Redox potential effect of bisulfite in brackish water with the presence of chlorine dioxide, chlorite, chlorate and metals

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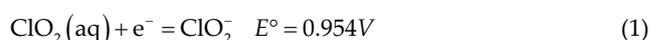
ABSTRACT

In desalination plants, disinfection is necessary to control biofouling, one of the main problems in the long-term performance of reverse osmosis membranes. The addition of both chlorine and the dechlorination reagents affects oxidation and reduction potential (ORP). The present investigation evaluates the evolution with time between bisulfite dose and ORP values, to assess the impact of chlorine dioxide, chlorite, chlorate and dissolved metals in the redox potential. Results showed that using chlorine dioxide as an oxidant (1 mg/L), it was needed at least 45.8 mg/L of bisulfite to reduce ORP values below 300 mV. In the presence of chlorite ion (0.65 mg/L) and adding 100 µg/L of different dissolved metals, the redox potential values did not increase higher than 300 mV except for cobalt (Co^{2+}); at 3 mg/L of chlorite, it was needed at least 46.9 mg/L of bisulfite to reduce the ORP below 300 mV. The influence of bisulfite without chlorination species in brackish water, but with dissolved metals showed redox values always below 300 mV, except for 15 mg/L of bisulfite with 250 and 500 µg/L of dissolved Co^{2+}. Overall, the presence of chlorine dioxide, chlorite and dissolved metals, particularly Co^{2+}, has a strong influence on the behavior of the redox potential after the addition of bisulfite.

Keywords: Redox potential; Chlorine dioxide; Chlorite; Chlorate; Dissolved metals

1. Introduction

Reverse osmosis (RO) membrane desalination of brackish water and/or seawater has become an important strategy to provide water for municipal and industrial use. In pretreatment, disinfection is necessary to control biofouling, one of the main problems in the long-term performance of reverse osmosis membranes [1–4]. Chlorine dioxide (ClO_2) has been mainly used in desalination plants to prevent biofouling [5] and to avoid bromate formation in desalinated seawater [6]. It functions as a highly selective oxidant due to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-) [5,7]. In drinking water, chlorite (ClO_2^-) is the predominant end product of chlorine dioxide, with approximately 50% to 70%, and 30% to chlorate (ClO_3^-) and chloride (Cl^-) [8–10]:

$$ClO_2\left(aq\right) + e^- = ClO_2^- \quad E° = 0.954V \tag{1}$$

Other important half reactions are:

$$ClO_2^- + 2H_2O + 4e^- = Cl^- + 4OH^- \quad E° = 0.76V \tag{2}$$

$$ClO_3^- + H_2O + 2e^- = ClO_2^- + 2OH^- \quad E° = 0.33V \tag{3}$$

To prevent RO membrane damage caused by chlorine dioxide, chlorite and chlorate, dechlorination is required to reduce oxidation and reduction potential (ORP) values

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below the critical values provided by membrane manufacturers (<300 mV) [11]. There are several available treatment options for lowering chlorine dioxide and chlorite ion concentrations in desalination plants. They include granular activated carbon [12,13], sulfur-reducing agents, such as sulfite, metabisulfite and thiosulfate [14], and ferrous iron (Fe^{2+}), and anion exchange [14]. Furthermore, precise operation ("tuning"), proper maintenance and the generation technology employed with the chlorine dioxide generator has a large bearing on the chlorine dioxide production efficiency and the rate at which chlorite and chlorate are formed [15]. As much as 35% of the chlorate concentration found in a distribution system can be attributed to the type and performance (tuning) of the chlorine dioxide generator. Currently, there is no readily available and low-cost treatment available to remove chlorate ion once it has been formed. Although anion exchange and reverse osmosis are possible technologies for the removal of chlorate [16], they are high-cost treatment options. Granular activated carbon is generally not effective, as chlorate is reversibly adsorbed on granular carbon [17].

In practical applications, sodium bisulfite, sodium metabisulfite or similar chemicals are the preferred dechlorination agents and their doses are normally controlled at 1.5 parts for every part of free residual chlorine present in the water [18,19]. Excessive concentration of bisulfite that is used for dechlorination may facilitate scale formation [20]. By means of bisulfite, chlorine dioxide should be reduced to chloride ion, which is an innocuous species against reverse osmosis membranes, but both chlorine and the dechlorination reagents may affect the ORP [7,21]. Seawater is known to have an ORP between 150 and 300 mV in sallow columns [19]. There is a lack of knowledge, however, on how chlorination and dechlorination, and salinity might influence ORP quantitatively. The importance of understanding such relationships will benefit (1) dose determination of the chlorine chemicals and dechlorination agent with high confidence and minimum chemical wastage, (2) robust control of the chlorination/dechlorination unit operations, and (3) prevention of RO membrane oxidation. Therefore, the knowledge of these redox reactions is of great importance in the desalination process. For these reasons, the objectives of this work were to study the evolution with time between the dose of bisulfite and ORP values and to assess the impact of chlorine dioxide, chlorite, chlorate and dissolved metals in the redox potential.

2. Materials and methods

2.1. Materials

Experiments were performed with brackish water samples from the ultrafiltration (UF) outlet of a desalination plant (~5 mS/cm). Permeate water samples from reverse osmosis membranes were also used to study the evolution of the redox potential of RO racks' preservation solution. This desalination plant was operating with brackish water from the lower part of a river with marine influence. Chemicals used were analytical reagents of high purity. Dissolved metals (aluminum, iron, chromium, nickel, molybdenum, copper, manganese, zinc and cobalt) were from High-Purity Standards (Charleston, USA). The multi-elemental spike solution

(IES-WWK) used in the isotopic dilution was from ISC-Science (Oviedo, Spain). Sodium chlorate ($NaClO_3$, Fischer Scientific, Analytical reagent grade, conforms to EP and ACS, >80%) and sodium chlorite ($NaClO_2$, Fischer Scientific, Analytical reagent grade, conforms to EP and ACS, >80%), were used for standard solutions of chlorate and chlorite, respectively. Sodium bisulfite ($NaHSO_3$, Acros Organics) was used as a reducing agent. The chlorine dioxide stock solution was prepared by acidification of the sodium chlorite solution with 50% (v/v) sulfuric acid. Chlorine dioxide evolved was removed with an air stream and dissolved in cold water. The stock solution was kept refrigerated and was protected from light to avoid its photochemical decomposition. The purity of the chlorine dioxide stock solution was checked each day prior to use for chloride, chlorite, and chlorate impurities after purging out its ClO_2 content. Glass volumetric flasks and 0.5 L polypropylene reaction vessels were cleaned with 10% HCl and rinsed several times before use.

2.2. Analysis

The ORP experiments were conducted by slowly stirring the brackish water solution (~500 mL) with an IKA RET basic magnetic stirrer. After the addition of bisulfite, chlorine dioxide, chlorite or chlorate, the changes in ORP were monitored using a pH meter (CRISON microPH 2002), which measures mV, with a metallic electrode made of platinum (CRISON 52 61). The system performance was verified using a standard redox of 220 mV at 25°C. Dissolved metals, such as aluminum, iron, chromium, nickel, molybdenum, copper, manganese, zinc and cobalt were added in some brackish water solutions. Ionic chromatography analyses were carried out with a liquid chromatograph equipped with an eluent generator and coupled to a conductivity detector (ICS-3000). The employed column was a hydroxide selective anion exchange IonPac AS19 (method 300.1, EPA), in conjunction with an anionic suppressor ASRS 300 4 mm. Mobile phase flow was 1 mL/min and the analyses were kept at a constant temperature of 33°C. Chlorine dioxide analyses were carried out with a DR 5000 spectrophotometer using a colorimetric kit supplied by Hach Lange.

3. Results and discussion

3.1. Chlorine dioxide redox studies

Chlorine dioxide was evaluated in terms of the redox potential evolution with time after the addition of different amounts of bisulfite. Experiments were performed with brackish water samples from the UF outlet (~5 mS/cm) at 1 mg/L of ClO_2 and 5.9–56.7 mg/L of bisulfite concentrations (Fig. 1). The initial redox potential value was ~675 mV, much higher than the maximum ORP value accepted by RO membrane manufacturers (300 mV). Bisulfite concentrations decreased the redox potentials during the first 30 s; however, after this time, values remained stable above 300 mV for low bisulfite concentrations (5.9–34.7 mg/L). To reduce ORP values below 300 mV it was needed at least 45.8 mg/L of bisulfite. Other studies showed that photodecomposition of chlorine dioxide with UV light was also an effective removal method for the direct destruction of chlorine dioxide [22].

All of these decomposition reactions yield chlorate. Chlorate is a strong oxidizer in acidic conditions (reduction potential of +1.47 V) and a moderate oxidizer in alkaline conditions (reduction potential of +0.63 V) that must be removed prior to polyamide membranes. Previous studies also suggested other methods for neutralizing chlorine dioxide, employing sodium thiosulfate or sodium sulfite [5,23,24]. Theoretically, 1 ppm of thiosulfate is required per 1 ppm of chlorine dioxide, and 2.95 ppm of sulfite is required per 1 ppm of chlorine dioxide. Thus, our results suggested that the dechlorination efficiency of chlorine dioxide with bisulfite is not as efficient as the observed with thiosulfate or sodium sulfite.

3.2. Chlorite ion redox studies

3.2.1. Effect of salinity and bisulfite dose

Chlorite ion (ClO_2^-) is the main by-product from a disinfection process of ClO_2. Therefore, it is essential to know the redox potential evolution of ClO_2^- when reacting with bisulfite to prevent oxidation of reverse osmosis membranes. In order to know the influence of salinity some
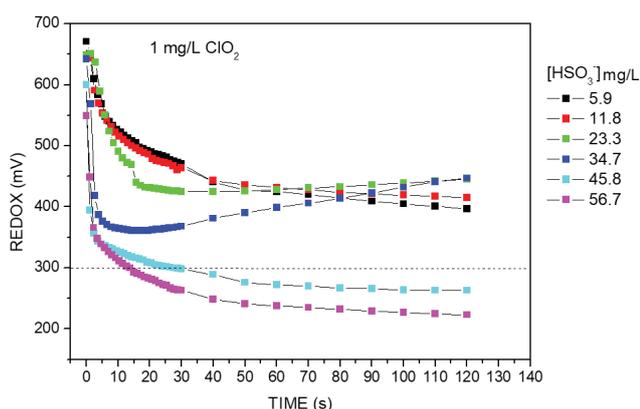

Fig. 1. Representation of ORP values vs. time of experiments performed with 1 mg/L of chlorine dioxide and different bisulfite concentrations in brackish water samples after ultrafiltration.

experiments were performed with Milli-Q water, and adding NaCl (15 mS/cm), at 12 mg/L of bisulfite and chlorite ion concentrations of 0.3, 1.5 and 3 mg/L (Fig. 2). Experiments with Milli-Q water (no conductivity) and adding 12 mg/L of bisulfite showed ORP values below 300 mV after 5, 20 and 70 s, at chlorite concentrations of 0.3, 1 and 3 mg/L, respectively. Experiments with Milli-Q water and NaCl (15 mS/cm) showed similar ORP patterns than without conductivity for 0.3 and 1 mg/L of chlorite after adding 12 mg/L of bisulfite; however, at 3 mg/L of chlorite it was not possible to reduce the redox potential below 300 mV with 12 mg/L of bisulfite (Fig. 2). Therefore, salinity affected the redox potential of high chlorite ion concentration (3 mg/L). These results are in accordance with a previous oxidation-reduction study of NaOCl (0, 1, and 2 mg/L) in deionized and saline water. In general, ORP values of deionized water decreased with the additions of $Na_2S_2O_5$; however, for saline water, ORP increased slightly as the $Na_2S_2O_5$ titration continued and greater increments were observed with higher salinities [21].

The efficiency of bisulfite to reduce chlorite ion to its innocuous products was examined under varying concentrations of chlorite (0.65 and 3 mg/L) and bisulfite (from 2.3 to 49 mg/L) (Tables 1 and 2). Experiments were performed with brackish water samples from the UF outlet (~5 mS/cm). At chlorite concentration of 0.65 mg/L the evolution of ORP values was always below 300 mV indistinctly of bisulfite concentrations. However, at 3 mg/L of chlorite, some redox experiments (using bisulfite concentrations from 15.5 to 46.9 mg/L) showed redox values above 300 mV. At bisulfite concentration of 15.5 mg/L, ORP values were higher than 300 mV after 65 s, at 19.8 mg/L after 25 s, at 27.5 mg/L (15 s), at 34 and 39.6 mg/L (10 s), at 44.6 mg/L (20 s) and at 46.9 mg/L (90 s). It was needed at least 46.9 mg/L of bisulfite to reduce the ORP below 300 mV (Tables 1 and 2). Bisulfite, when oxidized, yields persulfate or peroxodisulfate anions [25,26]. These compounds react with chlorite to reproduce chlorine dioxide [5]. When this occurs within the concentration polarization boundary layer of the membrane, it results in significant oxidation of the polyamide membrane. These findings elucidate that the addition of bisulfite to reduce chlorite ion may result in unwanted
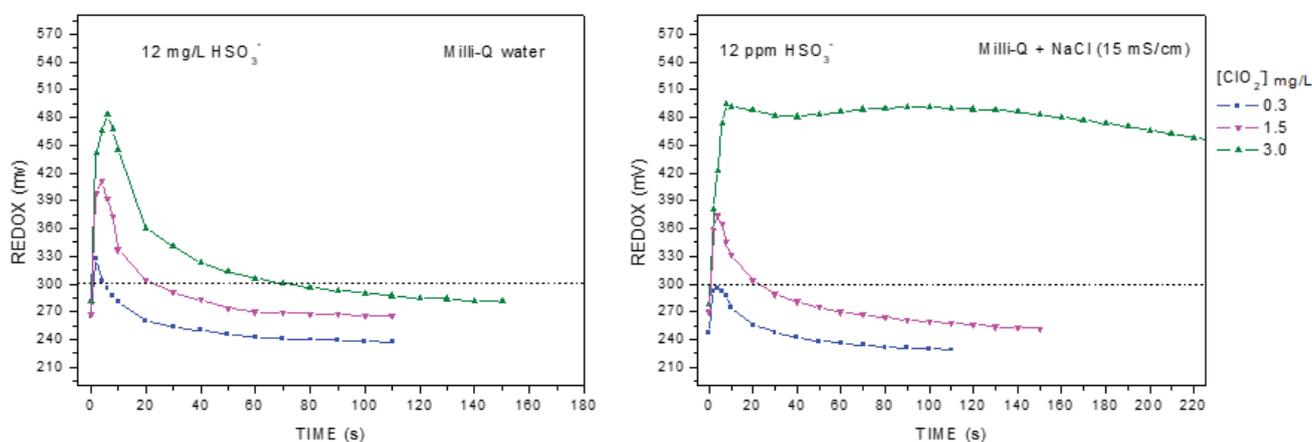

Fig. 2. Redox potential vs. time at three different chlorite concentrations (0.3, 1 and 3 mg/L) with 12 mg/L of bisulfite in different water samples. (a) Milli-Q water and (b) Milli-Q water with NaCl (15 mS/cm).

Table 1
Redox experiments with time (0–120 s) to evaluate the efficiency of bisulfite to reduce chlorite ion (0.65 mg/L) varying concentrations of bisulfite (from 2.3 to 28.8 mg/L).

Time (s)	2.3 mg/L	4.6 mg/L	6.7 mg/L	8.8 mg/L	12.8 mg/L	16.4 mg/L	23 mg/L	28.8 mg/L
0	163	163	163	174	165	173	163	162
1	164	177	165	185	208	185	169	196
2	167	178	188	211	210	211	211	220
3	168	176	185	204	211	219	215	223
4	169	175	182	200	212	222	218	226
5	168	174	180	198	213	224	224	229
6	169	173	179	196	214	225	229	234
7	168	172	178	194	214	228	231	238
8	167	171	177	193	215	230	233	240
9	167	171	176	192	215	231	237	241
10	167	170	176	192	216	231	238	243
11	167	170	176	192	216	232	239	245
12	167	170	176	192	216	232	241	246
13	167	170	175	191	216	233	241	247
14	167	170	175	191	216	233	243	248
15	167	170	175	191	216	234	244	248
16	167	170	175	191	216	234	244	249
17	167	170	175	191	216	235	244	249
18	167	170	175	191	216	236	246	250
19	167	170	175	191	216	236	246	250
20	167	170	175	191	216	237	247	251
30	167	171	175	191	216	239	254	254
40	168	171	176	190	216	241	258	255
50	168	171	176	190	215	241	258	256
60	168	172	176	190	215	241	259	256
70	169	172	176	190	215	242	260	258
80	169	172	177	190	215	242	262	260
90	169	172	177	191	215	243	264	260
100	171	172	177	191	215	243	265	260
110	171	173	177	191	215	244	266	262
120	173	173	178	191	214	244	266	262

higher ORP values at intermediate bisulfite concentrations, and not immediately after bisulfite addition (after >1 min). Thus, in desalination plants it is important to monitor ORP values after a sufficient time (>1 min) of bisulfite addition.

3.2.2. Influence of chlorite and dissolved metals

To evaluate the influence of chlorite and dissolved metals on brackish water from the UF outlet, redox experiments were performed at 100 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}), 0.65 mg/L of chlorite using 2, 10, 30 mg/L of bisulfite, and 3 mg/L of chlorite with 10, 34 and 48 mg/L of bisulfite (Figs. 3 and 4). At 0.65 mg/L of chlorite, redox potentials did not exceed 300 mV except for cobalt (Fig. 3). In this case, at 100 µg/L of cobalt, ORP values increased higher than 300 mV in tested bisulfite concentrations (2, 10 and 30 mg/L, after 115, 80 and 60 s, respectively). The general pattern in all dissolved metals was an increasing of ORP values after adding 30 mg/L

of bisulfite. Meanwhile, at lower bisulfite concentrations (2 and 10 mg/L), there was always a decreasing tendency of the redox potentials. At 3 mg/L of chlorite, tests performed in the presence of dissolved cobalt showed a different ORP trend than in other dissolved metals (Fig. 4). Redox potential values increased rapidly with time reaching values above 300 mV in 20, 25 and 50 s, using bisulfite concentrations of 34, 10 and 48 mg/L, respectively. However, in the other dissolved metals, ORP values were below 300 mV, except for 34 mg/L of bisulfite. In most cases, with a high excess of bisulfite (48 mg/L), the redox potential showed a slight decrease followed by an increase, ending at higher redox values than the initial ones and only exceeding 300 mV with dissolved cobalt and molybdenum. These results may be explained by the fact that some metals catalyze the oxidation of the sulfur(IV) compounds, including bisulfite [25,27,28]. Sodium bisulfite generates some oxidizing agents in the case of coexistence of heavy metals such as Cu and Co, and chloride ion [29]. Other studies, even suggested

Table 2
Redox experiments with time (0–120 s) to evaluate the efficiency of bisulfite to reduce chlorite ion (3 mg/L) varying concentrations of bisulfite (from 2.3 to 49 mg/L).

Time (s)	2.3 mg/L	4.6 mg/L	6.7 mg/L	8.8 mg/L	10.8 mg/L	15.5 mg/L	19.8 mg/L	27.5 mg/L	34 mg/L	39.7 mg/L	44.6 mg/L	46.9 mg/L	49 mg/L
0	220	162	168	160	177	178	163	171	187	175	178	169	171
1	222	169	176	250	227	236	203	193	227	240	205	224	282
2	223	177	186	245	236	244	256	251	245	277	236	238	283
3	224	179	190	237	235	241	254	244	255	271	248	246	274
4	223	180	193	232	232	236	254	248	261	273	261	258	272
5	222	180	195	229	230	237	256	257	267	278	268	263	272
6	222	181	196	226	232	239	258	266	271	281	273	265	274
7	222	182	198	228	232	241	260	271	276	286	278	267	272
8	222	182	200	230	234	245	263	275	280	290	281	269	270
9	222	183	202	232	235	246	268	278	284	295	285	272	268
10	222	183	204	234	237	248	271	282	288	299	290	273	267
11	222	183	206	236	240	250	276	287	295	304	292	274	266
12	222	183	208	237	242	252	277	293	299	307	293	276	265
13	222	184	210	238	244	255	280	295	302	309	294	277	264
14	222	184	211	239	245	258	282	296	305	313	294	277	263
15	222	184	212	240	246	261	284	298	310	315	292	278	262
16	222	184	214	241	247	263	286	301	312	318	292	278	261
17	222	184	216	242	248	266	287	303	315	320	294	279	261
18	222	185	217	242	249	268	290	305	318	322	297	279	260
19	222	185	217	243	249	269	293	306	322	325	299	279	259
20	222	185	218	247	250	270	296	309	323	332	300	279	259
30	221	185	220	249	253	275	305	320	337	350	311	281	257
40	221	185	222	251	257	279	310	342	351	368	321	283	252
50	221	185	224	255	260	290	322	360	362	379	328	285	248
60	221	186	226	259	263	297	334	370	373	394	331	287	245
70	221	186	228	262	265	305	340	381	387	403	342	292	246
80	221	186	228	264	268	312	345	395	399	408	350	294	246
90	221	186	230	266	271	318	352	402	407	416	357	297	247
100	221	187	232	268	273	322	361	409	412	423	361	301	247
110	221	187	234	268	275	327	370	415	417	431	368	305	248
120	221	188	235	270	277	330	380	419	424	443	373	307	250

that the preferred methods for neutralizing chlorite could employ other reducing salts, such as ferrous chloride or ferrous sulfate, or filtration through activated carbon, but neither of those methods is ideal for pretreatment prior to membrane desalination systems [5,23]. The use of ferrous chloride or ferrous sulfate generates iron oxide (a membrane foulant) via oxidation of Fe^{3+} by chlorite [30], and filtration through activated carbon can yield chlorate if any free chlorine is present [6,17]. All in all, to prevent oxidation of reverse osmosis membranes it is also important to know the heavy metal composition of the feed water and to evaluate previously the efficiency of the reducing agent.

3.3. Chlorate ion redox studies

3.3.1. Effect of salinity and bisulfite dose

Chlorate ion (ClO_3^-) is also a by-product of a chlorine dioxide disinfection process. Thus, it is important

to study its redox potential evolution when reacting with bisulfite, which is a common reducing agent used in desalination plants to prevent oxidation of reverse osmosis membranes. To know the influence of salinity, some experiments were performed with Milli-Q water, and adding NaCl (15 mS/cm), at 12 mg/L of bisulfite and chlorate ion concentrations of 0.3, 1.5 and 3 mg/L (Fig. 5). Experiments with Milli-Q water (no conductivity) and 12 mg/L of bisulfite showed ORP values below 300 mV after 5 and 10 s, at chlorite concentrations of 1.5 and 3 mg/L, respectively. Experiments with Milli-Q water (0.3 mg/L of chlorate) and NaCl (15 mS/cm) at 0.3, 1.5 and 3 mg/L of chlorate and 12 mg/L of bisulfite showed always decreasing ORP patterns below 300 mV (Fig. 5). Therefore, salinity did not affect the redox potential of chlorate ion concentrations.

It was also evaluated the efficacy of bisulfite to reduce chlorate ion at different concentrations of chlorate (0.65 and
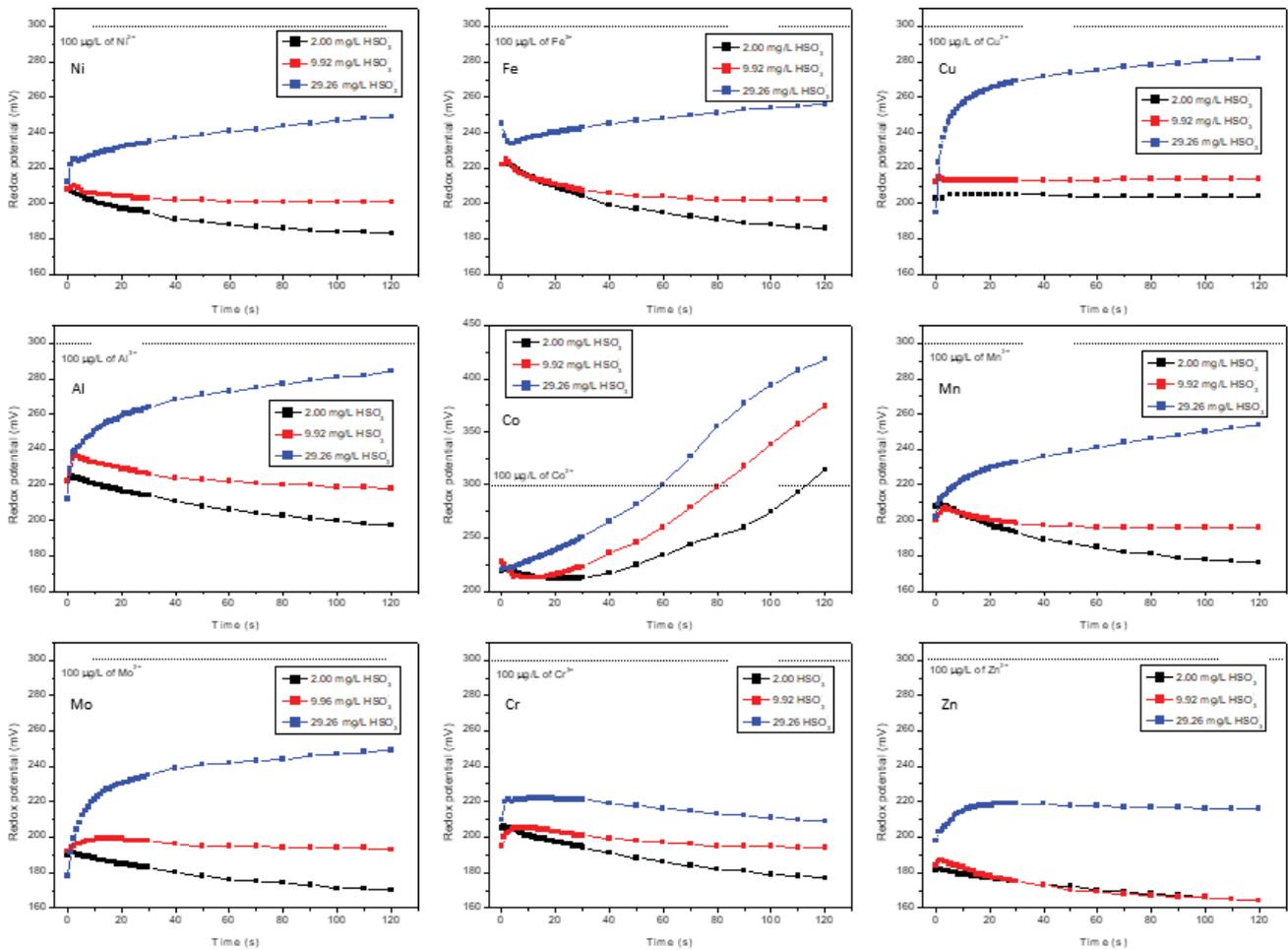
Fig. 3. Evolution of ORP values with time at 0.65 mg/L of chlorite using 2, 10, 30 mg/L of bisulfite, and 100 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in brackish water samples after ultrafiltration.

3 mg/L) and bisulfite (from 2.3 to 49 mg/L) using brackish water samples from the UF outlet (~5 mS/cm) (Fig. S3). Experiments at chlorate concentrations of 0.65 and 3 mg/L showed always ORP values below 300 mV indistinctly of bisulfite concentrations. It is important to note that whereas intermediate bisulfite concentrations increased ORP values in chlorite solutions (Fig. 3), in chlorate concentrations, bisulfite was able to reduce completely its redox potential (Fig. S3), even without increasing the redox potential at any moment. Although chlorate is a strong oxidizer, as much as chlorite [31,32], these results showed that bisulfite was much more effective in reducing chlorate ion, even at a high concentration of chlorate and adding low bisulfite concentrations.

3.3.2. Influence of chlorate and dissolved metals

The influence of dissolved metals on chlorate brackish water solutions was studied by means of redox experiments at 100 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed at 0.65 mg/L of chlorate using 2, 10 and 30 mg/L of

bisulfite, and at 3 mg/L of chlorate with 10, 34 and 48 mg/L of bisulfite (Figs. S2 and S3). At 0.65 mg/L of chlorate, redox potentials of the different metals solutions did not exceed 300 mV (Fig. S2). The general pattern of ORP values in the metals solutions was a decreasing tendency after adding bisulfite, except for Co^{2+} and Cu^{2+} solutions where its redox potentials slightly increased after bisulfite addition (2, 10 and 30 mg/L). In the Co^{2+} solution, the redox potential started to increase after 40 s of adding bisulfite, and in the Cu^{2+} solution just after bisulfite addition. At higher chlorate concentration (3 mg/L), redox experiments did not exceed either 300 mV, but tests performed with 10 mg/L of bisulfite in the presence of dissolved Co^{2+} showed a different ORP trend than in other dissolved metals. The redox potential increased rapidly with time reaching values close to 300 mV in 120 s (Fig. S3). These results showed that depending on chlorate and bisulfite concentrations, the presence of dissolved cobalt and copper changed the ORP tendencies of the brackish water solution. However, unlike what was observed with chlorite, these redox patterns never exceed 300 mV, showing that bisulfite is much more effective in reducing chlorate ion.
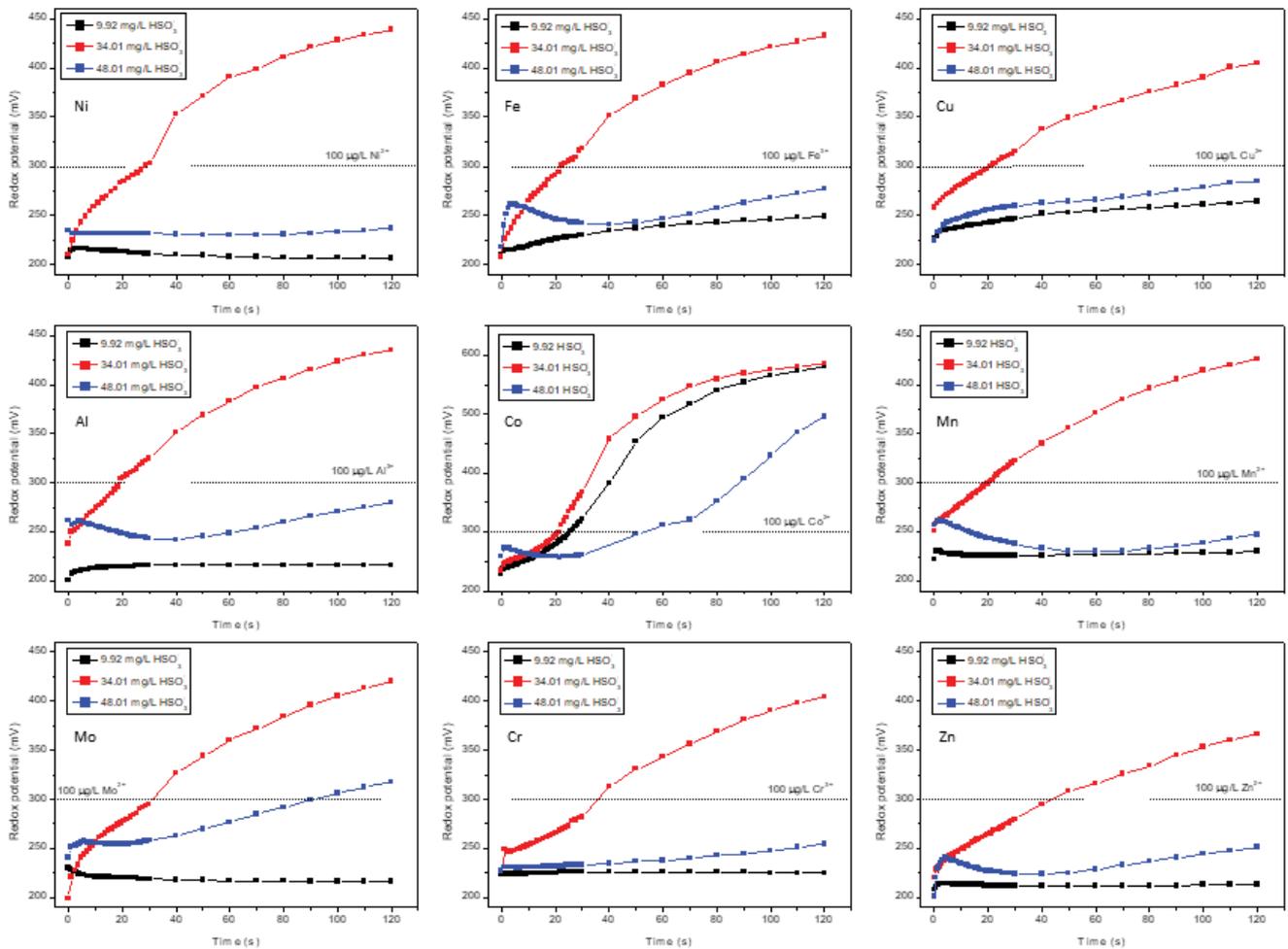
Fig. 4. Redox potential values with time at 3 mg/L of chlorite using 10, 34, 48 mg/L of bisulfite, and 100 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in brackish water samples after ultrafiltration.
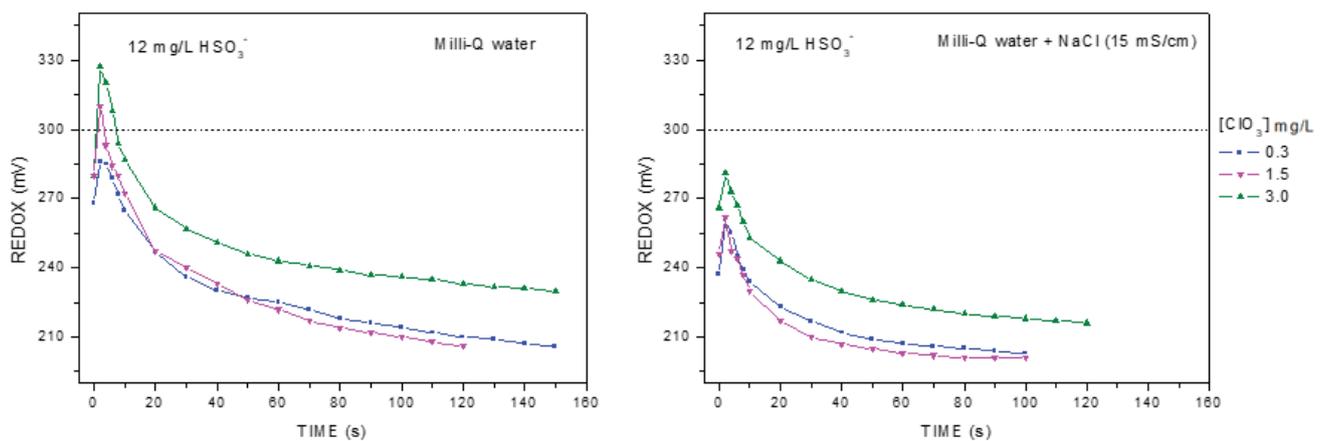

Fig. 5. Evolution of the redox potential with time at three different chlorate concentrations (0.3, 1 and 3 mg/L) with 12 mg/L of bisulfite in different water samples. (a) Milli-Q water and (b) Milli-Q water with NaCl (15 mS/cm).

3.4. Bisulfite studies with dissolved metals

To evaluate the influence of bisulfite in brackish water after UF with dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}), the redox potential evolution of three different concentrations of bisulfite (5, 15 and 30 mg/L) was evaluated in three different concentrations of the dissolved
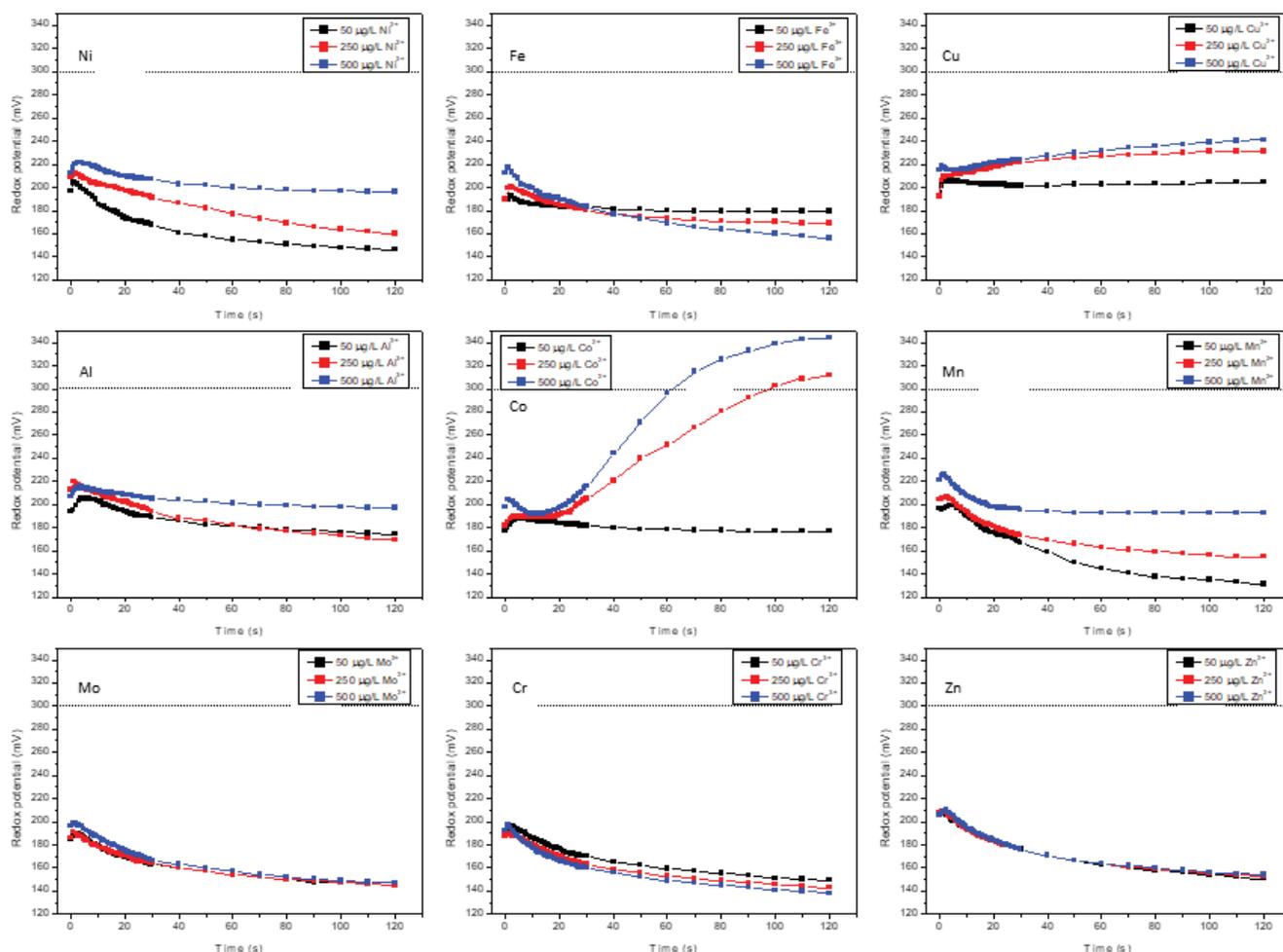
Fig. 6. ORP values vs. time at 15 mg/L of bisulfite and 50, 250 and 500 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}) in brackish water samples after ultrafiltration.

metals (50, 250 and 500 µg/L). Results showed that redox values were always below 300 mV (Figs. S4, S5 and Fig. 6), except for 15 mg/L of bisulfite in brackish water with 250 and 500 µg/L of dissolved Co^{2+}. In this case, ORP values showed an increasing curve after 20 s of bisulfite addition, and redox potentials were above 300 mV even after 120 s (Fig. 6). Cu^{2+} solution at 15 mg/L of bisulfite also showed an increasing pattern, but very slightly and not reaching 300 mV. At 5 and 30 mg/L of bisulfite, the general ORP pattern in the metals solutions was a decreasing tendency after adding bisulfite, except for Co^{2+} and Cu^{2+} solutions where its redox potentials slightly increased after bisulfite addition (Figs. S4 and S5). Overall, these results show that bisulfite can increase the redox potential of brackish water even without the presence of chlorine dioxide, chlorite or chlorate, but with the presence of some dissolved metals (Co^{2+} and Cu^{2+}). This can be explained by the fact that bisulfite generates some oxidizing agents in the case of coexistence of heavy metals such as Cu and Co [29]. Thus, to prevent oxidation of reverse osmosis membranes it is important to know the heavy metal composition of the feed water. Further, it should be noted that the addition of

bisulfite intermediate concentration (15 mg/L) just with the presence of dissolved Co^{2+}, results in unwanted higher ORP values (>300 mV) after 1 min of its addition. However, with lower and higher bisulfite concentrations (5 and 30 mg/L) this phenomenon does not occur.

3.4.1. Bisulfite preservation solution of RO membranes

It was studied the evolution of the redox potential of RO racks' preservation solution with 1% of bisulfite and the presence of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}) in permeate water samples (Fig. S6). The redox values slightly increased in Fe^{3+} and Cu^{2+} solutions after adding bisulfite (1%). These redox enhancements took place during the first stage of the reactions, and after 10–20 s, the redox potentials started to decrease. The achieved redox potential values were higher when higher metal concentrations were tested; however, in all experiments, the redox values remained always below 300 mV (Fig. S6). These results may be explained by the fact that some heavy metals and dissolved O_2 in solutions whose pH is neural can catalyze the oxidation of bisulfite,

yielding persulfate and peroxodisulfate anions [25,27,29]. Thus, in the preservation of RO membranes, it is very important to know the heavy metal concentration of feed water and not to add different bisulfite concentrations without being tested previously.

4. Conclusions

This study evaluates the redox potential effect of bisulfite and different oxidants, chlorine dioxide and its decomposition by-products, chlorite and chlorate, and dissolved metals in brackish water with saline intrusion. Using chlorine dioxide as an oxidant, the initial redox potential value was much higher than the maximum ORP value accepted by RO membrane manufacturers (300 mV). To reduce ORP values below 300 mV it was needed high concentrations of bisulfite, at least 45.8 mg/L, much higher than it would be needed with thiosulfate or sodium sulfite. In the presence of chlorite and bisulfite, experiments with a solution of NaCl, and a conductivity of 15 mS/cm, showed similar ORP patterns than without conductivity (Milli-Q water) at low chlorite concentrations (0.3 and 1.5 mg/L); however, at higher chlorite concentration (3 mg/L) it was not possible to reduce the redox potential below 300 mV with bisulfite (12 mg/L). Therefore, salinity affected the redox potential of high chlorite ion concentration. In brackish water, at 0.65 mg/L of chlorite concentration the evolution of ORP values was always below 300 mV indistinctly of bisulfite concentrations, but at 3 mg/L of chlorite, it was needed at least 46.9 mg/L of bisulfite to reduce the ORP below 300 mV. Further, experiments with chlorite and different dissolved metals (100 μg/L) (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}), showed that at 0.65 mg/L of chlorite, redox potentials did not exceed 300 mV except for cobalt. At 3 mg/L of chlorite, and intermediate bisulfite concentration (34 mg/L), all dissolved metals solutions showed ORP values increasing with time and reaching 300 mV.

Experiments with chlorate ion showed that salinity did not affect its redox potential, and bisulfite was much more effective in reducing chlorate than chlorite, even at a high concentration of chlorate and adding low bisulfite concentrations. Further, the general pattern of ORP values in different metals solutions was a decreasing tendency after adding bisulfite, except for Co^{2+} and Cu^{2+} solutions where its redox potentials slightly increased after bisulfite addition. Experiments of bisulfite in brackish water with dissolved metals showed that redox values were always below 300 mV, except for 15 mg/L of bisulfite in 250 and 500 μg/L of dissolved Co^{2+}. At 5 and 30 mg/L of bisulfite, the general ORP pattern in metals solutions was a decreasing tendency after adding bisulfite, except for Co^{2+} and Cu^{2+} solutions, where its redox potentials slightly increased after bisulfite addition. All in all, the addition of bisulfite intermediate concentration (15 mg/L) just with the presence of dissolved Co^{2+}, resulted in unwanted higher ORP values (>300 mV) after 1 min of its addition. However, with lower and higher bisulfite concentrations (5 and 30 mg/L) this phenomenon did not occur. Thus, these results show that bisulfite can increase the redox potential of brackish water even without the presence of chlorine dioxide, chlorite or chlorate, but with the presence of some

dissolved metals (Co^{2+} and Cu^{2+}). Overall, these findings elucidate the fact that some metals catalyze the oxidation of bisulfite. The addition of bisulfite to reduce chlorine dioxide, chlorite and chlorate may result in unwanted higher ORP values, particularly at intermediate bisulfite concentrations, and not immediately after bisulfite addition. Thus, in desalination plants, to prevent oxidation of reverse osmosis membranes, ORP values should be monitored after a sufficient time (>1 min.) of bisulfite addition. Further, it would be important to characterize the heavy metal composition of the feed water and to evaluate the efficiency of the reducing agent previously.

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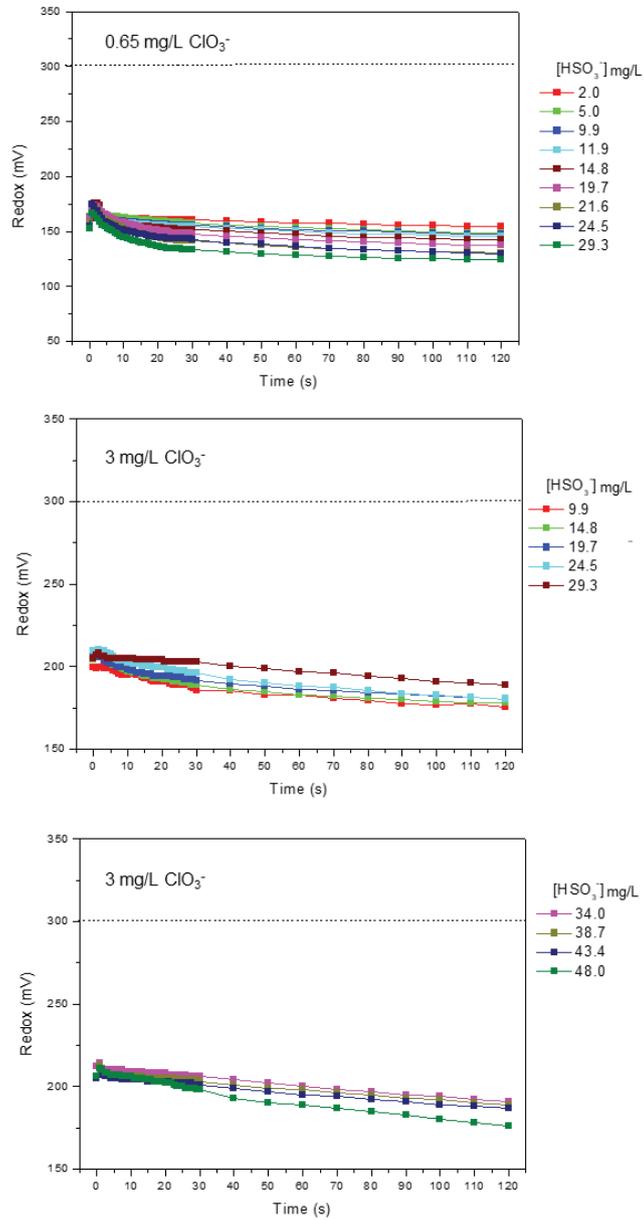
Supplementary information

Fig. S1. Redox experiments to evaluate the efficiency of bisulfite to reduce chlorate ion varying concentrations of chlorate (0.65 and 3 mg/L) and bisulfite (from 2 to 48 mg/L).
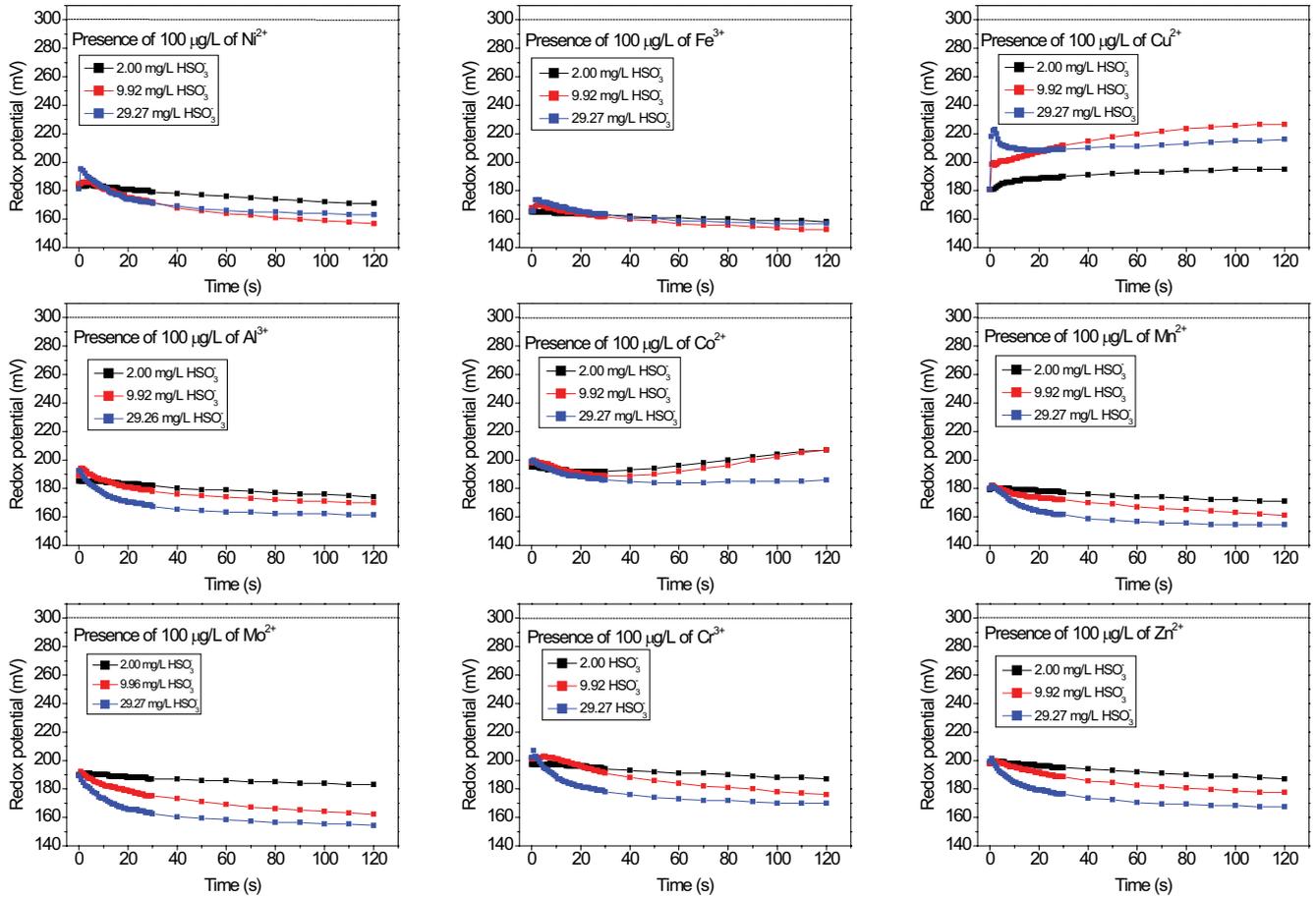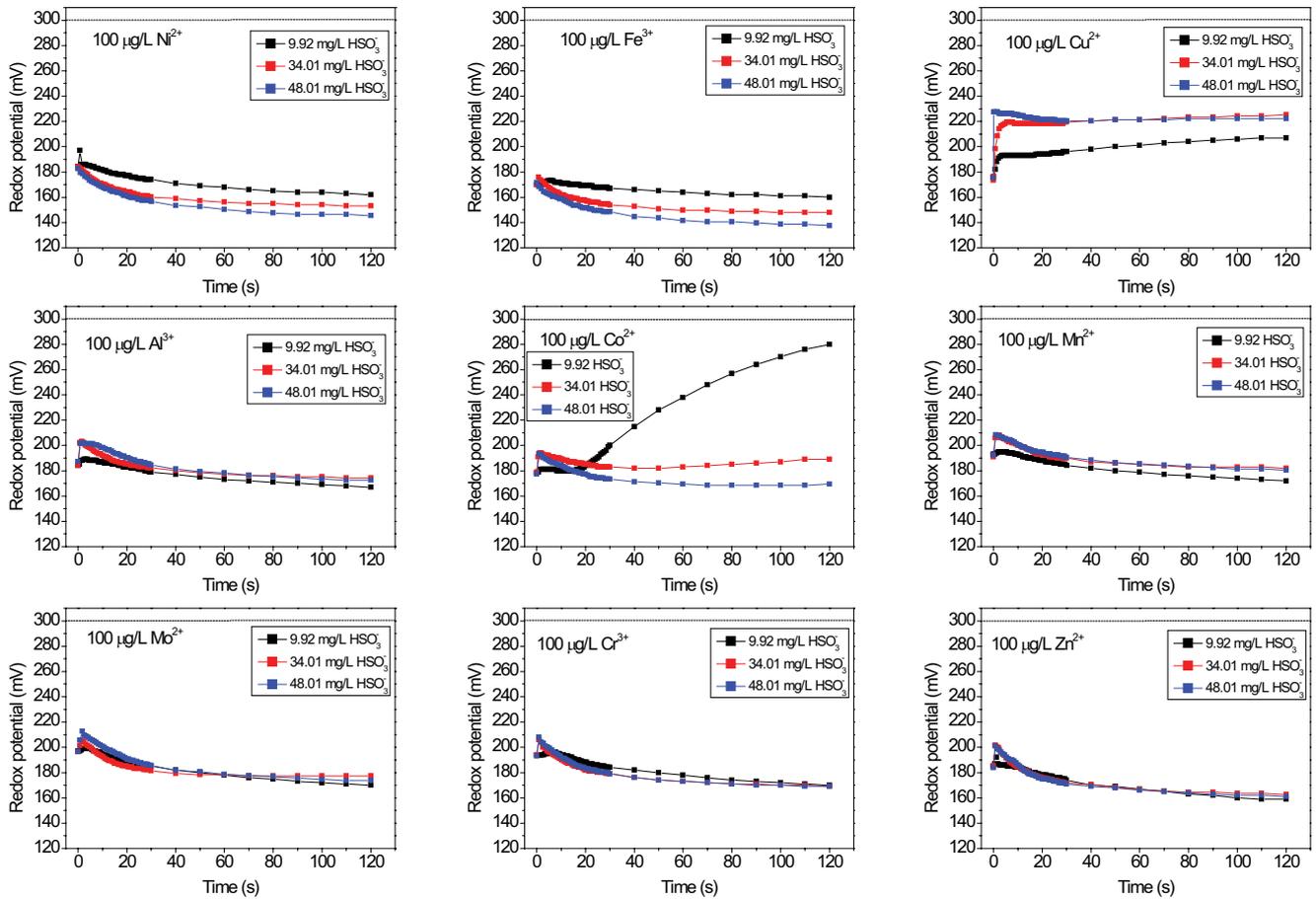
Fig. S2. Evolution of ORP values at 0.65 mg/L of chlorate using 2, 10, 30 mg/L of bisulfite, and 100 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in brackish water samples after ultrafiltration.
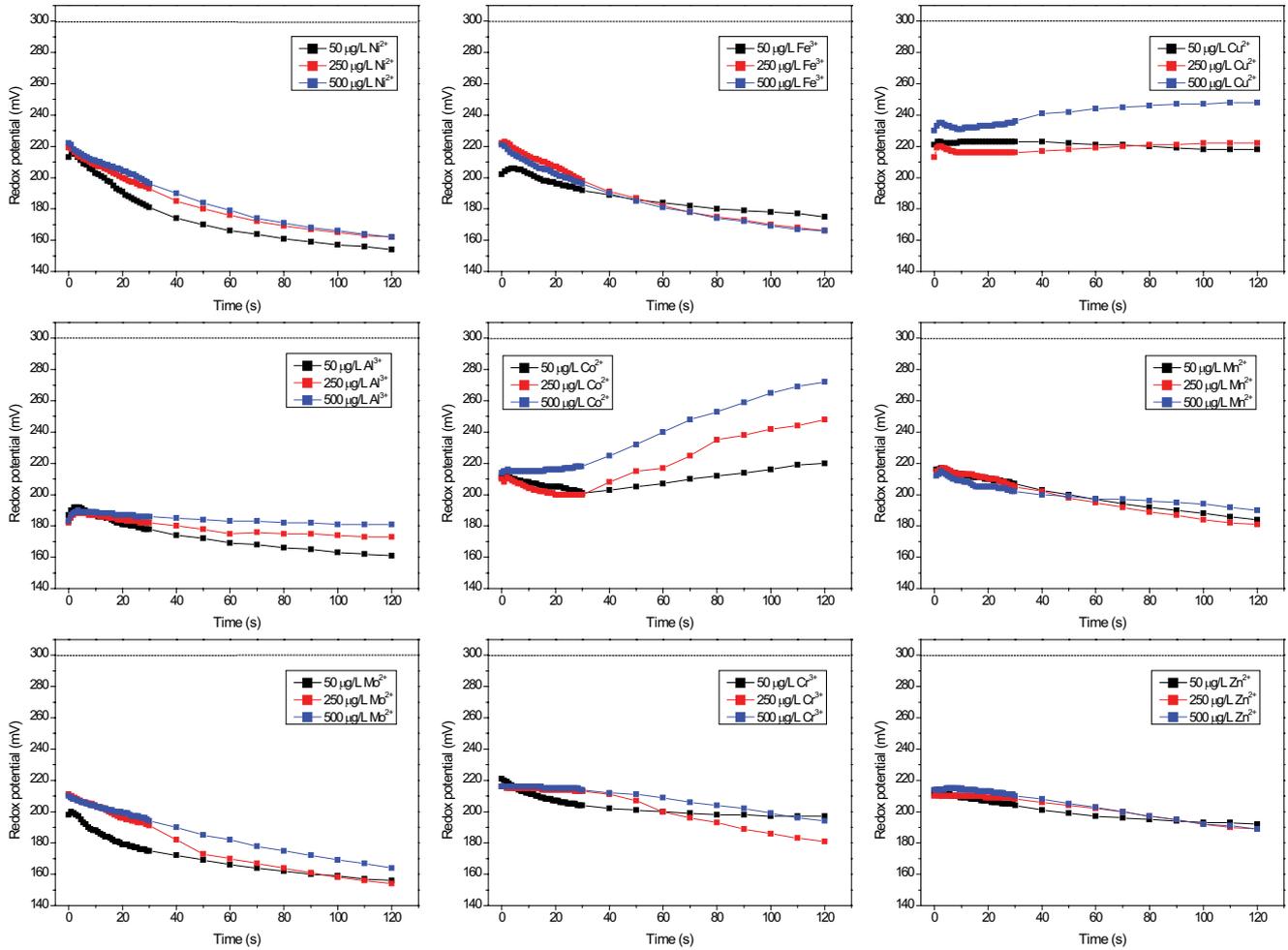
Fig. S3. Evolution of ORP values at 3 mg/L of chlorate using 10, 34, 48 mg/L of bisulfite, and 100 μg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in brackish water samples after ultrafiltration.
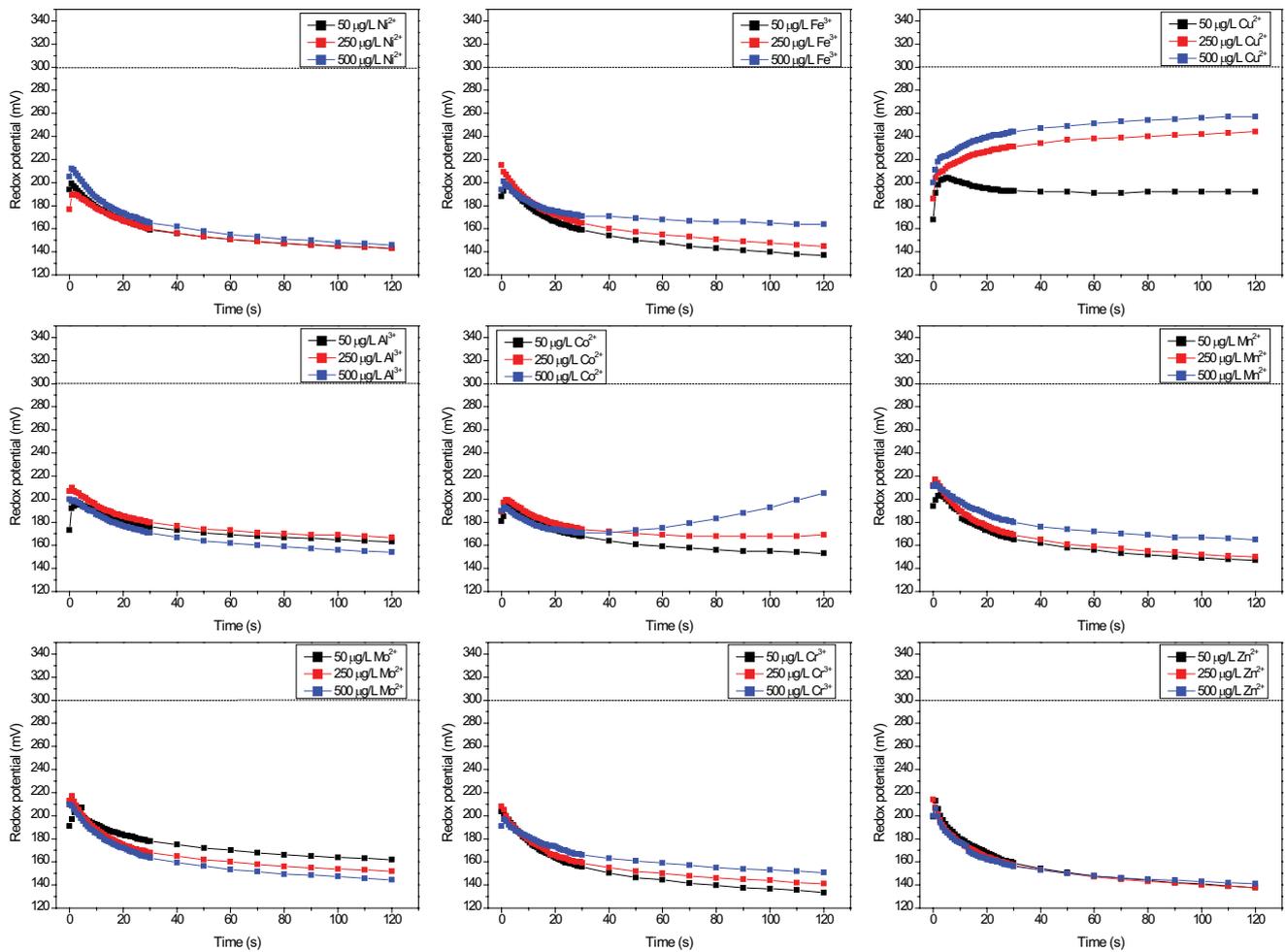
Fig. S4. Evolution of ORP values at 5 mg/L of bisulfite using 50, 250 and 500 μg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in brackish water samples after ultrafiltration.

Fig. S5. Evolution of ORP values at 30 mg/L of bisulfite using 50, 250 and 500 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in brackish water samples after ultrafiltration.
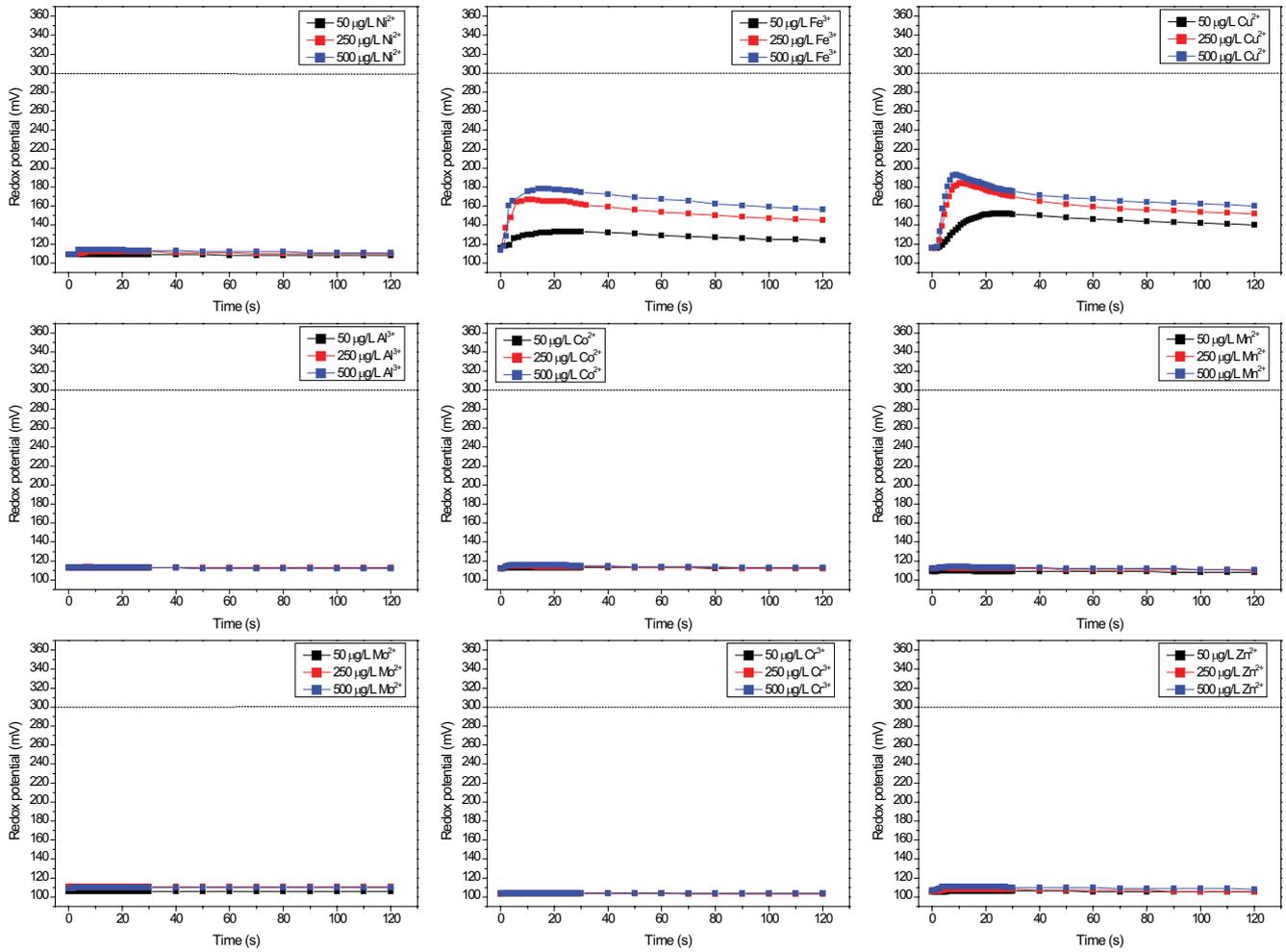
Fig. S6. Evolution of ORP values at 1% of bisulfite solution using 50, 250 and 500 µg/L of different dissolved metals (Ni^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, Mo^{2+}, Cr^{3+}, Zn^{2+}). Experiments were performed in permeate water samples after reverse osmosis.