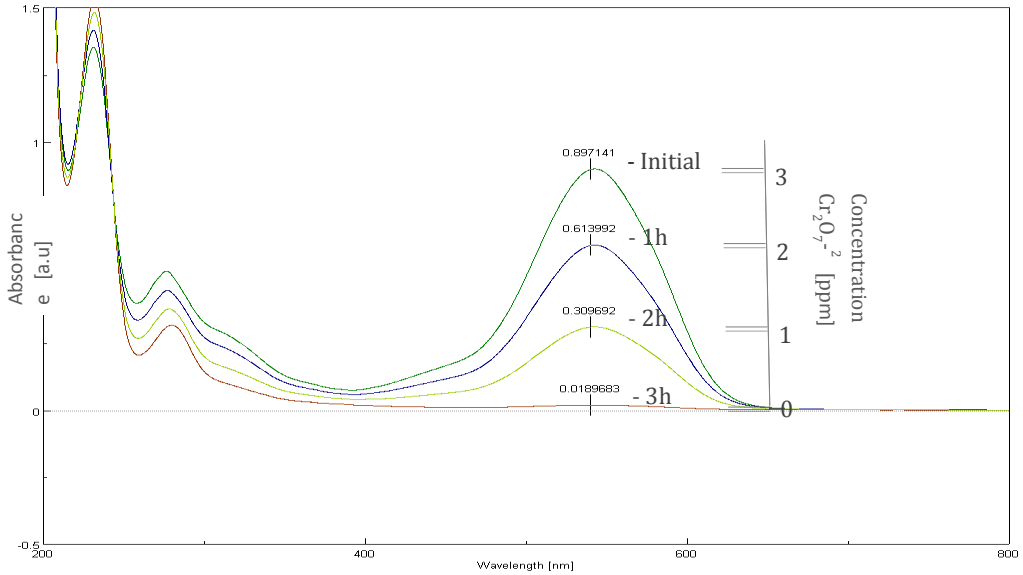


Figure: UV-VIS spectra progress of complex formed between 1,5-diphenylcarbazide and dichromate during the reaction.

In the Cr VI determination a standard photometric method is followed. The rate of dichromate elimination is presented in the next Figure.

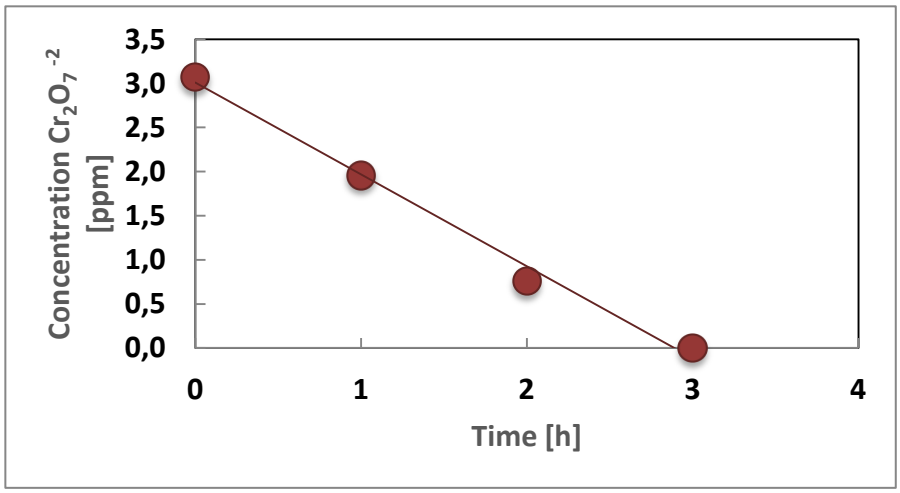


Figure: Dichromate reduction using catalytic ceramic hollow fiber membrane reactor.

Chromate reduction process: main parameters

The experimental conditions of the presented results are as follow:

- Tap water: 3 ppm $Cr_2O_7^{2-}$
- Room temperature
- Water volume: 50 ml
- Membrane reactors surface: 7x10-4 m^2
- Hydrogen supply: 5 Nccm/h

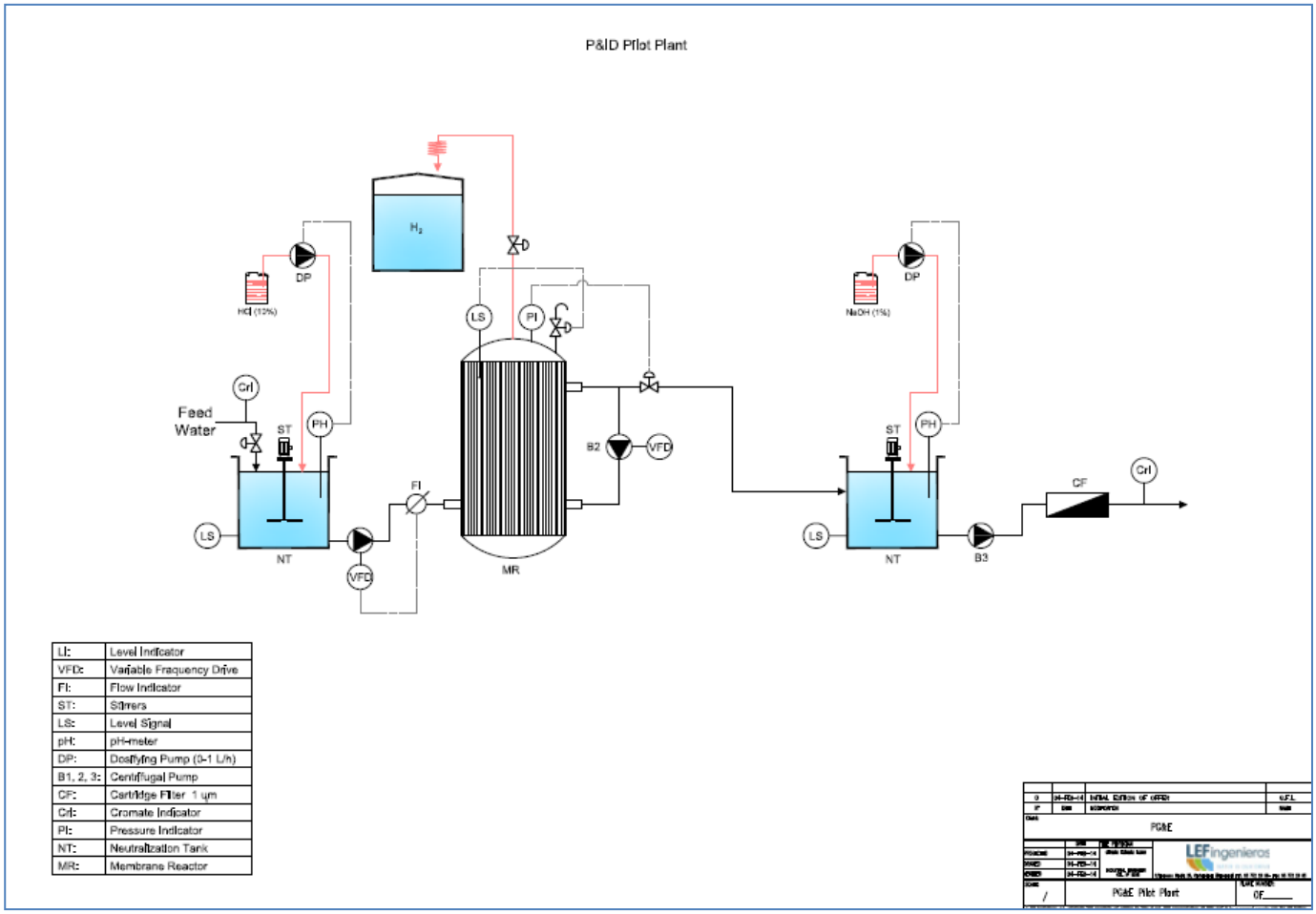
The membrane reactor has been tested at different initial dichromate concentration, (100ppb, 200 ppb, 3 ppm, 4ppm and 20 ppm) in consecutive runs. It has not been observed deactivation of the catalytic phase. The different tests demonstrated that the rate of Cr VI reduction varies linearly with the initial dichromate concentration.

The following parameters can be pointed for the case of California contaminated water sources by dichromate:

- Cr VI reduction rate (mg/m^2*h): 80*
- H_2 supply (NL/m^2*h): 100
- H_2 consume per ppm Cr (VI) reduced: 0,2 ppm.
- Operation mode: semi batch or continuous
- H_2 supply pressure (bar): between 1-6
- Water treatment capacity: due to the modular character of the catalytic membrane reactors there are not scalability limitations.
- Water pretreatment requirements: water pH adjusted in the range 3-4
- Residence time Dichromate reduction: 3-4 hours

*It is considered 3 ppm of initial dichromate concentration

Pilot plant description



Feed water is pumped to a neutralization tank in which a pH sensor read and controll, depending on the resultant value, the dosing Pump (DP) of HCl to achieve the desired value. The pump drives the fluid to Membrane Reactor (MR) has a Variable Frequency Drive (VFD) controlled by a Flow Indicator (FI) to achieve the desired flow rate. The output of the MR valve will remain locked until the expected PI values. Once past the MR, the water is drived to a neutralizing tank (NT) to achieve a neutral pH. The neutralized water passes through a cartridge filter (CF). The chromium concentration indicators (Crl) are continuously measured the concentration of Cr input and output.

Treatment costs

Concentration of Cr (VI) income water: 1 ppm.

Variable cost

Consume of H_2: 0,2 ppm.

Cost of H_2: 35,-$/Kg H_2.

Fixed cost (independent on Cr(VI) concentration)

Consume of HCl: 20 ppm

Cost of HCl: 1,5,-$/Kg HCl (100%)

Consume of NaOH: 15 ppm

Cost of HCl: 3,-$/Kg HCl (100%)

Cr (VI)		COST
0,1	ppm	$0,04
0,5	ppm	$0,04
1	ppm	$0,04
2	ppm	$0,05
3	ppm	$0,06
4	ppm	$0,06