

EVALUATING ARSENIC AND MANGANESE REMOVAL FROM WATER BY CHLORINE OXIDATION FOLLOWED BY CLARIFICATION

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Abstract - This paper investigates the simultaneous removal of arsenic [As(V) or As(III)] and manganese [Mn(II)] from natural waters of low and high turbidity by clarification (with polyaluminum chloride and aluminum sulfate as primary coagulants) associated or not with chlorine pre-oxidation. The results showed that the clarification process exhibited low Mn(II) removal, that varied from 6% to 18% and from 19% to 27% for natural waters of low and high turbidity, respectively. The use of chlorine as pre-oxidant increased Mn(II) removal up to 77% and was associated with the formation of birnessite. Regarding As(V) removal by clarification, particularly for high turbidity water, a concentration lower than that established by the National Drinking Water Quality Standards (10 µg.L⁻¹) was achieved in almost all tests. Oxidation preceding the clarification led to As(III) removal efficiencies from 80% to 90% for both coagulants and types of water.

Keywords: Arsenic; Manganese; Clarification; Oxidation; Water treatment.

INTRODUCTION AND RELEVANCE

Among the chemical characteristics of natural water, manganese and arsenic concentrations play an outstanding role in the raw water quality due to the importance of both parameters in the national and international drinking water standards and the significant frequency at which they appear in water sources.

Manganese is one of the most abundant metals in the earth's crust and, like other transition metals, it presents several forms and oxidation states (0 to +7). It is present in several types of rocks and in the environment, not as a pure metal, but as oxides (MnO₂), hydroxides (Mn(OH)₂), bicarbonates (Mn(HCO₃)₂) and sulfates (MnSO₄), being less soluble and result-

ing in concentrations in surface waters rarely higher than 1.0 mg.L⁻¹, except in the same circumstances as iron in groundwater of deep wells with low concentrations of dissolved oxygen.

The prevalence of each species of manganese depends on the pH, Eh and temperature, and, in the usual range of Eh values of surface waters (0.5 to 1.0 V), manganese is divalent and largely soluble to pH close to 8.0. Keeping the Eh conditions and increasing the pH, manganese appears in the form of low-solubility oxides and hydroxides. Thus, an increased pH or Eh would be more favorable for the removal of manganese.

As it is more stable in the reduced form than iron, manganese oxidation is more difficult, and simple aeration is generally insufficient for its removal.

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Additionally, it may be chelated by organic matter. Although this does not affect substantially the removal mechanisms, it can result in the formation of by-products when pre-disinfection is performed with chlorine compounds.

At the concentrations usually found in natural water, manganese does not present a health hazard and the inconveniences are of an aesthetic nature; at concentrations higher than 0.01 mg.L^{-1} , it has an adstringent flavor. Concentrations higher than 0.05 mg.L^{-1} – the limit of the American and Canadian Drinking Water Quality Standards – it can cause the appearance of stains on garments and sanitary facilities. The World Health Organization (WHO, 2011) establishes a significantly higher value (0.4 mg.L^{-1}), emphasizing the possibility of complaints from users about appearance, taste and odor. However, higher concentrations may result in damages of a neurological and psychological nature (WHO, 2011).

The relevance of Mn is evidenced by the successive monitoring of water quality performed in Minas Gerais state (Brazil), which shows this metal to be the second most frequent parameter of violation for the streams of classes 1 and 2, for which the maximum allowable concentration of 0.10 mg.L^{-1} coincides with the provisions of the Brazilian Water Quality Standards established by Regulation 2914 (Health Brazil, 2011). This Regulation allows the concentration of Mn to be higher than the maximum contaminant level, provided that this element is chelated with chemical products of proven low risk to health and the total concentration of Mn does not exceed the value of 0.4 mg.L^{-1} .

Arsenic is part of the earth's crust, prevailing in the form of arsenopyrite (FeAsS), orpiment (As_2S_3) and realgar (AsS). In the four states of oxidation (-3, 0, +3 and +5), it usually appears in natural water as arsenite (+3) and arsenate (+5). The prevalence of either form is governed by the Eh and pH, and within the range from pH 6.5 to 8.5, usual for most of the surface and groundwater, the arsenite form (H_3AsO_3) prevails, while the arsenate form (HAsO_4^{2-}) is present in the pH range from 7.0 to 11.5 (Montgomery, 2005). This metalloid appears mostly in the dissolved, more toxic form (+3) – this form is estimated to be 25 to 60 times more toxic than arsenate – prevailing mostly in groundwater with low concentration of dissolved oxygen.

Besides the natural sources, arsenic may be conveyed to the natural water from anthropogenic activities related to mining, agriculture – from fungicide, insecticide and herbicide use -, the wood industry

and several industrial activities (especially glass and electronic products), besides the burning of fossil fuels and subsequent leaching by rain.

Studies of the possible damages to human health due to the extended consumption of water containing arsenic made in the past decades report the development of tumors in the kidney, liver and bladder, besides damages to skin and the circulatory system. In countries like Mongolia, China, India, Argentina, USA, Chile, Hungary, Mexico and others, part of their population is supplied by groundwater with significant concentrations of As.

The cumulative character of arsenic has resulted in a progressive reduction of the maximum concentrations established by the several drinking water quality standards. Particularly in Brazil, the limit established by the mentioned Regulation 2914 (0.01 mg.L^{-1} , the same as that established by the American standard and by WHO) is ten times lower than that recommended by the standard that prevailed in January, 1993.

The techniques for arsenic and manganese removal include clarification, adsorption, oxidation, ion exchange and reverse osmosis. In water treatment plants, the techniques usually applied for removal of arsenite [As(III)] involve pre-oxidation followed by adsorption or coprecipitation of the arsenate [As(V)] formed, whereas for manganese its oxidation from Mn(II) to Mn(IV) leads to the formation of a black precipitate. In either case, oxidation can be performed with ozone, hydrogen peroxide and chlorine compounds.

Arsenic removal in developed countries usually employs adsorption by granular activated carbon, particularly for groundwater in which a low concentration of particles hinders coagulation. However, due to their high implementation cost, granular activated carbon filters are not used in Brazil. In water treatment plants for public supply in almost all developing countries, the application of this process is restricted to the rare use of powdered activated carbon.

In view of this, the general purpose of this paper was to evaluate, on a bench scale, arsenic and manganese removal in surface waters by clarification, associated or not with pre-oxidation. The intent was to evaluate the influence of the characteristics of raw water, of the initial concentration of As and Mn and of the type of coagulant, aluminum sulfate (AS) and polyaluminum chloride (PAC), on the removal of these elements, as well as to obtain a better understanding of the mechanisms for removal of As and Mn.

METHODOLOGY

Experimental Apparatus, Characteristics of the Raw Waters and the Chemical Products

The clarification and oxidation tests were performed simultaneously in two Jar Test apparatuses, fitted with six 2 L jars with rotating blades and rotation control, which are a compulsory tool for a more accurate operation of water treatment plants.

These apparatuses are suitable to apply velocity gradients ranging from 10 to 2000 s^{-1} – required for rapid mixing and flocculation – and simultaneous dispersion of the chemical products and collection of the settled water 7 cm from the liquid surface.

The tests were performed with two surface natural waters, with low and high turbidity, aiming at simulating the operational conditions prevailing in most of the treatment plants in the country in the rainy and dry seasons. Manganese chloride ($MnCl_2 \cdot 6H_2O$), sodium arsenate [$Na_2HAsO_4 \cdot 7H_2O$, for As(V)] and sodium arsenite [$NaAsO_2$ for As(III)] were used to increase the concentrations of the elements of interest. For both elements, the removals at concentrations close to the limits of the national drinking water standard and 10 to 15 times higher than those limits were evaluated, as concentrations of this magnitude are frequent in the natural waters in the region of Minas Gerais state. After the collection, the water was stored in polyethylene reservoirs and submitted to stirring prior to the withdrawal of samples for execution of the tests, aiming at avoiding sedimentation of the suspended particles. The characteristics

of the waters used in the clarification and oxidation tests are presented in Table 1. Two aliquots of Type 1 water were contaminated with sodium arsenite ($NaAsO_2$, Vetec, 99% purity) aiming at providing concentrations of As(III) of $328 \pm 16 \mu g \cdot L^{-1}$ and $173 \pm 12 \mu g \cdot L^{-1}$, especially prepared for the pre-oxidation tests.

The characteristics of the waters listed in Table 1 were determined with equipment traditionally used in water treatment – turbidimeter, potentiometer, colorimeter, among others – duly calibrated as recommended by the manufacturers.

Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) and polyaluminum chloride 10/12 ($Al_n(OH)_mCl_3$), primary coagulants extensively used in water treatment plants, were applied in the clarification tests. Additionally, calcium hydroxide ($Ca(OH)_2$, 20% m.v) – to increase the coagulation pH –, sodium hypochlorite ($NaOCl$, 12% m.v) – for the pre-oxidation tests –, sodium thiosulfate ($Na_2S_2O_3$, 99%) for dechlorination, and nitric acid PA (HNO_3 , 99.8%), for preservation of samples, were used.

Hydraulic Parameters for the Clarification Tests

For definition of the optimum coagulation conditions – coagulant dose and respective coagulation pH to be employed in the subsequent arsenic and manganese removal tests –, the hydraulic parameters (Table 2) used in the Jar Test equipment were established in conformity with recommendations of the literature and the Brazilian Technical Standards Association (ABNT 1992).

Table 1: Average and standard deviation of the characteristics of the waters used in the tests.

Characteristic	Water			
	Type IA	Type IB	Type IIA	Type IIB
Turbidity (ntu)	13.4 ± 0.5	12.2 ± 0.6	208.4 ± 1.5	201.6 ± 2.6
pH	7.2 ± 0.1	7.2 ± 0.0	7.1 ± 0.1	7.1 ± 0.1
Electric conductivity ($\mu S \cdot cm^{-1}$)	156.2 ± 3.5	158.8 ± 2.6	152.3 ± 2.1	149.2 ± 2.8
Temperature ($^{\circ}C$)	21.2 ± 0.2	21.6 ± 0.3	20.5 ± 0.3	20.9 ± 0.1
Dissolved oxygen ($mg \cdot L^{-1}$)	6.5 ± 0.2	6.4 ± 0.4	6.4 ± 0.3	6.3 ± 0.3
Redox potential (mV)	427 ± 6	436 ± 4	439 ± 2	435 ± 8
Total alkalinity ($mg \cdot L^{-1} CaCO_3$)	17.0 ± 0.3	16.6 ± 0.6	16.2 ± 0.2	16.0 ± 0.4
Apparent color (Hu)	28.1 ± 0.6	26.3 ± 0.2	231.3 ± 1.0	242.1 ± 1.2
Concentration of manganese ($\mu g \cdot L^{-1}$)	990 ± 12	150 ± 8	1120 ± 14	120 ± 6
Concentration of arsenic ($\mu g \cdot L^{-1}$)	157 ± 10	32 ± 5	149 ± 9	36 ± 6

Table 2: Hydraulic parameters used in the tests for definition of the optimum coagulation conditions.

Coagulation		Flocculation		Sedimentation
Rapid mix detention time (s)	Rapid mix velocity gradient (s^{-1})	Flocculation time (min)	Flocculation velocity gradient (s^{-1})	Settling velocity ($cm \cdot min^{-1}$)
15	600 ± 20	20	35 ± 5	2.0

Regarding the parameters adopted, the ABNT recommends velocity gradients (G) ranging from 700 to 1100 s^{-1} for rapid mixing, with a detention time (T) shorter than 5s, resulting in a GT product higher than 3500. For all the tests performed, the parameters shown in Table 2 provided a GT product higher than 9000 and ensured a homogeneous dispersion of the coagulants, for any coagulation conditions.

Later on, for the optimum coagulation conditions for both primary coagulants and in the same rapid mixing conditions, sedimentation and flocculation optimization tests were performed – keeping the flocculation velocity gradient value ($35 \pm 5 s^{-1}$) fixed. These tests were essentially based on the turbidity removal for both waters.

Definition of the Optimum Coagulation, Flocculation and Sedimentation Conditions

As previously mentioned, the first experimental tests aimed, based on the remaining turbidity after sedimentation, at the definition of the optimum coagulation conditions for both coagulants and both waters. For this purpose, the coagulant doses and the coagulation pH with and without application of alkalinizing agent were varied in this step, without addition of salts to increase the concentrations of arsenic and manganese.

Under the optimum coagulation conditions, the flocculation time ranged from 5 to 30 min, keeping the flocculation gradient ($35 \pm 5 s^{-1}$) constant. After definition of the four flocculation times – for two waters and two primary coagulants -, the sedimentation times ranged from 1 to 7 min.

Once again, the variation of the flocculation and sedimentation times was based on the design parameters of water treatment plants referred to in ABNT (1992). Both the flocculation time and the settling velocity govern the dimensions and, certainly, the construction cost of these units. In this context, ABNT (1992) refers to 30-40 min flocculation times for mechanical flocculators and to 20-30 min for hydraulic units. The evaluated sedimentation times led to settling velocities ranging from 1.0 to 7.0 $cm \cdot min^{-1}$, also based on the recommendations of ABNT (1992) that associates these velocities - from 1.74 to 2.80 $cm \cdot min^{-1}$ – with the influent flow rate to the water treatment plant.

Pre-Oxidation Tests

Prior to the clarification, pre-oxidation tests were performed with sodium hypochlorite, with initial

chlorine doses of 2.5, 3.0 and 3.5 $mg \cdot L^{-1}$, associated with 5, 30, 60 and 120-min contact times. After addition of the oxidant, during the mentioned contact times, the volume of the jar was submitted to stirring at a velocity gradient of $35 \pm 5 s^{-1}$ to prevent sedimentation of particles. After the contact time had elapsed, samples were collected for analysis of residual chlorine, arsenic and manganese, and the clarification was started under the previously optimized conditions. At the end of the clarification, the collected sample was submitted to dechlorination with sodium thiosulfate for subsequent determination of the concentrations of As and Mn.

Sludge Characterization

The sludges obtained during the clarification of waters of high turbidity (without the spike with As or Mn) with both coagulants were harvested and characterized by X-ray diffraction (XRD) and used to determine their point of zero charge (PZC) and the isotherms for As adsorption.

The adsorption isotherms were determined according to the ASTM D3860 Standard (2000) and performed at the temperatures of 20, 30 and 40 °C. For this, seven 200 mL erlenmeyers containing 131 $\mu g \cdot L^{-1}$ of As(V) received masses of 0.4, 1.0, 2.0, 3.0, 4.0, 10.0 and 20.0 mg of dry sludge (adsorbent). 200 mL of the adsorbate solution was poured into another erlenmeyer, without adsorbent, for the blank. The erlenmeyers were then placed, under 180 rpm stirring, in a shaker incubator for two hours. After that time, aliquots of each sample were filtered and the residual concentration of arsenic determined in the filtered sample. Each condition was performed in triplicate.

XRD analyses were performed using a Shimadzu XRD-6000 diffractometer, with graphite monochromator, nickel filter, $FeK\alpha$ radiation ($\lambda = 1.9360 \text{ \AA}$), 40 kV and 20 mA. A scan of 2-90° 2 θ was used at a rate of 2° 2 θ /minute and the results were converted to $CuK\alpha$ ($\lambda = 1.5406 \text{ \AA}$) for data processing, as detailed by Teixeira *et al.* (2013).

The PZC was determined according to the procedures described in Aquino *et al.* (2010). For this, six erlenmeyers containing different masses of sludge had their pH initially adjusted to 3.0 with 0.1 mol/L HNO_3 and/or 0.1 mol/L NaOH and then kept under constant mixing (130 rpm) at ambient temperature for 24 hours to attain equilibrium. After such period the pH was measured and a graph relating the mass percentage of sludge with final pH was plotted. The procedure was repeated changing the initial pH to 7.0 and then to 11.0.

Statistical Analyses

The data analysis tool of the software Excel was used in order to verify whether the statistical differences among the removal efficiencies of the elements studied in the different conditions were significant. Data comparisons were performed by evaluating the p-value attained. For p-values lower than 0.05, the hypothesis of equality among the results compared was rejected with a confidence interval of 95%.

RESULTS AND DISCUSSION

Evaluation of the Arsenic and Manganese Removal Exclusively by Clarification

The results (20 tests) for optimization of the flocculation and sedimentation are presented on Table 3. Although it is not the main purpose of this work, the higher efficiency of polyaluminium chloride in the removal of the suspended particles should be emphasized, both in the time required for formation of the flocs and in the magnitude of the remaining turbidity itself.

The results of the clarification tests without pre-oxidation, shown in Table 4, refer to 12 analyses of each element (out of a total of 192 analyses) with the concurrent use of two Jar Test apparatuses.

Regarding the manganese removal, the results show that the concentrations of this element were slightly reduced in the tests performed. At the Eh value of the waters (amounting to 0.4V) and the co-

agulation pH value (amounting to 7.2), most of the manganese is present in the divalent form and, therefore, dissolved. So, manganese removal is due to the adsorption of this element on the particulate material present in the sample or on the aluminum hydroxide flocs. Although of low magnitude, greater removals of both coagulants with the higher turbidity water tend to confirm this assertion.

Also according to the stability diagram ($E_h \times pH$) for Mn (Figure 1), keeping the same Eh conditions for the waters, the increase of the coagulation pH above 8.0 would favor the formation of manganese oxide-hydroxide (MnO-OH) and subsequent precipitation.

The arsenic removal occurred more significantly for the higher turbidity waters at both concentrations, probably favored by its adsorption on the aluminum hydroxide precipitate formed. The greater formation of precipitate (sludge) for both coagulants, resulting from the higher concentration of suspended particles and higher dose applied, increased the surface area required for the adsorption of the arsenate ion ($HAsO_4^{2-}$), which predominates under the conditions of coagulation (Figure 2). Additionally, the higher coagulant dose applied in these conditions also leads to the formation of other species that, in turn, are able to develop positive charges on the surface of the precipitate, as shown in Figure 3, which would possibly aid the removal of the dissolved arsenate anion by adsorption. This fact is explained by Smedley and Kinniburgh (2002), who established that the adsorption/desorption of arsenic from particulate material are primarily responsible for the changes in the concentrations of this anion in natural waters.

Table 3: Optimized coagulation, flocculation and sedimentation conditions for Type I and Type II Water.

Study Water	Coagulant	Dose* ($mg.L^{-1}$)	Coagulation pH	Flocculation time (min)	Settling velocity ($cm.min^{-1}$)	Remaining turbidity (ntu)
Type I	AS	15 (0.60)	7.4 ± 0.3	15	2.0	2.48 ± 0.45
	PAC	4 (0.24)	7.1 ± 0.2	10		1.17 ± 0.39
Type II	AS	38 (1.52)	7.1 ± 0.2	20	2.0	1.40 ± 0.61
	PAC	35 (2.10)	7.3 ± 0.3	5		1.11 ± 0.50

*The figures in parentheses refer to the calculated concentrations of Al^{3+} .

Table 4: Results of the clarification tests in terms of arsenic and manganese removal.

Water Type	Coagulant	Manganese		Arsenic	
		C_r ($\mu g.L^{-1}$)	ER (%)	C_r ($\mu g.L^{-1}$)	ER (%)
IA	AS	839 ± 14	15	72.6 ± 2.8	54
	PAC	807 ± 13	18	82.5 ± 3.0	48
IB	AS	141 ± 4	6	7.8 ± 1.0	76
	PAC	137 ± 7	8	9.6 ± 1.4	70
IIA	AS	835 ± 21	25	10.3 ± 0.6	93
	PAC	820 ± 19	27	8.2 ± 0.9	94
IIB	AS	98 ± 10	19	2.8 ± 0.4	92
	PAC	89 ± 9	26	2.0 ± 0.4	94

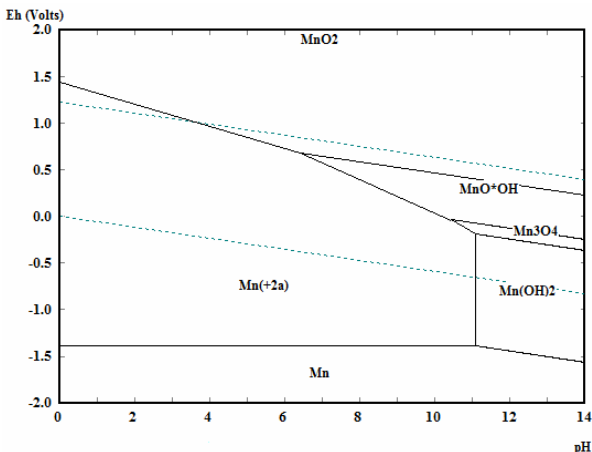


Figure 1: Stability diagram of the manganese in water at 25 °C and 10^{-5} molal concentration.

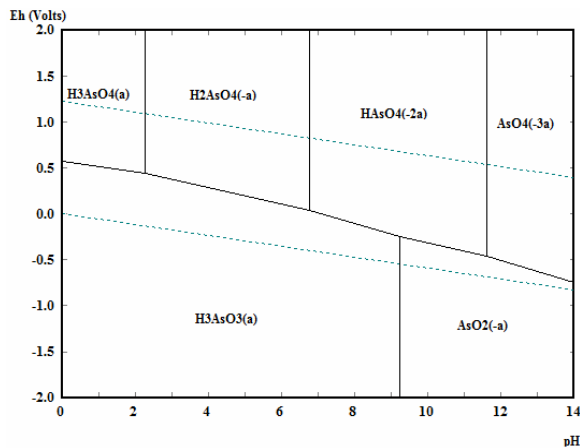


Figure 2: Diagram for stability of arsenic at 25 °C and 10^{-6} molal concentration.

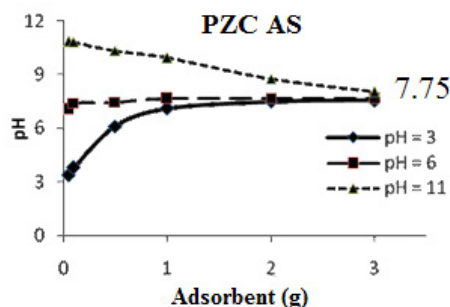
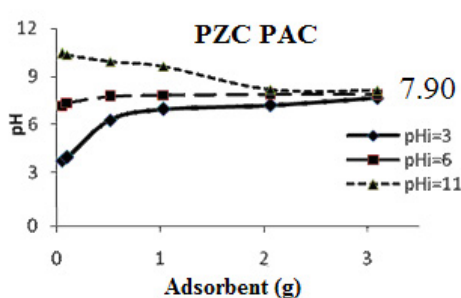


Figure 3: Determination of the Point of Zero Charge for the sludge from coagulation with polyaluminum chloride and aluminum sulfate.

In this context, the reorganization of the electric charges on the coating surface of the hydroxide and of the species formed from coagulation that involve the flocs has been considered to be the main mechanism in the arsenate adsorption process, forming complexes. This process is controlled by changes in the chelated surface that, in turn, depend on the pH of the medium. Under conditions of pH values lower than the PZC value of each coagulant (Figure 3), there are excess positive charges on the solid surface of the sludge, which may cause adsorption of the arsenate ions. This hypothesis is supported by the higher PZC values of the sludge generated with aluminum sulfate (PZC = 7.75) and polyaluminum chloride (PZC = 7.90) when compared to the coagulation pH values ($\text{pH} < 7.5$).

As arsenic, under the conditions of study, is found prevalently in the form of HAsO_4^{2-} , the possibilities of electrostatic interactions between the arsenic ions and the generated sludge are evidenced. The isotherms of AsV adsorption to the sludge tend to confirm the interaction of the arsenate anions and the

solid phase by the electrostatic attraction mechanism, as shown in Figures 4 and 5.

The coefficient of determination values (R^2) suggested that, for both coagulants, the Langmuir model best fitted the experimental data. Since the adsorbent is in excess and associated with the single-layer, homogeneous adsorption and, according to the parameters obtained, it has a maximum adsorption capacity (q_{max}) of $5.3 \text{ mg}\cdot\text{g}^{-1}$ and $7.0 \text{ mg}\cdot\text{g}^{-1}$ for the sludges generated with aluminum sulfate and polyaluminum chloride, respectively. The values of q_{max} in this work are in conformity with those found for the granular iron hydroxide ($5.0 \text{ mg}\cdot\text{g}^{-1}$) and higher than that reported for Portland cement slurry ($4.0 \text{ mg}\cdot\text{g}^{-1}$), but significantly lower than that obtained for cesium (IV) oxide containing iron ($70.4 \text{ mg}\cdot\text{g}^{-1}$) (Yokoi *et al.*, 2004).

By performing XRD tests on the sludge formed during clarification of high turbidity waters, even with high concentrations of arsenic, it was not possible to visualize how this element was present in the precipitate formed.

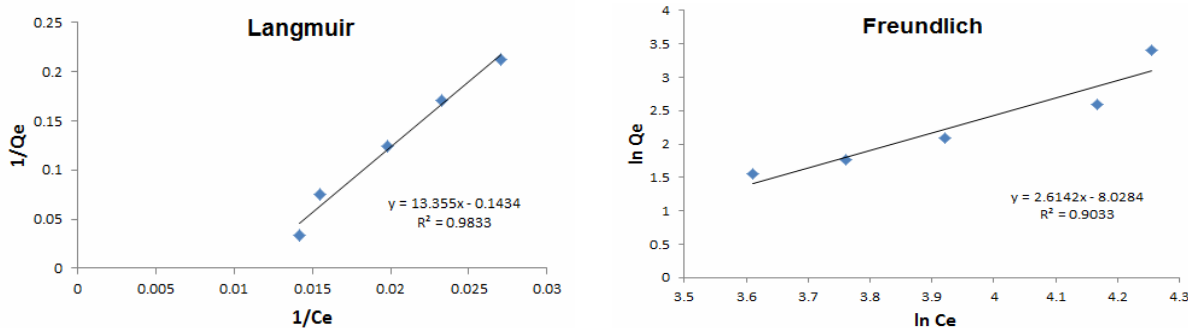


Figure 4: Adsorption isotherms of the arsenate anion in sludge generated by coagulation with polyaluminum chloride.

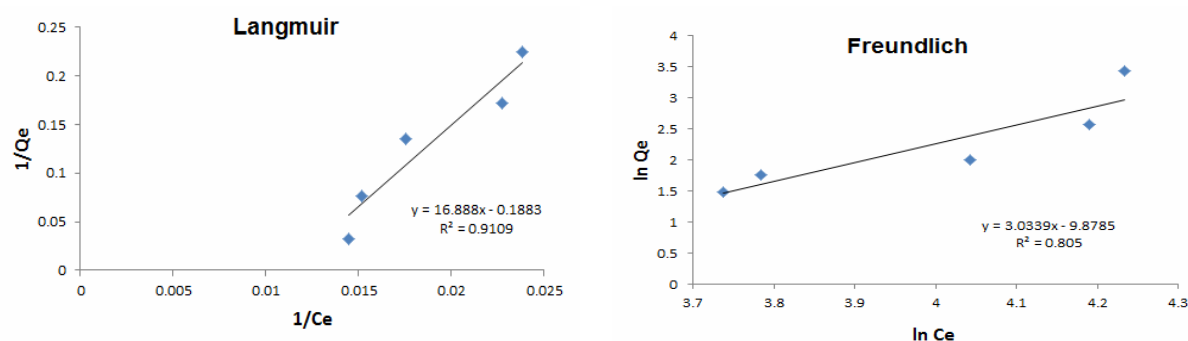


Figure 5: Adsorption isotherms of the arsenate anion in sludge generated by coagulation with aluminum sulphate.

This fact might be due to the low sensitivity of the equipment and the small amount of As with relation to the total mass of sludge, or that the As precipitate had low crystallinity. For Mn, the XRD data (not shown) indicate that the partial removal of this metal (see Table 4) was accomplished by the formation of birnessite, a manganese oxide mineral liable to be associated with calcium, potassium and sodium. This mineral $(\text{Na}_{0.3}\text{Ca}_{0.1}\text{K}_{0.1})(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5 \text{H}_2\text{O}$ has a dark brown or black color, and it can be found in lakes and groundwaters as a consequence of the oxidation of the soluble manganese. Therefore, these data indicate that part of the Mn(II) was oxidized to Mn(IV) during the jar test experiments, probably due to oxygen solubilization, mainly during rapid mix.

Evaluation of the Influence of the Pre-Oxidation Associated with Clarification

The subsequent pre-oxidation tests were intended for evaluating the relevance of the use of chlorination for removal of these metals. As expected, the pre-oxidation with chlorine increased the manganese removal in the 12 conditions evaluated for each water (low and high turbidity). The average removals ranged from 37% (Type IA water) to 86% (Type IIB

water), and the chlorine consumption, governed by the initial concentration of manganese, ranged from 0.3 to 1.0 $\text{mg}\cdot\text{L}^{-1}$. There were no significant differences between the CT (product of chlorine concentration and time) values tested, and the minor supremacy of the polyaluminum chloride appeared again in all the 48 comparisons. For each water, the practically equal results for the different contact times favor the application of chlorine at the entrance of the water treatment plant, instead of such application being made in the water intake unit, while the pre-oxidation occurs along the raw water pipe line. The comparisons of the three different chlorine doses to the ratio between the final concentration and initial concentration of manganese are listed in Figures 6 and 7.

When sodium hypochlorite is added to water, a hydrolysis reaction takes place producing hydroxyl ions, resulting in a slightly increased pH, which may contribute to the manganese removal. However, the pH increase was not enough to justify the removal of Mn via $\text{Mn}(\text{OH})_2$ precipitation (see Figure 1). Therefore, it is likely that the main Mn removal would result from the formation of $\text{MnO}\cdot\text{OH}$ and MnO_2 , following the oxidation of Mn(II) to Mn(III) and Mn(IV), respectively.

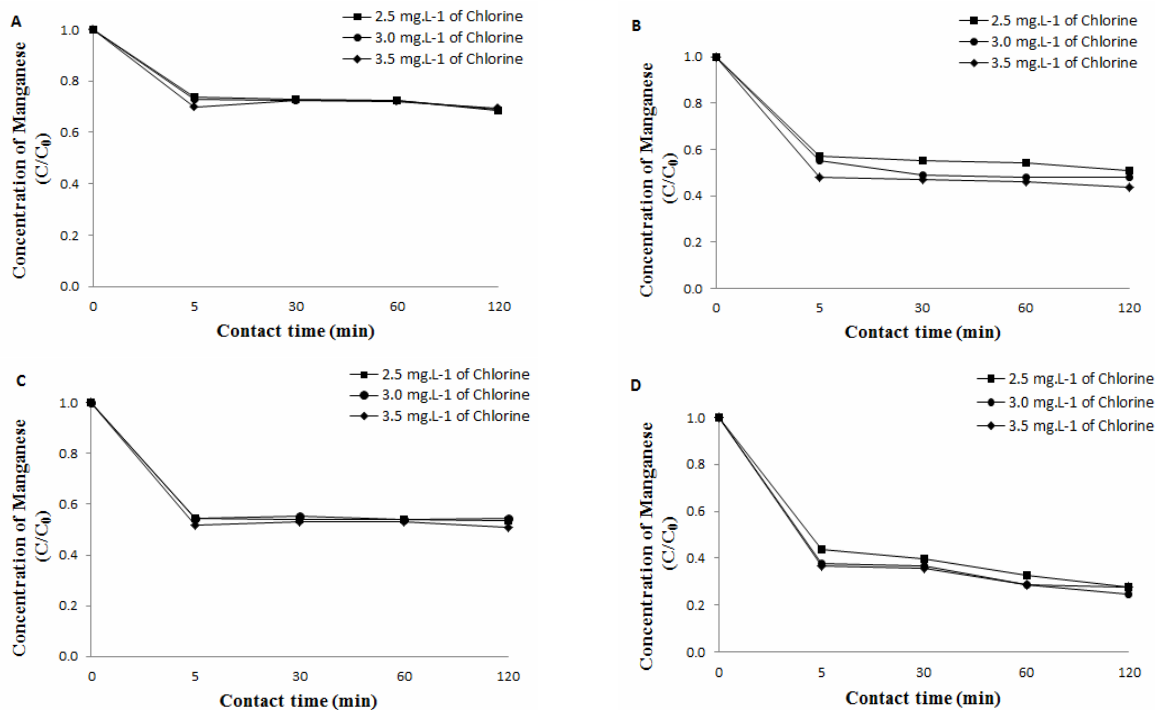


Figure 6: Temporal decay of Mn concentration in view of the concentration of chlorine applied in the pre-oxidation, followed by clarification with aluminum sulfate for IA (A), IB (B), IIA (C) and IIB (D) type waters.

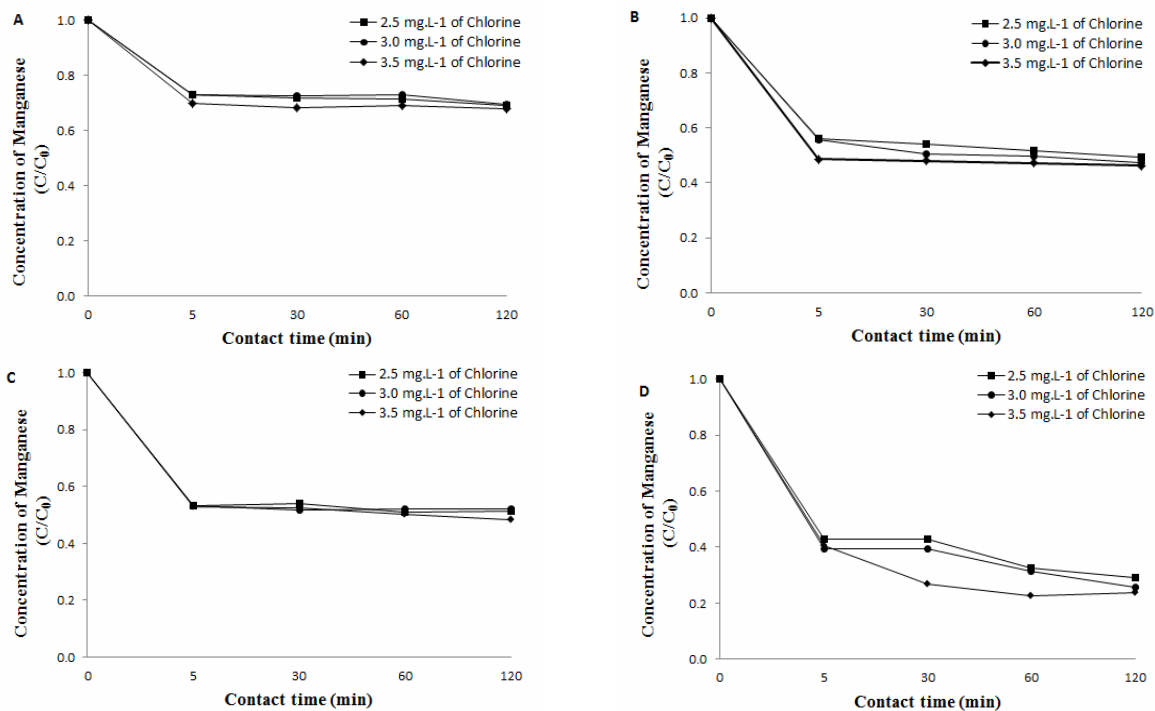


Figure 7: Temporal decay of Mn concentration in view of the concentration of chlorine applied in the pre-oxidation, followed by clarification with PAC for IA (A), IB (B), IIA (C) e IIB (D) type waters.

By performing X-ray diffraction tests (Figure 8) on the sludge formed during this treatment process using high-turbidity waters, it has been possible to verify that, as estimated by the stability diagram (Figure 1), the main form of manganese removal was by the formation of birnessite, which contains both Mn(III) and Mn(IV).

Regarding the initial concentration of chlorine, it was noted that, at the pH value at which the experiment was performed, it was considerably higher than that required by the stoichiometric amounts of oxidant. Nevertheless, the percentage of manganese removal for high initial metal concentration are still insufficient to comply with the maximum limit established by the Regulation 2914. It is worth mentioning that additional removal can also be achieved in the filtration unit.

On the other hand, the pre-oxidation kept the ar-

senic removal within the same levels of efficiency listed in Table 4, for all the conditions evaluated and waters. The increase of pH value close to 7.8, due to the hydrolysis of the hypochlorite, contributes to minimize the arsenic removal, as the pH gets closer to the PZC value of the generated sludge (Figure 3), weakening the capacity to adsorb the arsenic anions.

The pre-oxidation presented a higher significance for As(III), as 80 to 90% removals were achieved for both coagulants at low and high concentrations of this element at several CT values, as shown in Figure 9. However, it was observed – even with significant removals – that the final concentration of As(III) increased as its initial concentration also increased. This way, the use of this process is feasible for waters with lower concentrations of arsenic, since the drinking water guidelines for this metalloid are pretty low (0.01 mg.L^{-1}).

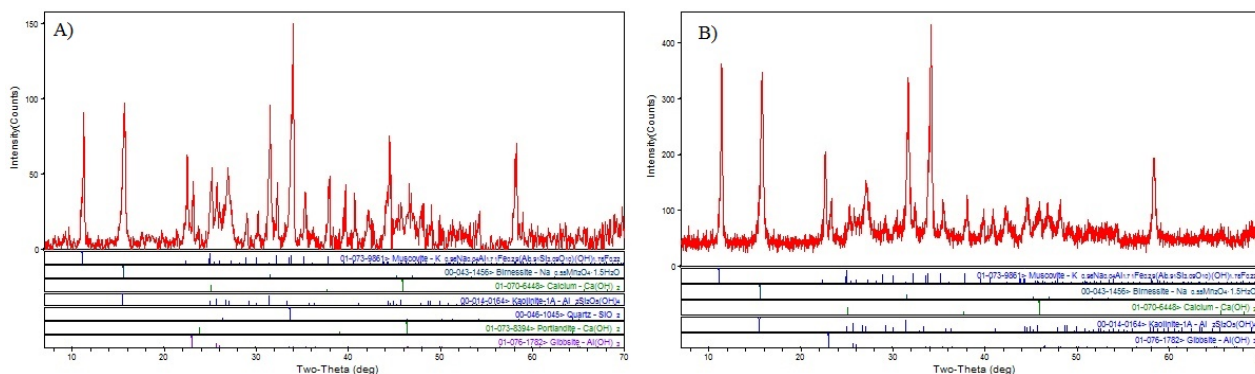


Figure 8: Results of the X-ray diffraction tests with the sludge generated from the treatment with the coagulants PAC (A) and SA (B).

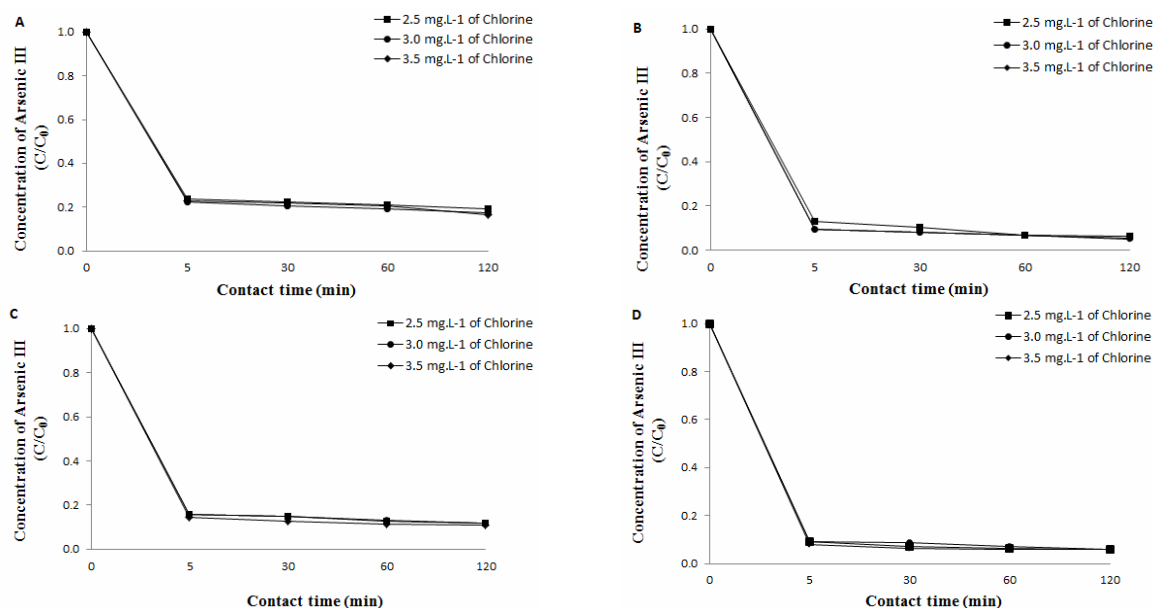


Figure 9: Temporal decay of the concentration of As(III) in view of the concentration of chlorine applied in the pre-oxidation, followed by clarification with SA for IIIA (A) and IIIB (B) type waters and clarification with PAC for IIIA (C) and IIIB (D) type waters.

Statistical Analyses

The first statistical analysis was based on the comparison between the coagulants tested in terms of manganese removal by clarification after pre-oxidation for high-turbidity water (Type II). For that purpose, the 144 results for each coagulant achieved, with polyaluminum chloride, a 70.7% average removal and a 1.0% variance, and, with aluminum sulfate, 68.4% and 1.0%, respectively. The application of the hypothesis test led to the rejection, at a 95% significance level, of the null hypothesis, thus confirming the supremacy of polyaluminum chloride.

Following that, the intent was to prepare a multiple linear regression model that would involve the initial and final concentrations of manganese, the chlorine dose, and the contact time in the oxidation preceding the clarification with polyaluminum chloride as primary coagulant. This way, Equation 1 was established with a 0.99 adjusted determination coefficient, in which the residual and initial concentrations of manganese refer to $\mu\text{g.L}^{-1}$ and the chlorine doses refer to mg.L^{-1} , with the subsequent clarification – under optimum conditions – being performed with polyaluminum chloride.

$$\text{Residual conc. of Mn} = 0.42 * (\text{Initial conc. of Mn}) - 10.54 * \text{Chlorine dose} \quad (1)$$

Taking into consideration the recommendation of Regulation 2914 regarding the maximum chlorine concentration of 2 mg.L^{-1} in the drinking water, and taking into consideration the 10% average reduction in the concentration of free chlorine after dosage and oxidation, it can be stated that the maximum applicable chlorine dose is 2.2 mg.L^{-1} . This way, it is possible to state that, for the manganese removal by the *pre-oxidation + clarification* process to be sufficient to adjust the drinking water to the allowable maximum limit, the initial concentration of manganese in the raw water should be lower than $293 \mu\text{g.L}^{-1}$. It can also be concluded that this equation is more suitable for lower values of Mn.

A similar procedure was performed for Type II water, although intended for evaluating the contingent relevance of the pre-oxidation in As(V) removal. For that purpose, 96 test results were used, with polyaluminum chloride as primary coagulant and clarification either preceded or not by the oxidation. Only the clarification with polyaluminum chloride, for IIA and IIB Type waters, led to an average AsV removal of 94.7% which was reduced to 86.8% when preceded by oxidation. The application of the hypothesis test at the 95% significance level confirmed

that the AsV removal just by clarification is more efficient when associated with pre-oxidation. As previously mentioned, the slightly increase in pH observed after the pre-oxidation and the closeness to the sludge PZC value seemed to reduce the capacity of the solid to adsorb the arsenic anions.

The influence of both coagulants on [As(III)] removal by clarification associated with pre-oxidation was evaluated for a total of 192 results. The use of polyaluminum chloride led to a 70.2% average removal, which was reduced to 63.5% when the coagulant was the aluminum sulfate. However, the application of the hypothesis test at a 95% significance level confirmed that both coagulants had statistically similar efficiencies for As(III) removal.

The multiple linear regression model (with 0.89 adjusted determination coefficient), represented by Equation (2), allows one to estimate the remaining concentration of As(III) after clarification with polyaluminum chloride associated with pre-oxidation under optimum conditions.

$$\text{Residual conc. of As(III)} = 0.18 * (\text{Initial conc. of As(III)}) - 5.96 * \text{Chlorine dose} \quad (2)$$

This way, for a maximum chlorine dose (2.2 mg.L^{-1}) liable to being applied in pre-oxidation, it is possible to estimate that natural waters with characteristics similar to the waters tested here and with concentration of As(III) lower than $128 \mu\text{g.L}^{-1}$ can be adapted to the prevailing drinking water standard by associating these processes.

CONCLUSIONS

From the review of the literature and the test results, it is possible to conclude that:

i) In terms of manganese removal, even under the optimized conditions for both coagulants, the clarification – either associated or not with the pre-oxidation – was insufficient to comply with Regulation 2914 ($100 \mu\text{g.L}^{-1}$), particularly for the higher concentrations of the metal. For both waters, the greatest obstacle to manganese removal is probably the coagulation pH close to neutrality, favoring the prevalence of the dissolved form of the metal;

ii) Regarding the As(V) removal by clarification only, the results were more promising, particularly for waters of more significant turbidity, for which a concentration lower than that established by Regulation 2914 ($10 \mu\text{g.L}^{-1}$) was achieved in almost all the tests with both coagulants. The As(V) removal focused essentially on the adsorption of the anions

HAsO₄²⁻ to the positively charged particles of the generated sludge, and this was of greater magnitude when polyaluminum chloride was used as primary coagulant;

iii) For waters of lower turbidity and high concentration of As(V), the production of settled water in conformity with the Drinking Water Quality Standards failed, even when pre-oxidation was associated with the clarification, suggesting that other technologies (e.g., adsorption) should be employed to produce potable water regarding this metalloid;

iv) Oxidation preceding the clarification is valid when, in low-turbidity waters, the arsenic prevails as As(III) (in concentrations up to 18 times higher than the limit established by Regulation 2914). In this context, the contact time did not play a relevant role in arsenic removal.

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