

The Dechromatation Step in Wastewater Treatment Plants: Fundamental Role and Optimization

Giuseppe Trunfio and Grégorio Crini*

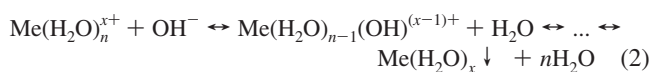
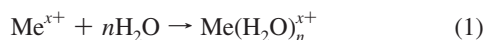
Université de Franche-Comté, Chrono-environnement, UMR 6249 UFC/CNRS usc INRA,
Place Leclerc 25030, Besançon cedex, France

Chromium compounds represent an important class of chemicals and are widely used in many industrial processes. Their release in the aquatic environment constitutes a concerning source of toxicity for flora and fauna. Chromium exists mainly in the trivalent and hexavalent forms, with the latter being much more soluble and toxic and requiring specific treatment before discharge. A review of the literature data reveals that there are few treatment methods applicable on an industrial scale, mainly because of efficiency and maintenance issues. Among them, the reduction at acidic pH by NaHSO₃ and the further precipitation of the more insoluble Cr³⁺ species formed at neutral pH is the most employed technique, given the opportunity to automatically monitor the reaction by means of simple pH and ORP sensors. On this account, we optimized the setting of pH and ORP parameters, applying the method to synthetic solutions and real industrial wastewater from surface-treatment industries. The experimental results showed that optimization of the parameters (i.e., pH = 2.5 and ORP = 280 mV) leads to a reduction of reducing agent employment and fewer chemical compounds in the solution and final sludge.

Introduction

Metal ions represent the most important wastewater pollution source. In fact, their water solubility, mainly at acidic pH, enables them to dissolve easily in the natural aquatic environment, leading to their uptake by animals and plants and resulting in toxic risk.¹ Toxicological tests have clearly demonstrated the deleterious action of certain metals on flora and fauna, even at very low concentrations.^{1–11} The toxicity varies with the specific metal, with some being dangerous/lethal even at trace levels.^{2–6,9,10}

Each metal behaves, when dissolved in water or in other media, according to its own characteristics. All are completely soluble at strongly acidic pH, and most precipitate under appropriate neutral/basic conditions, depending on their concentration and their solubility constant (K_s). Dissolved metal ions form relatively stable complexes with the surrounding water molecules and exchange the water with hydroxide ions as the pH increases, until the insoluble hydroxide is formed, as schematized in eqs 1 and 2:



At higher pH values, aluminum, copper, and other metals with amphoteric behavior continue to incorporate OH⁻, forming soluble metalate ions, which contribute to further increasing the metal solubility. On the other hand, other hydroxides start precipitating at higher pH values and stay soluble until relatively strong basic values are reached.^{12–14} The precipitation of metal hydroxides remains the basis of almost all wastewater treatment processes, leading, when conducted at the appropriate pH, to a considerable proportion of the heavy metals being separated out.^{15–18} Nevertheless, the efficiency of the method is affected by many drawbacks, such as a high, and more importantly

variable, pollutant load or the presence of organic matter, recalcitrant to precipitation and, which can interfere with metals, inhibiting their insolubilization.¹⁴ However, its simplicity makes it very popular among small and medium enterprises.¹⁵

As already stated, not all metals have the same behavior, with some presenting characteristics that vary with the oxidation state. That is the case of chromium, which exists mainly in two forms, +3 and +6, although it can present various valence states ranging from +2 to +6.^{19–30} While Cr(III) readily precipitates at about neutral pH, the latter form is considerably less insoluble.^{15,16,23,25–34} Many studies have been conducted on the toxicity of the two main forms of chromium to different organisms (Table 1), evidencing that the hexavalent form is significantly more toxic for all of the organisms, which implies much lower discharge tolerance regulations and thus proper treatment before water release.^{15,16,23,25–46} Chromium's toxicity

Table 1. Reported Toxicity for Cr(III) and Cr(VI) on Representative Freshwater Fish, Crustaceans, and Vegetables^a

form	studied species	parameter	effect	concentration (mg L ⁻¹)	reference
Cr(VI)	<i>Daphnia magna</i>	14d NOEC	mortality	0.03	36
Cr(III)	<i>Daphnia magna</i>	21d NOEC	mortality	3.40	37
Cr(VI)	<i>Oncorhynchus mykiss</i>	LC50	mortality	0.18	38
Cr(III)	<i>Oncorhynchus mykiss</i>	LC50	mortality	24.0	39
Cr(VI)	<i>Lactuca sativa</i>	EC50	biomass	0.16	39
Cr(VI)	<i>Lactuca sativa</i>	NOEC	biomass	0.04	39
Cr(III)	<i>Lactuca sativa</i>	NOEC	biomass	5.90	40
Cr(VI)	<i>Scenedesmus subspicatus</i>	72 h EC 10	mortality	0.03	41
Cr(III)	<i>Scenedesmus subspicatus</i>	24 h NOEC	mortality	>0.31	42
Cr(VI)	<i>Gammarus</i> sp	48 h LC50	mortality	0.81	43
Cr(III)	<i>Gammarus</i> sp	48 h LC50	mortality	6.40	44

^a NOEC for No Observed Effect Concentration: highest concentration for which the difference between the control and test organisms is not statistically significant. EC for Effective Concentration for which the measured parameter (growth, root growth) will be reduced by 50% or 10%. LC50 for Lethal Concentration to 50% of the organisms in the given time.

* To whom correspondence should be addressed. Tel.: +33 3 81 66 57 01. Fax: +33 3 81 66 57 97. E-mail: gregorio.crimi@univ-fcomte.fr.

leads it to being on the list of priority pollutants defined by the U.S. Environmental Protection Agency and by the French Water Agency.³⁵

Many processes have been proposed to remove Cr(VI), such as adsorption using different solid materials, membrane filtration, ion exchange, liquid–liquid extraction, and electrocoagulation,^{23,25,33–36,46–50} but no processes have been found to be economically feasible. In fact, the high concentrations generally presented by industrial effluents containing Cr(VI) make all of the above techniques economically unviable, so performing a preliminary reduction to the less harmful Cr(III) followed by a subsequent precipitation of the latter form is the most used shortcut to further precipitate chromium as Cr(OH)₃.

Industrially, the reduction is generally conducted at acidic pH by means of sodium bisulfite, and the reaction is monitored by a simple Oxidation Reduction Potential (ORP) meter immersed in the reaction mixture. It is fixed at a specific value and is used to establish both the effluent and the reducing agent injections. In order to make the reaction complete, the ORP is often fixed at a value which ensures an excess of bisulfite feed. The HSO₃[−] that has not reacted with Cr(VI) then passes through the following treatment steps, potentially leading to unwanted reactions, such as the reduction of other species (i.e., the organic matter) or the production of more abundant sludge. Other reducing agents can be used, but only other sulfur compounds with oxidation states lower than +6 and iron, both in the 0 and +2 state, can be used on the industrial scale.¹⁵

Given the poor availability of literature data on this topic, this paper is intended to present a broad analysis of the current methods used to reduce toxic Cr(VI) species from real wastewaters and to propose the optimization of the classic widely employed reduction to Cr(III) with NaHSO₃, by means of a more precise determination of the optimal redox potential. This, in turn, also leads to a lower consumption of the reducing agent and optimization of the operating pH, leading to less final pollution.

Brief Review of Cr(VI) Reduction Treatment

The reduction of Cr(VI) to Cr(III) becomes mandatory until efficient alternative processes are satisfactorily improved for application on an industrial scale. Despite the relevance of the reaction, few related works can be found in the literature.²⁷ Table 2 summarizes some relevant literature works that have appeared during the past 15 years on the reduction of Cr(VI), reporting the reducing agent and the method employed. As can be seen, the reducing agents generally used to detoxify Cr(VI)-containing waters include iron, both elemental and as Fe(II); Cu(I); sulfur compounds not completely oxidized, such as sulfites and sulfides; hydrogen peroxide; pyrite, which can simultaneously supply ferrous iron and sulfides for reduction and further metal precipitation; some oxides used as photocatalysts; and also various organic compounds.^{15,18,23–27,29,32,34,48–60}

Pettine et al.²⁹ studied the reaction kinetics between H₂O₂ and chromium at different pH and hydrogen peroxide concentrations, finding that the reaction order is strictly interrelated with proton and H₂O₂ concentrations. In particular, the rate dependence on H⁺ varies from about 2 to less than 0.5 as a function of the increasing hydrogen peroxide amount.²⁹ On the other hand, H₂O₂ becomes an oxidant for Cr(III) at neutral and basic pHs,^{29,56} and reaction may be sped up by organic compounds, such as EDTA, often present in wastewaters as contaminants.²⁹ This, coupled with the different control of the reaction temperature on an industrial scale, implies that hydrogen peroxide cannot be used for the reduction of Cr(VI) in

Table 2. Literature Produced during Past 15 Years on the Reduction of Cr(VI) and Relative Reducing Agents

year	reducing agent	method	reference
2009		photocatalysis	23
2009	Fe ⁰ ; Al ⁰	electrocoagulation	15
2009	Stainless steel	electrocoagulation	34
2009	Fe ⁰	surface reduction mediated by organic compounds	25
2007	SiO ₂ /Fe ⁰ ; Sand/Fe ⁰	surface reduction	58
2007	CaS ₅	liquid reduction	49
2006	S(IV)	liquid reduction	48
2005	FeSO ₄	liquid reduction	26
2002	Fe ⁰	surface reduction mediated by microorganisms	32
2002	Fe ⁰	surface reduction	53
2002	H ₂ O ₂	liquid reaction	29
2001		photocatalysis	18
2001	Fe ⁰	surface reduction	54
2001	H ₂ O ₂	liquid reaction	56
2000	Cu(I)/O ₂ [−]	liquid reduction	24
1999	S(IV)	liquid reaction	55
1998	Fe(II)	liquid reaction	27
1997	Fe ⁰	surface reduction	51
1997	H ₂ O ₂	liquid reaction	52
1996	organic compounds	surface reduction mediated by oxides	60
1996		photocatalysis mediated by organic compounds	59
1995	FeS	surface reduction	57

wastewater, given the necessity to increase the pH for precipitating metal ions present in the solution: the excess H₂O₂ would inversely react with Cr(III), nullifying previous reduction. Moreover, as a strong reducing/oxidizing agent, the excess H₂O₂, which could be released with discharged water, is relatively toxic for the aquatic environment and for the bacteria of subsequent biological treatments, thus representing another source of toxicity.^{61,62}

Pyrite, used as fine particles, was studied by Zouboulis et al.⁵⁷ and was found to be an efficient reducing agent. The Cr(III) ions formed were precipitated and separated onto the same pyrite surface and also act as a coagulant and adsorbent. The reduction was pH-dependent and occurred rapidly at pH values less than 2.⁵⁷

Ferrous iron can also reduce Cr(VI) to Cr(III) at acidic–neutral pH, the reaction rate depending on pH, temperature, and ionic strength for a wide range of natural waters.²⁷ Ferrous sulfate can then be used to remediate groundwater contaminated by small amounts of Cr(VI).²⁶ Unfortunately, Fe(II) is rapidly oxidized by dissolved oxygen, which competes with chromium to oxidize ferrous ions, reducing its possible application on a large industrial scale.^{26,27} Also, zero-valent iron was demonstrated to be a strong reducing agent, with potential application in the detoxification of Cr(VI) contaminated waters.^{53,54} Melitas et al.⁵⁴ evidenced corrosion inhibition and passive oxide effects produced by the same chromate ions on the iron surface, even though, for slightly contaminated waters, zero-valent iron can be efficiently used. To overcome these disadvantages, Rivero-Huguet and Marshall²⁵ included organic molecules in the Cr(VI)–Fe⁰ remediation system. They were able either to reduce Cr(VI) or to form stable complexes with the reaction products, inhibiting the formation of insoluble precipitates of Cr(III) and Fe(III), thus reducing the passivation of the Fe⁰ surface, increasing both reaction rates and the performance of the solid catalyst.²⁵ The iron efficiency was also increased by means of an original bioaugmentation achieved by colonizing the Fe⁰ column with indigenous microorganisms. In this case, the hydrogen produced at the cathode when the iron corroded anaerobically stimulated anaerobic bioremediation by acting as

an electron donor for the biotransformation of reducible contaminants.³² However, although zero-valent iron is a potential reducing agent for Cr(VI), it has not yet been used to detoxify highly loaded wastewaters. Zero-valent iron activity can be improved by doping it with amorphous silica or sand, as shown by Oh et al.,⁵⁸ who found that this material can provide a large surface area to preferentially adsorb reaction products. In particular, silica demonstrated higher enhancing effects in comparison to sand because of its greater surface area, greater affinity for reaction products, and a buffering pH effect, which grant a greater longevity to Fe(0) for the reduction of Cr(VI).⁵⁸

Given the activity of iron to reduce Cr(VI), electrocoagulation has been exploited using both iron and aluminum as electrode materials. Mouedhen et al.¹⁵ used different anode/cathode configurations (Fe/Fe, PtTi/Fe/FeAl/Al, and PtTi/Al) to explain the reduction mechanism. They found that, at neutral pH, both electrochemical reduction at the anode and adsorption on Al(OH)₃-formed flocs can be responsible for the removal of Cr(VI), but they did not discriminate between the two mechanisms.¹⁵ On the other hand, electrochemical reduction by iron electrodes appeared to be very low (removal efficiency less than 5%), although the Fe(II) generated at the anode surface reduced the chromium, which readily precipitated as Cr(OH)₃ at neutral pH. The decrease of solution pH increased the electrochemical reduction of chromium, but there was a delay in the Cr(III) precipitation and contamination of the reacting medium by electrodispersed iron.¹⁵ Ölmez³⁴ optimized Cr(VI) reduction by electrocoagulation by studying the effects of applied electric current, application time, and electrolyte concentration on wastewater from a metal finishing plant. The optimal conditions he found were a current of 7.4 A, a NaCl electrolyte concentration of 33.6 mM, and an application time of 70 min.³⁴ Moreover, the amount of sludge produced was lower compared to that with chemical methods using FeSO₄, indicating that electrocoagulation is an effective method to remove Cr(VI), even though the long application time and the resulting cost of the current could constitute strong disadvantages for industrial application.³⁴

Wazne et al.⁴⁹ employed calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residues, finding removal efficiencies at basic pH of almost 60% over a period of 10 months. Sulfur compounds at low oxidation states can be efficiently used at acidic pH to reduce Cr(VI). In fact, S(IV), through its ability to condense with HCrO₄⁻ and its high reducing power, enabled the direct reduction of Cr(VI) to Cr(III) bypassing the formation of Cr(IV) and Cr(V) intermediates.⁵⁰ Pettine et al.⁴⁸ studied the reaction of S(IV) and Cr(VI) as a function of pH, temperature, and ionic strength, finding that it is independent of ionic strength in the range of 0.01–1 M NaCl in solution, there is a first order dependence on proton concentration, and there is a small influence from the temperature. They also found that small amounts of Fe(III) exert a catalytic effect, while formaldehyde reacts with S(IV) to form the CH₂OHSO₃⁻ adduct, which does not react with chromium.⁴⁸

Reducing agents and various metal oxides can be used as catalysts and photocatalysts for the detoxification of Cr(VI), speeding up the slow reaction between organic compounds and Cr(VI) and taking advantage of solar energy.^{18,23,58–60} Titanium dioxide and zinc oxide are the most frequently used, even if the currently obtained reaction rate is insufficient for industrial applications.^{23,25,59} Various works have demonstrated that the presence of different organic compounds accelerates the reaction, facilitating the charge transfer driven by light in the near UV–visible region⁵⁹ or reacting with Cr(VI) adsorbed on the

catalyst surface.⁶⁰ Deng and Stone⁶⁰ presented a detailed investigation into the reactivity of different organic reducing agents and oxide surfaces on surface-catalyzed Cr(VI) reduction, showing that many organic compounds can help reduction remediation of chromate, even though concentrations must be low and reaction rates are not fast.

Abu-Saba et al.²⁴ studied the reduction of Cr(VI) present in seawater photocatalyzed by copper in the presence of superoxides. They found that the Cu(I), produced during superoxide redox cycling, can reduce the hexavalent chromium, but there is a strict correlation with metal speciation and concentrations in surface waters with low ionic strength and pH < 7.²⁴

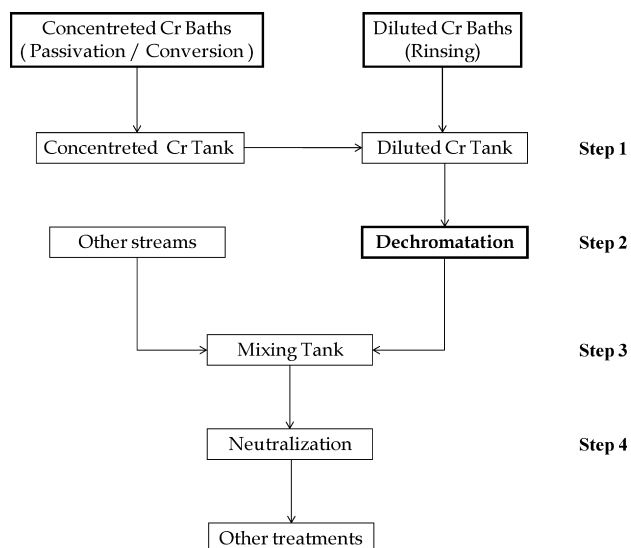
Sulfur presents many oxidation states, and several of its compounds with intermediate oxidation states are able to reduce Cr(VI). Pettine et al.⁴⁸ reported an interesting study on the reduction of Cr(VI) by S(IV), concluding that at acidic pH the reaction is rapid enough to be conducted on an industrial scale with engineered systems for the removal of Cr(VI) from wastewater. Then, the rapidity of the reaction and the opportunity to monitor its success by means of a simple ORP sensor allow industries to use sulfur(IV) compounds in their wastewater treatment plants for the preliminary reduction of Cr(VI).^{14,46} Then, it is evident that, for the reduction of Cr(VI) by means of NaHSO₃, the pH and ORP parameters play a key role.

Materials and Methods

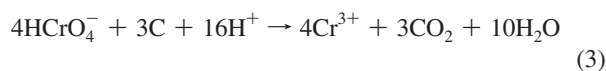
The experimental study for the reduction of Cr(VI) by means of NaHSO₃ was conducted as follows: K₂Cr₂O₇ was dissolved in distilled water to prepare solutions of 180, 340, and 680 mg L⁻¹ of Cr(VI), while a reducing solution was prepared by dissolving pure NaHSO₃ in a 10-fold volume of water. Then, 150 mL of each chromate solution was titrated, adding the bisulfite solution dropwise, measuring the ORP values after 15 min for each measurement to make the reaction complete. All reagents were of chemical grade, purchased from Sigma Aldrich (France). The pH of the medium was measured by a WTW pH meter equipped with a WTW SenTix 41 pH Electrode, while the redox potential was evaluated by means of a WTW ORP meter equipped with a Schott Instruments Platin Elektrode BlueLine 32 Rx.

The evolution of the reduction reaction was evaluated by assaying the Cr(VI) present in the solution during the titration using the colorimetric method. The Cr(VI) present in samples periodically withdrawn from the reaction solution were adjusted in the pH range 1–9, as required by the addition of NaOH, and reacted with diphenylcarbazide to form Cr(III) and diphenylcarbazone. The latter forms a red–violet complex determined by measuring its absorbance at 540 nm using a WTW SpectroFlex series 6100. COD was determined using the dichromate COD method based on the use of colorimetric measurement for high-range COD (0–1500 mg L⁻¹ range) using potassium hydrogen phthalate solutions as a standard. Samples and standards were placed on a preheated COD reactor (model FB15006, Fisher Bioblock Scientific, Illkirch, France) for 2 h at 148 °C. Following incubation and cooling at room temperature, the absorbance was measured at 605 nm using a photometer (model COD Vaxio, Aqualytic PCCompact, Dortmund, Germany) apparatus. It must be noted that the method is based on the oxidation of organic compounds by an acidic chromate solution, and Cr(VI) present in some samples, such as waters of the diluted chromium tank (Scheme 1), would affect the measure because this adds more chromium reactant to the solution. The COD results were then corrected by adding the

Scheme 1. Physicochemical Treatment Plant at Electrolyse d'Acéy (Vitreaux, Haute-Saône, France) with Particular Emphasis on the Dechromatation Step



oxygen corresponding to the added chromium. In fact, both Cr(VI) and molecular oxygen act as oxidants for organic compounds and, assuming in our calculation the oxidation state of carbon to be 0, we can write

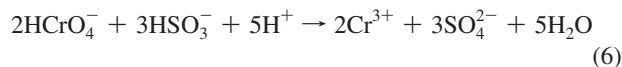


that is, 1 mol of oxygen equals 4/3 mol of chromium. From this evidence, the corresponding COD value masked by the presence of Cr(VI) in the samples can be calculated as

$$\text{COD} = \frac{\text{mg}_{\text{Cr(VI)}}}{52} \times \frac{3}{4} \times 32 \quad (5)$$

where $\text{mg}_{\text{Cr(VI)}}$ is the concentration, in milligrams per liter, of hexavalent chromium previously detected in the solution, 52 is the molecular weight of chromium, and 32 is the molecular weight of O_2 .

The reduction of Cr(VI) by means of NaHSO_3 was also carried out using a concentrated industrial effluent, withdrawn directly at the storage tank of the treatment plant of Electrolyse d'Acéy, (Vitreaux, Franche-Comté, France), whose Cr(VI) detoxification step is schematized in Scheme 1. Cr(VI) streams from concentrated baths are periodically sent to a tank used for the storage of the dilute chromate streams. Then, the mixed waters are continuously pumped into another tank used for the hexavalent chromium detoxification step. Here, the solution is stirred with NaHSO_3 under controlled pH and ORP, set at 2.1 and 230 mV, respectively. The ORP sensor measures the redox potential of the solution, determined by the dissolved matter, and low values, associated with a concentration of reducing agents higher than that of the oxidant ones, ensure the reduction reaction is complete and no Cr(VI) remains unreacted. The overall reaction can be written as follows:



The necessity to operate at acidic pH is therefore clear. Indeed, the reaction rate is acceptable for industrial application

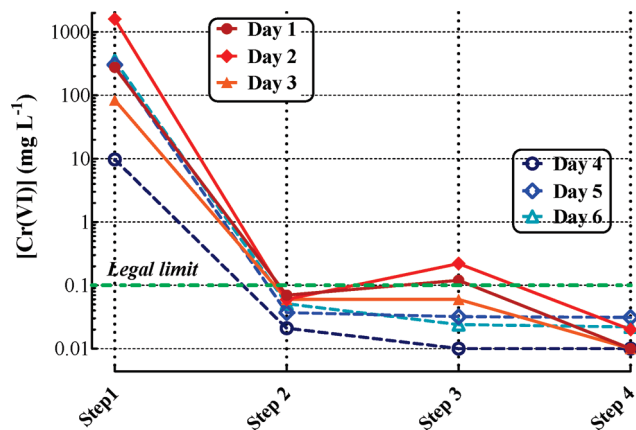


Figure 1. Cr(VI) concentration during different wastewater treatment steps (see Scheme 1). Full lines and symbols concern Electrolyse d'Acéy (days 1, 2, and 3); dotted lines and empty symbols are relative to the treatment plant missing the decyanidation step (days 4, 5, and 6).

at pH values lower than 3,^{15,48} thus often requiring the addition of an acid, monitored by a pH sensor. On the other hand, values lower than 1.8 are dangerous, owing to the release of noxious gaseous SO_2 emissions under these conditions.⁵⁵ The detoxified effluent is then pumped into a storage tank, where all of the streams are collected. Then, the wastewaters are forwarded to the neutralization tank and on to the flocculation step where heavy metals are precipitated as hydroxides, which are further decanted and separated from the water.

Results and Discussion

The reduction reaction between Cr(VI) and the reducing agent converts the highly toxic hexavalent form of chromium to the much less noxious trivalent form, which is then removed as Cr(OH)_3 by means of precipitation at neutral pH. This procedure leads to an efficient detoxification of the wastewater, as do other preliminary treatments, such as the destruction of CN^- by the addition of oxidants. Henceforth, this will be referred to as the "dechromatation" step.

This step, carried out at Electrolyse d'Acéy, was surveyed for three consecutive days to evaluate to effectiveness of the process, and the results are reported in Figure 1 in terms of Cr(VI) concentration during the different stages of the wastewater treatment. It can be easily deduced that the reduction reaction takes place quantitatively, reducing the chromate concentrations below the legal limit. In fact, irrespective of the initial level in the solution, after the dechromatation step, the hexavalent chromium concentration was practically 0. Unexpectedly, the concentration of Cr(VI) increased after mixing with other effluents and lowered during the neutralization step. It must be noted that, in the tank containing alkaline effluent for cyanide removal by oxidation treatment with bleach or hydrogen peroxide (step 2 in Scheme 1), excess oxidant is added. In fact, cyanide complexes being very stable, an excess of oxidant must be fed to ensure the complete reaction. In fact, the effluent is mixed with other acid streams (step 3 in Scheme 1), allowing undesired reactions such as the reoxidation of Cr(III) to Cr(VI). Many research works have also demonstrated the ability of various hydroxides, especially in the early stages of their formation, to adsorb Cr(VI), and this can be the case with the solid hydroxides formed during the neutralization step, which led to their reduction below legal limits (Figure 1).¹⁵ The same test conducted in another treatment plant (results relative to days 4, 5, and 6 in Figure 1) without decyanidation treatment, besides

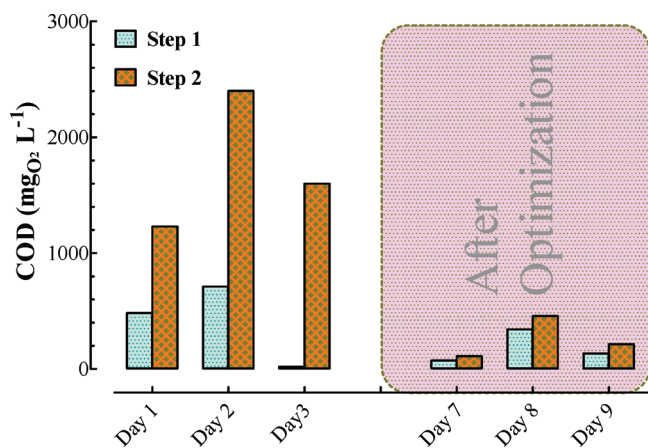


Figure 2. COD values for steps 1 and 2 before (days 1, 2, and 3) and after optimization of the dechromatation step (days 7, 8, and 9).

confirming the efficiency of bisulfite reduction, corroborates the assumption that oxidants from other reactors can reoxidize trivalent chromium.

Water streams from surface treatment industries are highly loaded with many pollutants such as various heavy metals and organic matter (oils and solvents). The aim of our group being to detoxify wastewater of all pollutants, during the survey, we measured different parameters such as the COD. The findings are represented in Figure 2 for samples analyzed before (days 1, 2, and 3) and after (days 7, 8, and 9) our further optimization. We would expect the same COD values before and after dechromatation treatment: concerning the reduction reaction just the Cr(VI) with, at least, a slight decrease of the COD values due to dilution by the bisulfite solution. However, after the dechromatation step, each sample presented a higher COD with respect to the same sample before treatment, even when the initial solution presented only a small amount of organic matter. The COD expresses the amount of oxygen necessary to oxidize the *oxidizable* substances present in solution, whether they are organic or not. NaHSO₃ used as a reducing agent can, then, increase the COD, indeed interfering with the measurement of organic compounds, explaining our unexpected results if used in excess. Total organic carbon (TOC) measurements could be used to provide a better evaluation of the presence of organic compounds in wastewater, but COD is the parameter generally taken to assess water toxicity. Thereafter, bisulfite, with its reducing power, could represent a further threat to aquatic life, even if it is just by consuming the oxygen present in the water and indispensable for river and marine populations.

On an industrial scale, reactions must be conducted automatically and the yield maximized. Thus, reduction must be complete, given the stringent necessity to eliminate Cr(VI), and rapid too, in order to continuously process the polluted streams, without storing them. A simple ORP sensor, measuring the redox potential of the solution, which is the result of summing the reducing power of Cr(VI) and the oxidizing power of NaHSO₃ (the contribution of organic compounds is ignored, due to their recalcitrance at ambient temperature, while other metals are already at their most favorable oxidation state), represents a very useful tool for reaction monitoring. On the other hand, the completeness of the reaction is ensured by feeding an excess of reducing agent into the medium, achieved by setting the ORP sensor under the optimal value, generally lying between 180 and 240 mV on an industrial scale. Thus, improvement of the dechromatation step, achieved by bisulfite reduction, relies on the optimization of the ORP value.

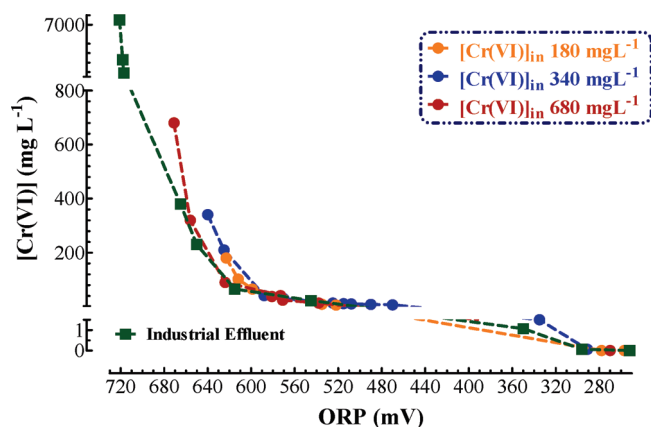


Figure 3. ORP values vs [Cr(VI)] for different pure Cr(VI) solutions and for a concentrated industrial effluent coming from Electrolyse d'Accey.

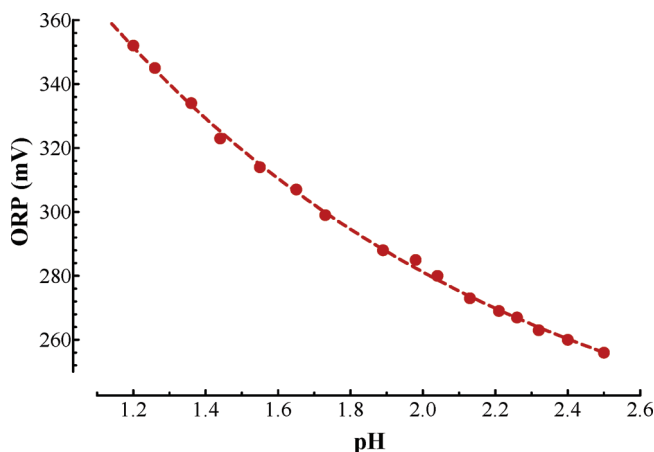


Figure 4. pH vs ORP for a solution with [Cr(VI)]_{in} = 340 mg L⁻¹ (see Figure 3) after the dechromatation procedure.

To exclude the influence of any other compounds, given the complex composition of industrial streams, Cr(VI) reduction was carried out in the laboratory using pure K₂Cr₂O₇ at different concentrations to determine whether the initial amount can influence the ORP measurement and, more importantly, the value at which the reaction is complete. The reaction was conducted at pH 2.5, which is the highest acceptable value for industrial purposes, given the lower reaction rate for greater values.^{15,48} In fact, attempts (not reported here) at lower pH values confirmed that the reaction takes place more easily and rapidly, while at higher values the reaction is too slow. Results are represented in Figure 3 for Cr(VI) concentrations of 180, 340, and 680 mg L⁻¹ and for a highly loaded effluent. All samples presented the same behavior, including the industrial one, with a rapid ORP decrease when the Cr(VI) concentration fell below 20 mg L⁻¹, conferring an asymptotic behavior on this particular conversion curve. The results definitely confirm the reduction efficiency and, crucial for our investigation, indicate that the ORP value at which Cr(VI) is not detected anymore is equal to 300 mV, suggesting an increase in its level to reduce the bisulfite feeding.

According to eq 6, the dechromatation reaction must be conducted at acidic pH. Thus, as the ORP measurements depend on pH, the sample with 340 mg L⁻¹ of Cr(VI) after total reduction was slowly acidified, and ORP values were recorded at different pHs. As expected (Figure 4), the redox potential of the solution increased as the pH fell, showing a slight exponential rate. This final evidence indicates the pH value as another opportunity to optimize the dechromatation step, with

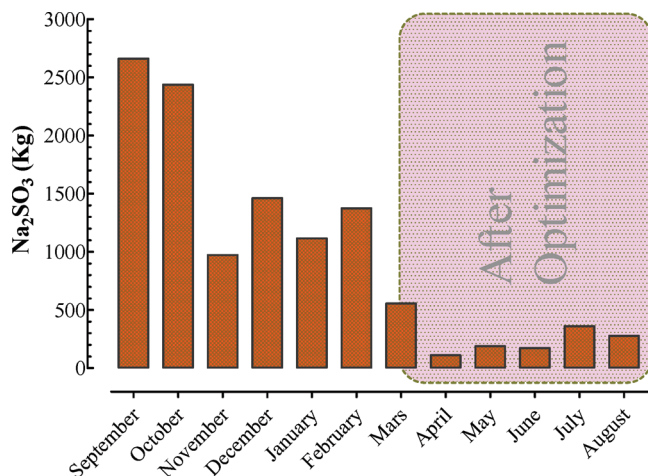


Figure 5. Monthly consumption of Na₂SO₃ before and after pH and ORP optimization at Electrolyse d'Acey.

a further possible increase of the setting of the ORP value for strongly acidic streams (bearing in mind the release of toxic gas for pHs lower than 1.8⁵⁵), or to raise the pH to 2.5 to consume less acid, for streams needing to be acidified.

Finally, all of our suggestions were adopted at Electrolyse d'Acey to confirm their relevance on the industrial scale, increasing the ORP value to 280 mV (a slight excess must ensure the absence of noxious hexavalent chromium) and a pH of 2.5 instead of 230 mV and 2.1, respectively. Samples withdrawn from the dechromatation and the neutralization tanks over two months confirmed our laboratory results with a constant absence of Cr(VI). In addition, as can be seen from the right side of Figure 2, the COD value after optimization of the dechromatation step is just slightly higher than before, confirming the relationship between the HSO₃⁻ excess and the higher value of the measured COD. A slight excess of bisulfite cannot be avoided, since it is preferable to have it, or its oxidation products, than Cr(VI) in the final solution. Finally, as shown in Figure 5, the consumption of bisulfite after the optimization is sensibly lower than before, confirming the crucial role of pH and ORP parameters in the control of the reduction.

Conclusions

The dechromatation step is crucial for reducing Cr(VI) from wastewaters before the precipitation treatment through a pH increase. On the industrial scale, the reaction is carried out using bisulfite as a reducing agent at acidic pH. The reduction is generally carried out at ORP values lower than 230 mV and at a pH equal to 2.1. Our survey on a real industrial stream and the subsequent laboratory tests led us to optimize the ORP and pH value settings, allowing minor consumption of chemical reagents and less environmental pollution. The monthly survey at the industrial site before and after optimization confirmed the practical, economical, and ecological interests of the process improvement. Indeed, the advantages are interesting in terms of simplicity and cost for industry, and also, from an ecological point of view, for the reduction of pollutant release. It must also be stated that less bisulfite means a lower COD value if it remains unreacted and less final sludge, given the precipitation of the SO₄²⁻ formed during subsequent treatments. In fact, since the precipitation of metals is made by means of lime, sulfate ions precipitate as CaSO₄, and the presence of a higher amount SO₄²⁻ ions would contribute to an increase in the final amount of sludge and, consequently, processing costs.

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