1 ## *Original Research Article*

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3 ## Risk of residual aluminum in treated waters with aluminum

4 ## sulphate

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8 Abstract

9 Waters treatment by aluminum sulphate is the most used process in waters treatment to remove

10 unwanted microorganisms. The inorganic coagulants are partially hydrolyzed salts; their

11 dissolution in water depends mainly on this one's pH. However, there are still aluminum residues

12 after dissolving. The determination of residual aluminum in the treated waters is determined by the

13 standard addition method. Treated waters from the treatment ~~plant~~ station in Skikda's city contains

14 210 g / L of residual aluminum for an average dose ~~of~~ equal to 40m /L of aluminum sulphate. The

15 residual aluminum in treated water exceeds WHO standards (200μg / L), and far from the

16 recommended standards of 100 g / L in all searches. We made trials with laboratory flocculators

17 under the same conditions. The residual aluminium obtained by the same method, is 182 mg / L,

18 13.33% less than the WHO standards. Another one trial is carried out with a dose of 40 mg / L

19 alum, as adjuvant we used a bentonite from M'Zila (Algeria) with a dose of 3mg / L. This test has

20 helped reduce the amount of residual aluminum in raw water (20.48%, lower than the

21 recommended standards).

22 In order to investigate the causes of this excess, we made trials with the laboratory flocculators

23 under the same conditions that station. The residual aluminum obtained by the same metered

24 addition method, is 182 mg / L (13.33%, less than the WHO standards).

25 The dry residues were characterized by analysis with a scanning electron microscope and EDX

26 (MEB-EDX) to show the different spectra of the aluminum in the dry residue. The crude bentonite

27 is characterized by the elemental chemical method using X-ray fluorescence.

28 Keywords. Aluminum sulphate, bentonite, residual aluminum, MEB-EDX, fluorescence X.

29 **INTRODUCTION**

30 The residual aluminum present in water that has been treated clarification with

31 aluminum sulphate may be the result of an overdose or no conditions favourable

32 to its hydrolysis (pH and temperature). The Flocculants bind to in suspension

33 particles and cause them to precipitate as sludge at the bottom of flocculators and

34 decanters. If the conditions are not met some of the aluminum remains in solution

35 (BOTTERO and al., 1980).

36 Epidemiological studies have shown the dangers of aluminum and some countries

37 have already taken their precautionary. The Canada, for example, tolerates only

38 than 100μg / L in the treated water (HILL., 1989). In France, epidemiology

39 research team of Professor Jean François Dartigues, University of Bordeaux has

40 published several articles in the American Journal of epidemiology (RONDEAU

41 and al., 2000; RONDEAU and COMMENGES, 2001; RONDEAU and al, 2006.)

42 treating the relation between aluminium and Alzheimer's disease. A lot of works

43 advocate a tolerable threshold limited to 100μg / L in water used for drinking,

44 while remaining vigilant about monitoring the waters treatment plants. The

45 inorganic monomeric aluminum represents their main fraction of aluminum after

46 treatment of the water (62% of total).

47 A study performed in Europe estimated that the intake of aluminum from drinking

48 water is less than 5% of daily intake from other sources like food, utensils,

49 medicines etc., (SOLLARS and al., 1989).

50 An estimated total daily average intake of 8.26 mg or the share contributed by the

51 water is less than 0.4 mg of aluminum.

52 Higher concentrations are found in drinking water in relation to the quality of raw

53 water over-loaded if the pH is not controlled properly during the steps of

54 treatment and optimizing the dose in steps of coagulation, decantation and

55 filtration (MEGHZILI and al, 2012; American Water Works Association Research

56 Foundation, 1993). In distribution networks, the process of disinfection can be

57 limited if we find high levels of residual aluminum that retains and protects

58 microorganisms (American Water Works Association Research Foundation, 1993.

59 COSTELLO., 1984). The best results are obtained with pH between 6 and 7,

60 minimum solubility range of aluminum hydroxide during coagulation

61 (LETTERMAN and DRISCOLL., 1988).

62 The chemistry of aluminum in water can be described by several forms (BAES

63 and MESMER, 1976; and MOTEKAITIS MARTELL, 1988; JEAN PIERRE

64 MARC HENRY JOLIVET and 1998):

65 → five monomers: Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ $Al(OH)_3^0$, $Al(OH)_4^-$

66 → three polymers: $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$, $[Al_{13}O_4(OH)_{24}$

67 $(H_2O)_{12}^{7+}$

68 → ~~a~~ One precipitate: $Al(OH)_3$

69 Aluminum mononuclear hydrolytic products are combined to form polynuclear

70 species in solution (Rondeau et al., 2000). Aluminum begins to polymerize when

71 the pH of an acidic solution substantially increases beyond 4.5: (BERTSCH and

72 PARKER., 1996)

73 $2Al(OH)(H_2O)_5^{2+} \rightleftharpoons Al_2(OH)_2(H_2O)_8^{4+} + 2H_2O$

74 Polymerization produces gradually larger structures and eventually lead to the

75 formation of the Al_{13} polycation (PARKER and BERTSCH., 1992a, 1992b).

76 According to Jones and BENOIT (1986) the aluminium present in the treated

77 water is found largely under dissolved forms. The dissolved aluminum is defined

78 as aluminum that passes through a 0.22μm filter (MEGHZILI and al., 2012).

79 In highly charged water, it is important to control the total aluminum content by

80 optimizing coagulation and filtration processes. We must control the dosage of the

81 coagulant and coagulation pH, because it must be accompanied by good stirring

82 allowing good flocculation of suspended solids and will facilitate their decantation

83 before the step of filtration.

84 The neglect of one of these steps may cause an increase of residual aluminum.

85 The pH is one of the factors that determine the form of aluminum present in water

86 and its solubility increases in lower pH (MARTELL and MOTEKAITIS., 1989).

87 **1. MATERIALS AND METHODS**

88   **1.1. Operating procedure**

89 Analytical results of the raw water and the treated water in station are

90 shown in Table I.

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95 Table I. Physic-chemical analysis of water supply (Central Laboratory of
96 the company's petrochemical industries, ENIP).

Parameters	Units	Raw water	*Treated water station*
Aspect	-	Disorder	*Limpid*
pH	-	8.10	*7.78*
Conductivity	µs/ cm	418	*425*
Salinity rate	mg/L	360	*340*
Suspended materials	mg/L	42	*Traces*
Chlorides	mg/L	78.55	*72.73*
Carbonates	mg/L	Traces	*Traces*
Bicarbonates	mg/L	132.41	*127.32*
Calcium	mg/L	50.79	*50.79*
Magnesium	mg/L	14.40	*14.40*
Total hardness	°F	18.6	*18.6*
Sulphates	mg/L	46.23	*44.20*
Phosphates	mg/L	Trace	*Traces*
Potassium	mg/L	4.9	*4.9*
Sodium	mg/L	9.3	*8.3*
Dissolved organic carbon	mg/L	38.02	*1.68*
Ammonium	mg/L	0.42	*Traces*
Nitrites	mg/L	Trace	*Traces*
Nitrates	mg/L	Traces	*Traces*
Total iron	mg/L	1.91	*1.88*
Cuivre	mg/L	0.37	*0.36*
Mercury	µg/L	3.80	*0.76*
Aluminum	µg/L	-	*210.00*
Turbidity	NTU	8.87	*2.96*
Organic matter content	Mg O_2/L	8.70	5.55

1.2. Determination of the content of aluminum in the treated water

1.2.1. Principle

The aluminum with cyanine Erichrome R forms a red complex at pH 6. After 5 minutes, the analysis is performed at the wavelength of 535 nanometers. The method used is the standard addition method.

- **Equipment**

    UV/visible type Shimadzu UV-1605.

- **reagents**

- Solution Erichrome cyanine R

- Acetic acid buffer solution pH 6

- Ascorbic Acid

- Solution 0.1 Mole EDTA (Éthylène Diamine Tétra-Acétique)

- Sulphuric acid 0.05 Mole

- Al Solution 0.1 g / L

    1.2.2. Procedure

Adjust the water sample at a pH of 3-3.5

Put 10ml of sample in 5 100mL flasks. In the first flask was added all reagents except the aluminum standard solution (to adjust the zero of spectrophotometer). In other vials, we put all reagents except EDTA and we add an increasing dose of standard aluminum. The absorbance of the solution of each flask was then measured is and traced in curve A = f (C), the absorbance versus concentration aluminum and from this curve the amount of aluminum was determined in the sample.

    1.2.3. Description of tests jar-test

Jar test is carried out as per the procedures outlined in paragraph 1.2.

The tests were conducted in a laboratory flocculator comprising six agitators and six 500mL beakers. The water to be treated is placed in each beaker. The rapid stirring is carried out at 200 rev / min; at time zero, we add increasing doses of aluminum sulphate in each of the beakers. The phase rapid stirring lasts three minutes. The rapid stirring is followed by 17 minutes of slow stirring at 45 t / min. After decanting for 30 minutes, we take a quantity of supernatant to analyze

128 residual aluminum. The optimum dose of aluminum sulphate is 40 mg / L

129 (determined by jar-test). In Table 2 we present the results of quality parameters

130 analysis.

131 **Table II. Results of analyzes of quality parameters**

Parameters	Raw water	(jar-test) Aliminum sulphate	*Treated water station (sulphate Al)*	Aliminum sulphate +Bentonite
Doses (mg/L)	-	40	40	40 +3
Temperature (°C)	28	29,5	28	29
Conductivity (µs/cm)	545	538	559	576
pH	8,10	7,32	7,61	7,79
Salinity	0,3	00	00	-
Turbidity(NTU)	4,47	1,04	2,10	3,37
Organic matter(mgO$_2$/L)	11,2	4,12	4,34	1,97
TH °F	21,00	20,40	26,20	-
TAC °F	11,50	9,70	8,10	-
% elimination turbidity	0	76,73	53,00	24,25
% élimination organic matter	0	63,21	61,25	42,41
Residual Aluminum (µg/L)	No detected	0,182	0,210	0,167

132 In Table II, we have considered only the monitoring of the residual aluminum in

133 the jar-tests and the water treated in station, then to the same dose ~~was~~ we add~~ed~~ a

134 dose of 3 mg / L of bentonite as an adjuvant. At the end, the results will be

135 compared between them.

136 **1.3. Analysis of solid materials**

137   1.3.1. Characterization bentonite

138 Bentonite is characterized by the National Entreprise of Non-Ferrous Mining

139 Products and Useful Products (ENOF) in 2007.

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141

142 **Table.III. Physico-chemical characteristics of the bentonite**

Specific surface m^2/g	pH	Specific mass g/cm^3	Exchange capacity (Meq/100g)	Exchangeable cations (meq/100g)			
				Ca^{2+}	Na^{2+}	Mg^{2+}	Na/ca
65,00	9,00	2,71	75,8	43,60	25,20	4,80	0,58

143

144 **Table IV. Mineralogical characteristics of bentonite**

Montmorillonite	Quartz	Carbonates	Feldspars	Biotites
45 à 60%	15 à 20%	8 à 10%	3 à 5%	8 à 10%

145   1.3.2. Electronic scanning microscopy

146 This operation allows to directly visualizing the morphology (shape, size) of
147 particles and their possible surface roughness (image 1, 2 and 3). It consists of
148 scanning, line by line, the surface of the particles by an incident beam of high
149 energy electrons, thereby causing the emission of secondary electrons of low
150 energy. These are sent to a detector which transmits the signal to a screen of
151 where the scanning is synchronized with the scanning of the sample. The contrast
152 of the image reflects the relief of the sample. These secondary electrons allow
153 reconstruction of a magnified picture of the surface.

154 In laboratory, images of the scanning electron microscope (SEM) were performed
155 using a Philips XL 30 microscope equipped with a field emission gun. The sample
156 is prepared by depositing the powder on the aluminum support coated with a thin
157 layer of graphite whose surface is adhesive. It is then metalized by vacuum, by
158 sputtering a layer of gold having a thickness between 10 and 20 nm.
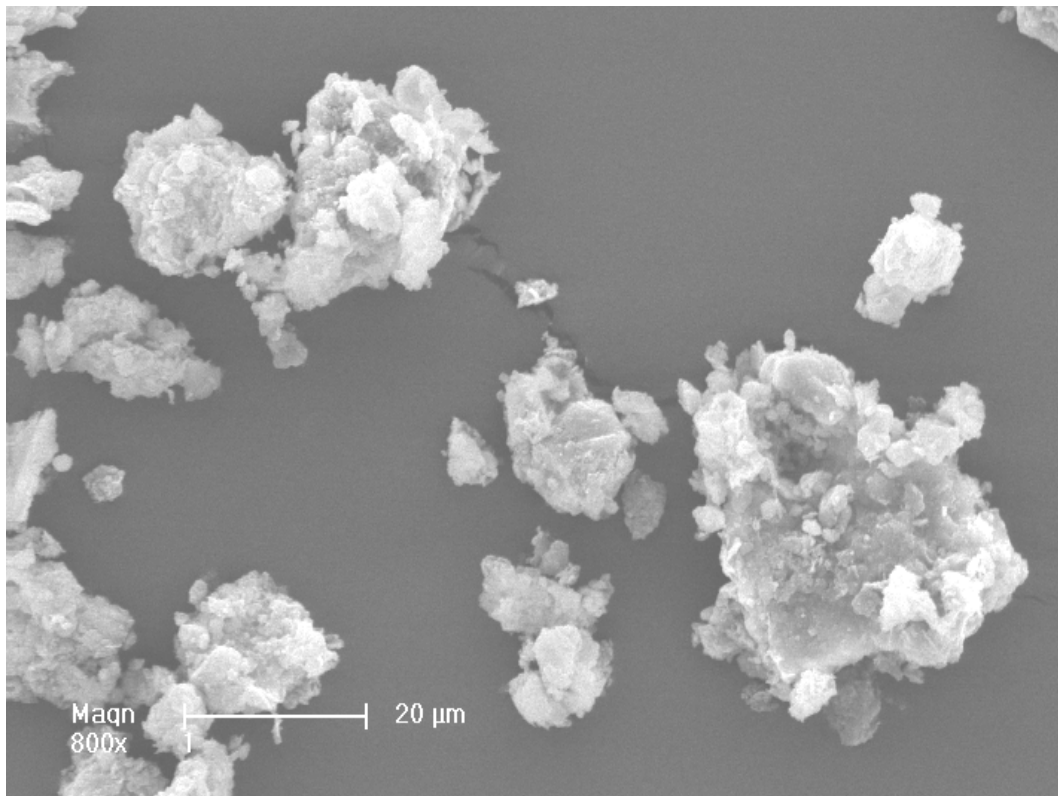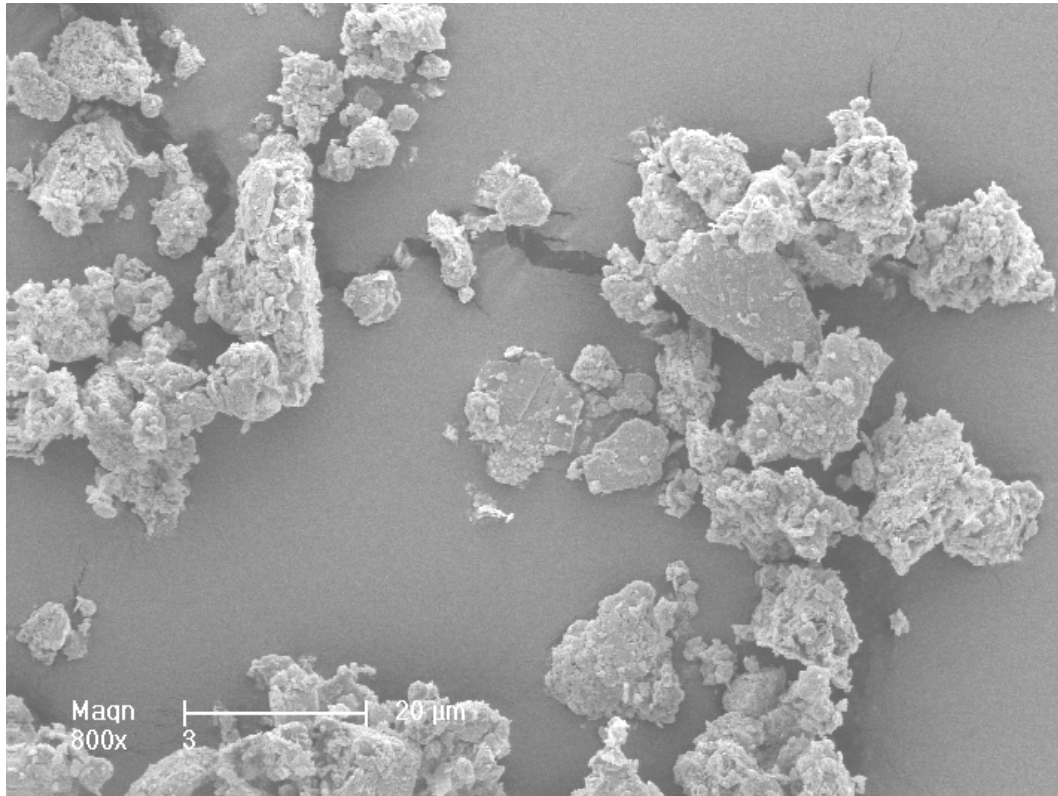
159

160   Figure 1. Image the morphology raw bentonite particles
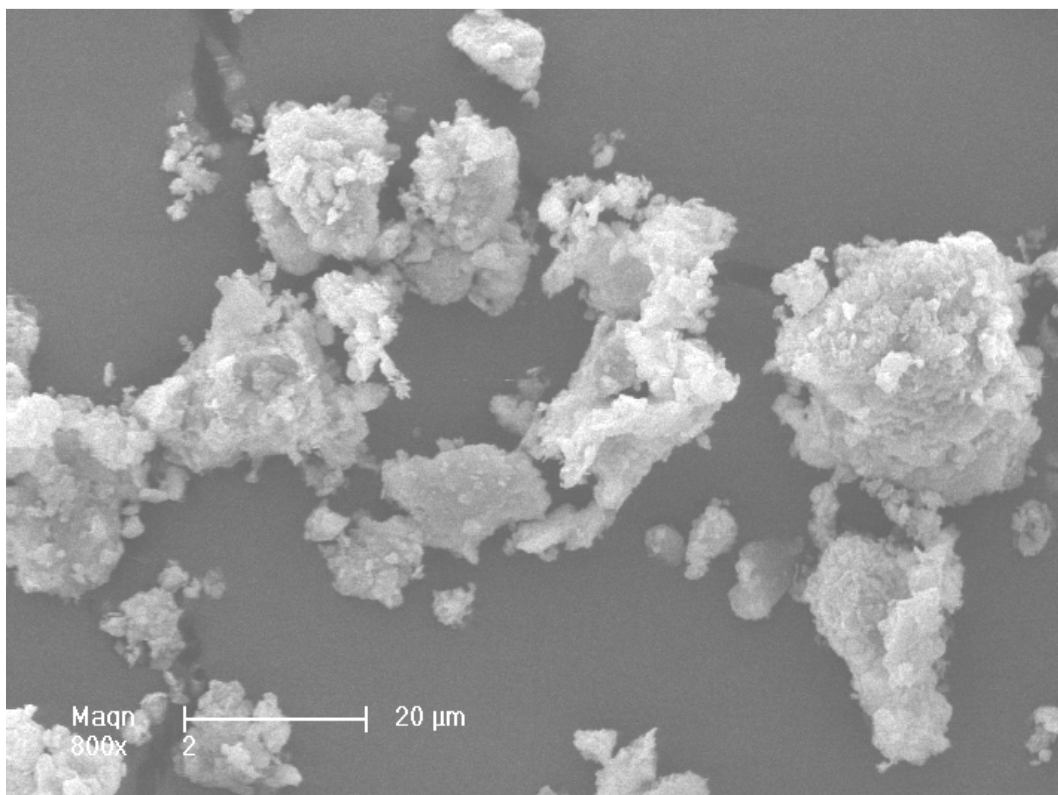
161

162   Figure 2. Sample image with a dose of aluminum sulfate 40 mg / L

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164 Figure 3. Sample image with a dose of aluminum sulfate 40 mg / L + 3 mg of
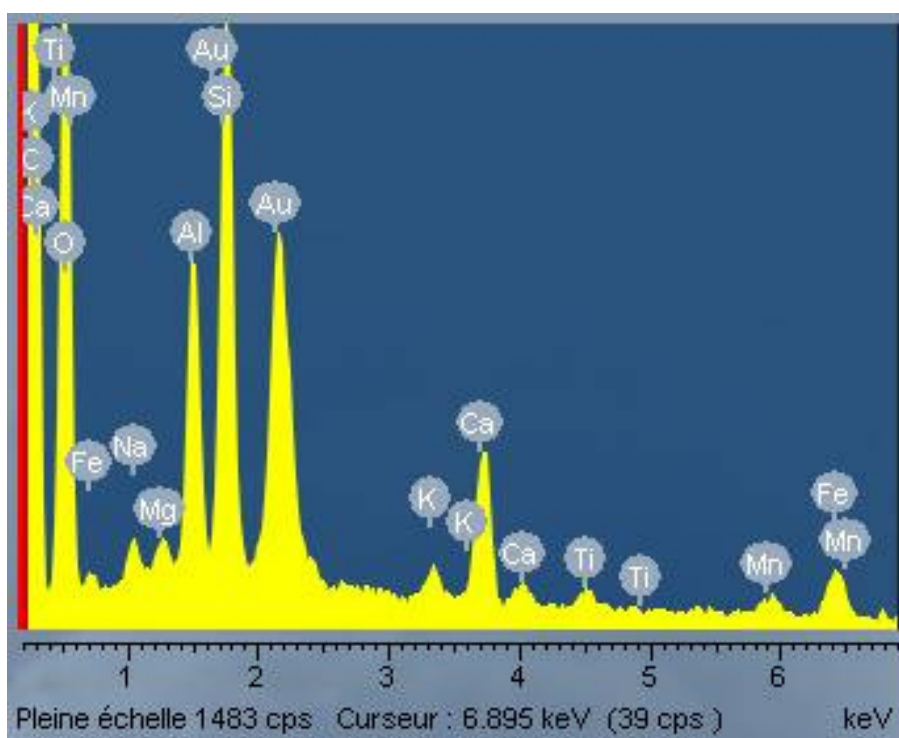
165 bentonite

166 1.3.3. MEB-EDX dry residues

167 Figure 4, 5, 6 shows the various spectra of the minerals present in different

168 samples. The peaks of aluminum vary from one sample to another. The higher

169 amounts of aluminum are located on the sample 3 and then the second and the

170 lowest peak on the sample 1. Figure 3 shows a larger concentration of aluminum

171 on the image 3

172
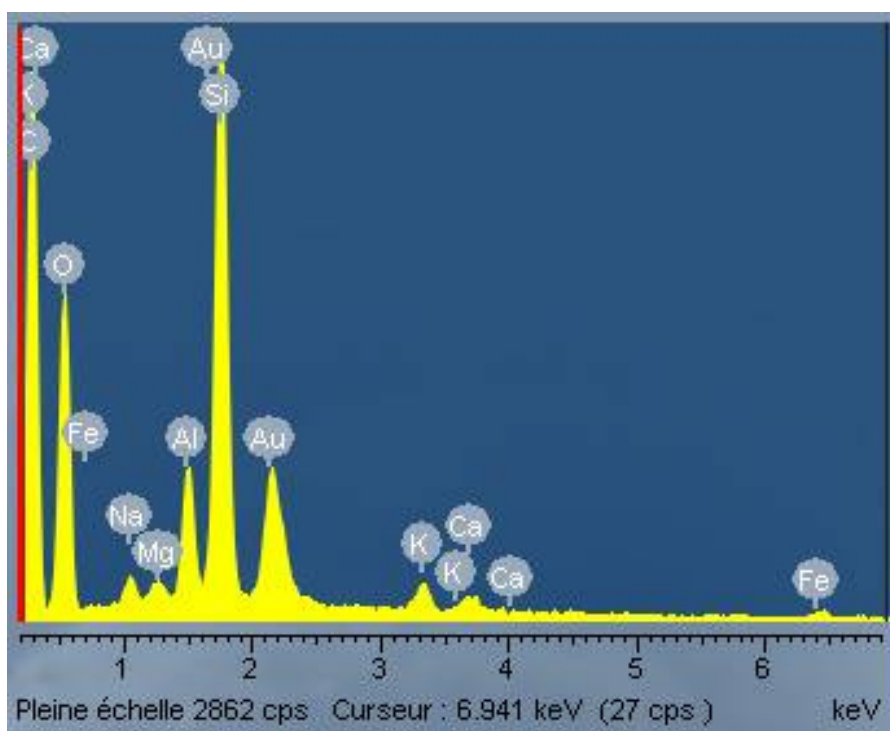
Figure 4. Raw bentonite

174

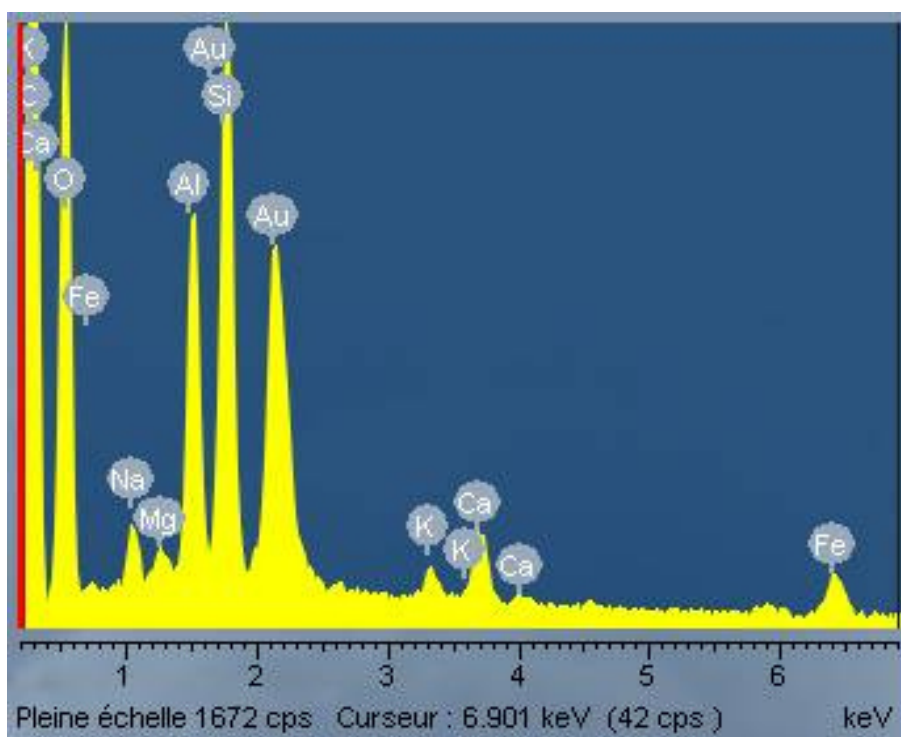**Figure 5. Dose of aluminum sulphate 40 mg / L**

Figure 6. Dose of aluminum sulphate 40 mg + 3 mg bentonite

1.3.4. Fluorescence (XRF)

Fluorescence spectrometry is an elemental analysis method using the physical property of the material to determine pure elements concentrations. The X-ray spectrum emitted by the material is characteristic of the sample composition. The spectrum analysis allows deducing the elemental composition of the mass concentrations. The powder to be analyzed is put into a cup, and then pressed onto a pellet of boric acid. The device used is a fluorescence spectrophotometer X MagiX Panalytical.

194 **Table V. Quantification of raw bentonite sample**

Analyte	Compound of formula	Concentration %	Méthod of calculating
Na	Na_2O	2.796	Calculated
Mg	MgO	2.913	Calculated
Al	Al_2O_3	14.031	Calculated
Si	SiO_2	69.665	Calculated
P	$P2O_5$	0.082	Calculated
S	SO_3	0.491	Calculated
K	$K2O$	2.407	Calculated
Ca	CaO	4.098	Calculated
Ti	TiO_2	0.350	Calculated
Mn	MnO_2	0.168	Calculated
Fe	Fe_2O_3	2.879	Calculated
Rb	Rb_2O	0.009	Calculated
Sr	SrO	0.041	Calculated
Cl	Cl	0.069	Calculated

195

196 **Table VI. Percentage of mass concentrations**

Element	Concentration %	Element	Concentration %
O	48.60	K	2.00
Na	2.07	Ca	2.93
Mg	1.76	Ti	0.210
Al	7.43	Mn	0.106
Si	32.6	Fe	2.01
P	0.0359	Rb	0.00844
S	0.197	Sr	0.0347
Cl	0.0690		

197 **2. DISCUSSION OF RESULTS**

198 We considered only the monitoring of residual aluminium.

199

Table VII. Monitoring the residual aluminum in the different samples

	Réactifs		Dose (mg/L)	Al residual	% Al residual/total Al
Water treatment station	Alumina sulphate		40	0,210	5,77%
Jar-test	Alumina sulphate		40	0,182	5,00%
Jar-test	Alumina sulphate		40	0,167	4,58%
	Bentonite	+	3		

The 40 mg dose of aluminum sulphate / L gives 3.64 mg / L of aluminum. water treated of station contains 5.77% of the total aluminum and thus constitutes the residual aluminum. The pH of raw water arriving at the station has a value of 8.10, less favorable for the polymerization leading to the formation of the Al13 polycation. After treatment the pH does not exceed 7.61 and the minimum solubility range of aluminum hydroxide during coagulation is at a pH between 6-7 for best yields (LETTERMAN and DRISCOLL., 1988).

Aluminum sulfate, in addition to its action on the reduction of suspended solids, it intervenes on lowering the pH. A pH of 7.61 obtained after treatment with aluminum sulfate confirmed that there was no optimization of the various steps of clarification (dose, pH, residence time, stirring etc.).

For the jar-test performed with SA of 40 mg / L, 5% of the total aluminum remains in solution, limit advised and recommended in all works on the residual aluminum in drinking water treatment.

The jar-test performed with 40 mg / L SA and 3mg / L of bentonite, residual aluminum is 4.58% of the total aluminum, well below the 5% recommended.

According to Sollars and al (1989), in a study of aluminum in drinking water in Europe have also shown that the aluminum contribution of drinking water is less than 5%.

The optimum dose determined by jar-test has eliminated 95% of the total aluminum after filtration.

Incidentally, during the process of agglomeration or coagulation, much of aluminum contained in the aluminum salts added is hydrolyzed to give/produce the aluminum hydroxide which precipitates and becomes part of the floculate. This aluminum is therefore part of the sludge generated by the treatment process.

226 It is possible that a small amount of added aluminum remains in the treated water,
227 whether in colloidal particle form (Al (OH) 3) or in soluble form (Al (OH) $_2$+, Al
228 (OH) $_4$ $^-$), according to the conditions of processing. A fault in the spillway of the
229 sludge, incorrect scraping, unsettled flow of the sludge pumps, can cause release
230 of the aluminum contained in the sludge and thus constitute a further addition to
231 the existed aluminum residual.

232 By studying the electronic scanning microscopy images and spectra in the jar-tests
233 1, 2 we find that the aluminum peaks are important in the second test. For a dose
234 of 40mg / L of SA, 5% of the total aluminum is residual; the remainder is with the
235 settled particles. In station, and under the same conditions, the residual aluminum
236 is 5.77% of the total aluminum. In the resort, this is explained by the non
237 homogeneity of treatment (agitation, dosage, residence time) because it must meet
238 the urgent need of drinking water because its capabilities are no longer sufficient
239 to satisfy a growing of population.

240 In addition a portion of the aluminum present in sludge may be salted out when
241 the sludge removal is not done automatically or when the sludge discharge pumps
242 are stopped. Bentonite, as adjuvant reduced the residual aluminum to a lower level
243 due to its cationic exchange capacity (75.8 meq / 100 g of bentonite) and the
244 possibilities of retention in their foliar spaces. The bentonite used contains
245 14.031% of Al_2O_3 compound, giving a 7.43% of aluminum, which may in its turn
246 be hydrolyzed to form other polymers, polycations Al_{13}, which promote good
247 decantation and reduce the residual aluminum.

248 **CONCLUSION**

249 The aluminum sulfate is used as a coagulant in the treatment of surface water;
250 generally its pH is close or greater than 8, what does not facilitate turbidity
251 removal, because their removal also results in reduction of pathogenic
252 microorganisms and also reduces the formation of by-products (organic matter)
253 before disinfection, to prevent the formation of compounds organochlorine
254 responsible for some cancers. Disinfection can be hindered by high levels of
255 residual aluminum. It is imperative, in the surface water treatment process, to

256   work in optimum conditions can lead to a minimum aluminum concentration in

257   drinking water. In loaded water, an adjuvant of the coagulation-flocculation can

258   help to reduce the residual of aluminum, as is the case with natural bentonite. The

259   Favorable conditions for hydrolysis of aluminum (pH, t °, agitation and water time

260   stay) allow the formation of the Al_{13} polycation responsible for a good

261   flocculation and reduced residual aluminum including its harmfulness described

262   in several studies. The tests have shown that if one respects the conditions of

263   hydrolysis of aluminum (Table II), we arrive at an acceptable level of residual

264   aluminum.

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