Original Research Article

Risk of residual aluminum in treated waters with aluminum sulphate

Abstract

Waters treatment by aluminum sulphate is the most used process in waters treatment to remove unwanted microorganisms. The inorganic coagulants are partially hydrolyzed salts; their dissolution in water depends mainly on this one's pH. However, aluminum residues may remain after dissolving. In this study, determination of residual aluminum in treated waters is performed by the standard addition method. Treated waters from the treatment station in Skikda's city contained 210 g / L of residual aluminum for an average dose equal to 40m /L of aluminum sulphate. The residual aluminum in treated water exceeds WHO standards (200µg / L), and far from the recommended standards of 100 g / L in all searches. Trials were made with laboratory flocculators under the same conditions. The residual aluminium obtained by the same method, is 182 mg / L, giving 13.33% less than the WHO standards. Another trial was carried out with a dose of 40 mg / L alum. As adjuvant, a bentonite from M'Zila (Algeria) was used with a dose of 3mg / L. This test helped to reduce the amount of residual aluminum in raw water (20.48%, lower than the recommended standards).

In order to investigate the causes of these excess, trials were made with the laboratory flocculators under the same conditions in that station. The residual aluminum obtained by the same standard addition method, is 182 mg / L (giving 13.33% less than the WHO standards).

The dry residues were characterized by analysis using a scanning electron microscopy (SEM) and EDX (MEB-EDX) to show the different spectra of the aluminum in the dry residue. The crude bentonite is characterized by the elemental chemical method using X-ray fluorescence.

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

INTRODUCTION

The residual aluminum present in water that has been treated clarification with aluminum sulphate may be the result of an overdose or no conditions favourable to its hydrolysis (pH and temperature). The Flocculants bind to particles in suspension and cause them to precipitate as sludge at the bottom of flocculators

and decanters. If the conditions are not met, some of the aluminum remains in solution (BOTTERO and al., 1980).

Epidemiological studies have shown the dangers of aluminum and some countries have already taken their precautions. Canada, for example, tolerates less than 100µg / L in the treated water (HILL., 1989). In France, epidemiology research team of Professor Jean François Dartigues, University of Bordeaux has published several articles in the American Journal of epidemiology (RONDEAU and al., 2000; RONDEAU and COMMENGES, 2001; RONDEAU and al, 2006.) treating the relation between aluminium and Alzheimer's disease. A lot of works advocate a tolerable threshold limited to 100µg / L in drinking water, while remaining vigilant about monitoring the waters treatment plants. The inorganic monomeric aluminum represents their main fraction of aluminum after water treatment (62% of total).

A study performed in Europe estimated that the intake of aluminum from drinking water is less than 5% of daily intake from other sources like food, utensils, medicines etc., (SOLLARS and al., 1989).

An estimated total daily average intake of 8.26 mg or the share contributed by the water is less than 0.4 mg of aluminum.

Higher concentrations are found in drinking water in relation to the quality of raw water over-loaded if the pH is not controlled properly during the steps of treatment and optimizing the dose in steps of coagulation, decantation and filtration (MEGHZILI and al, 2012; American Water Works Association Research Foundation, 1993). In distribution networks, the process of disinfection can be limited if we find high levels of residual aluminum that retains and protects microorganisms (American Water Works Association Research Foundation, 1993. COSTELLO., 1984). The best results are obtained with a pH between 6 and 7, minimum solubility range of aluminum hydroxide during coagulation (LETTERMAN and DRISCOLL., 1988).

The chemistry of aluminum in water can be described by several forms (BAES and MESMER, 1976; and MOTEKAITIS MARTELL, 1988; JEAN PIERRE MARC HENRY JOLIVET and 1998):

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

→ three polymers: $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

→ One precipitate: $Al(OH)_3$

Aluminum mononuclear hydrolytic products are combined to form polynuclear species in solution (Rondeau et al., 2000). Aluminum begins to polymerize when the pH of an acidic solution substantially increases beyond 4.5: (BERTSCH and PARKER., 1996)

$2Al(OH)(H_20)_5^{2+} \rightleftharpoons Al_2(OH)_2(H_20)_8^{4+} + 2H_20$

Polymerization produces gradually larger structures and eventually lead to the formation of the Al_{13} polycation (PARKER and BERTSCH., 1992a, 1992b).

According to Jones and BENOIT (1986), the aluminium present in the treated water is largely located in dissolved forms. The dissolved aluminum is defined as aluminum that passes through a 0.22µm filter (MEGHZILI and al., 2012).

In highly charged water, it is important to control the total aluminum content by optimizing coagulation and filtration processes. We must control the dosage of the coagulant and coagulation pH, because it must be accompanied by good stirring allowing good flocculation of suspended solids and will facilitate their decantation before the step of filtration.

If any one of these steps is neglected, it may cause an increase of residual aluminum. The pH is one of the main factors that determine the form of aluminum present in water; solubility of aluminum increases in lower pH (MARTELL and MOTEKAITIS., 1989).

1. MATERIALS AND METHODS

1.1. Operating procedure

Analytical results of the raw water and the treated water in station are shown in Table I.

Table I. Physic-chemical analysis of water supply (Central Laboratory of 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

Water sample is adjusted to pH of 3-3.5.then, 10 ml of sample are put in 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 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 according to 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 rev / min. After decanting for 30 minutes, we take a quantity of supernatant to analyze residual aluminum. The optimum dose of aluminum sulphate is 40 mg / L

(determined by jar-test). The results of quality parameters analysis are presented in Table II.

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

In Table II, we have considered only the monitoring of the residual aluminum in the jar-tests and the water treated in station, then to the same dose was added a dose of 3 mg / L of bentonite as an adjuvant. At the end, the results will be compared between them.

1.3. Analysis of solid materials

1.3.1. Characterization bentonite

Bentonite is characterized by the National Entreprise of Non-Ferrous Mining and Useful Products (ENOF) in 2007.

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

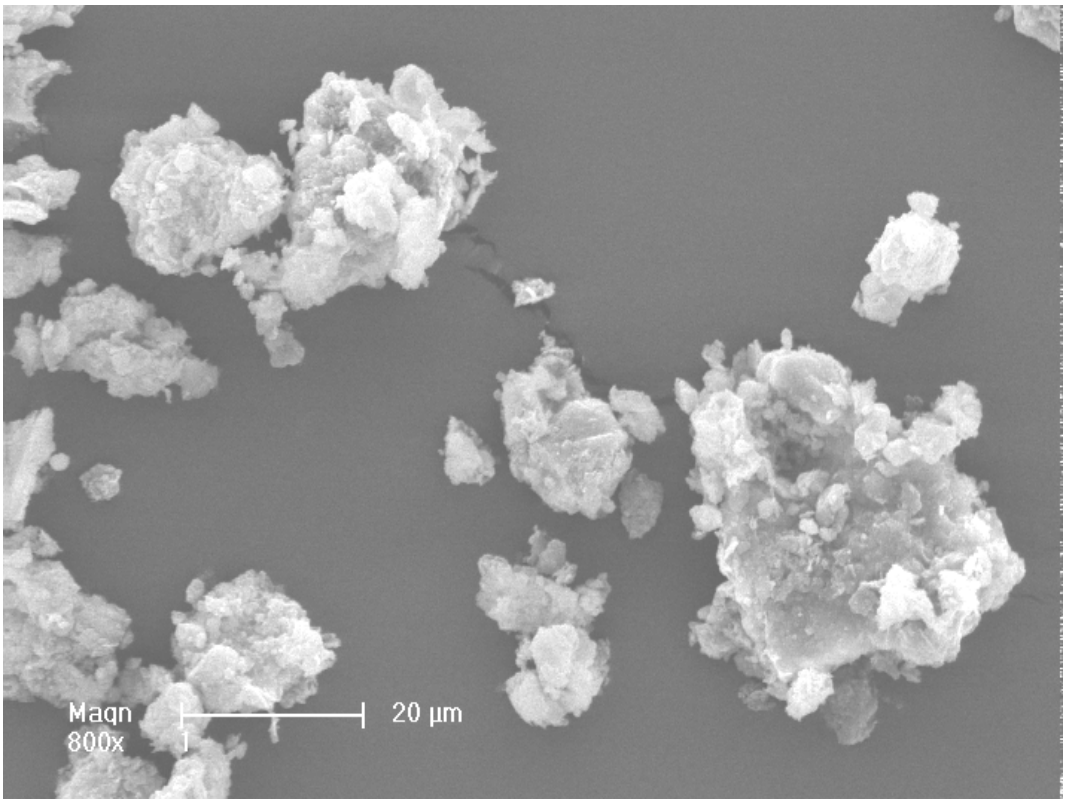
Table IV. Mineralogical characteristics of bentonite

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

1.3.2. Electronic scanning microscopy (EMF)

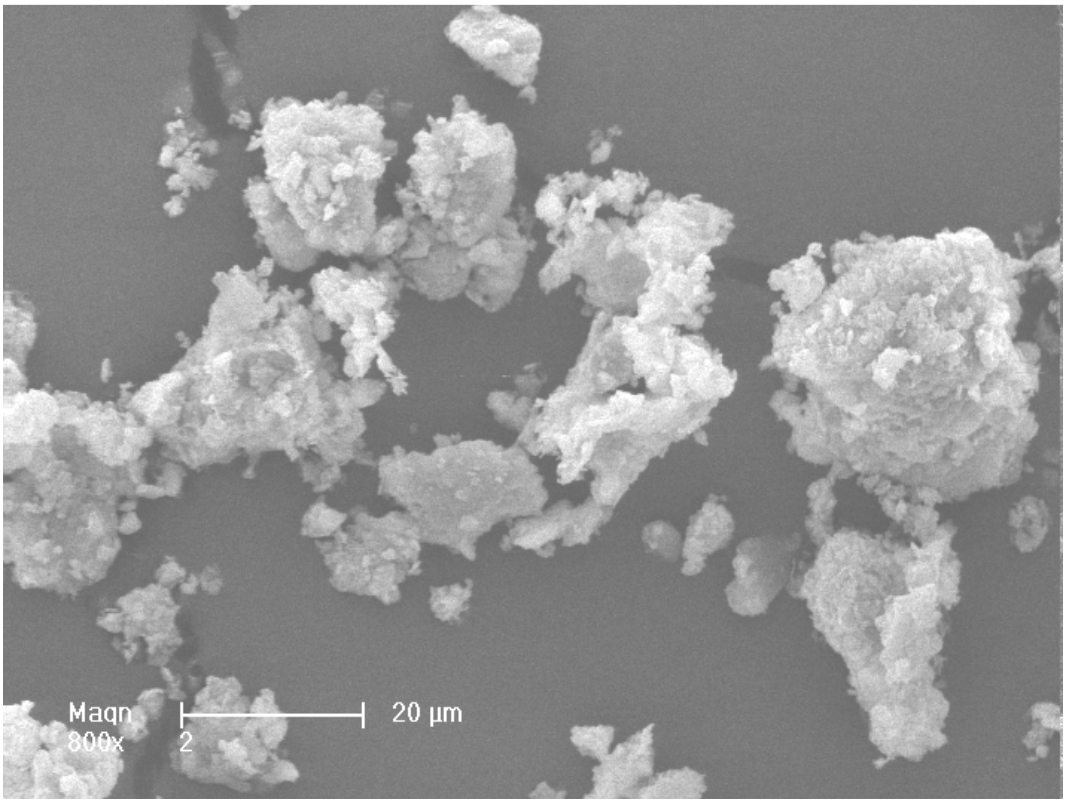
This operation allows to visualize the morphology (shape, size) of particles and their possible surface roughness (image 1, 2 and 3) directly. It consists to scan, line by line, the surface of the particles by an incident beam of high energy electrons, thereby causing the emission of secondary electrons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

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



160

161 Figure 1. Image the morphology raw bentonite particles



162

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

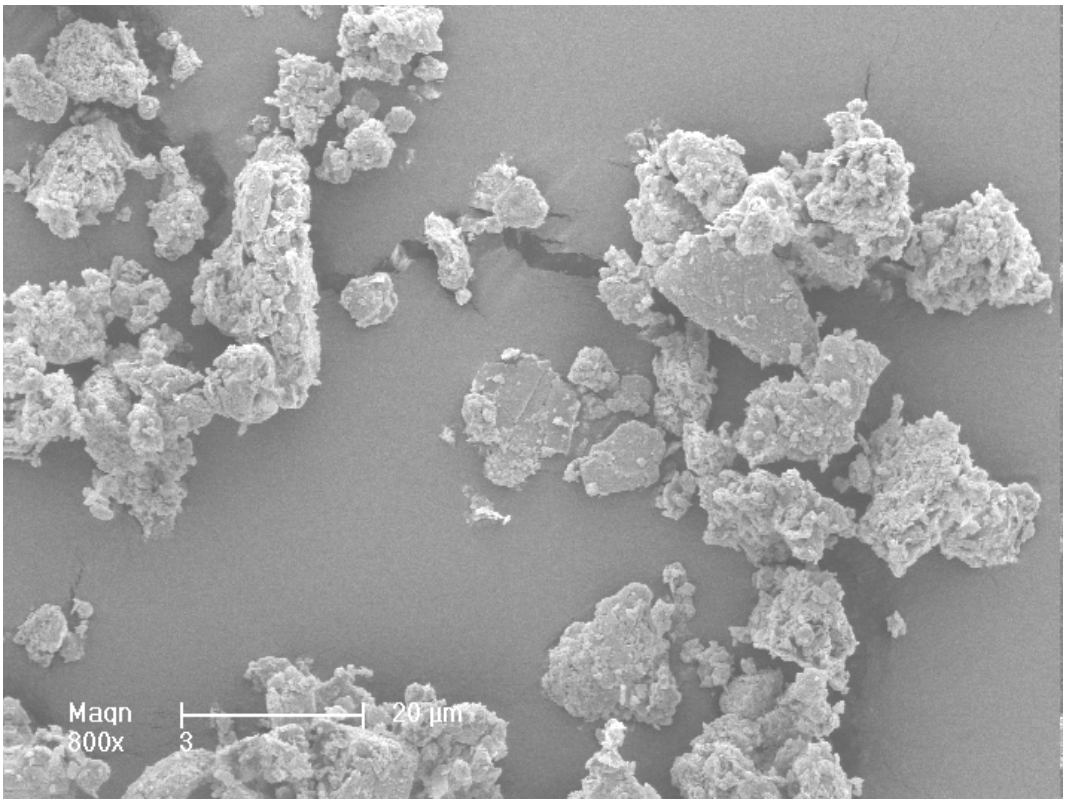


Figure 3. Sample image with a dose of aluminum sulfate 40 mg / L + 3 mg of bentonite

1.3.3. MEB-EDX dry residues

Figure 4, 5, 6 shows the various spectra of the minerals present in different samples. The peaks of aluminum vary from one sample to another. The higher amounts of aluminum are located on the sample 3 and then the second and the lowest peak on the sample 1. Figure 3 shows a larger concentration of aluminum on the image 3

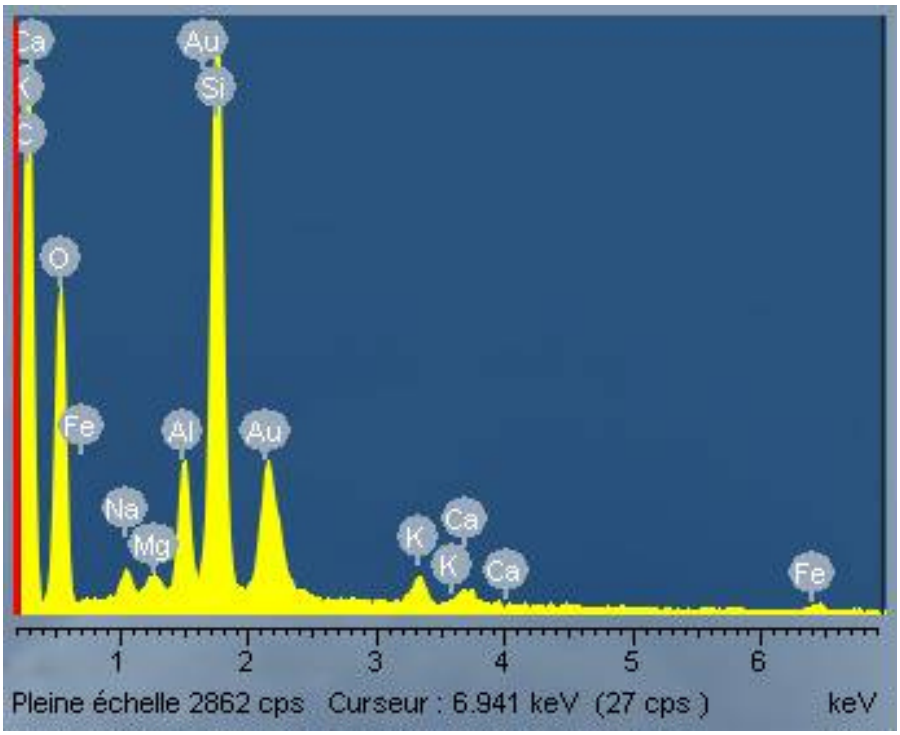


Figure 4. Raw bentonite

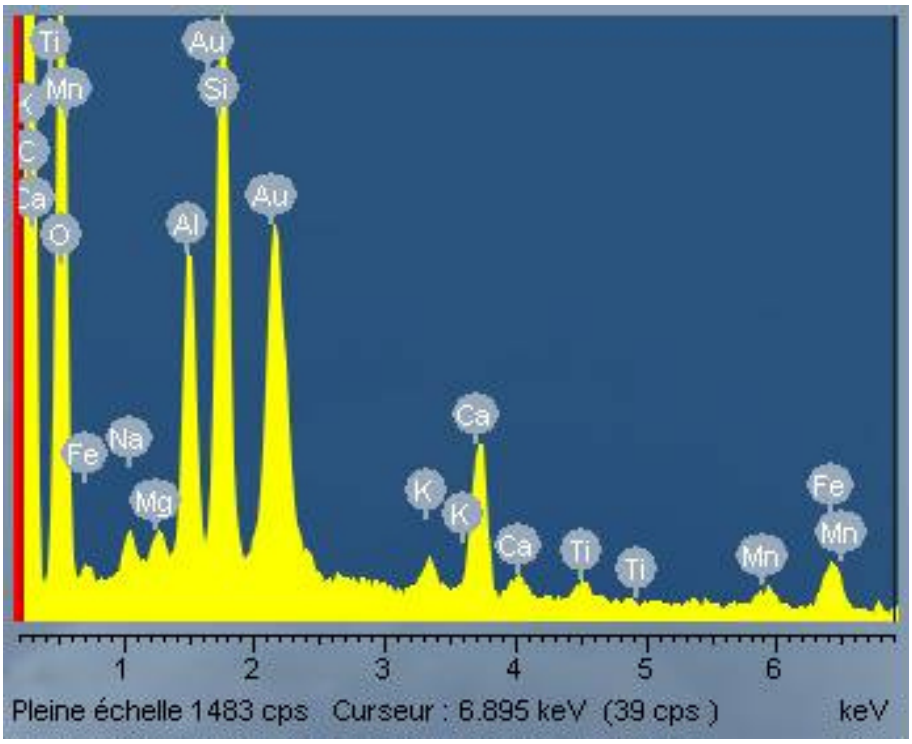


Figure 5. Dose of aluminum sulphate 40 mg / L

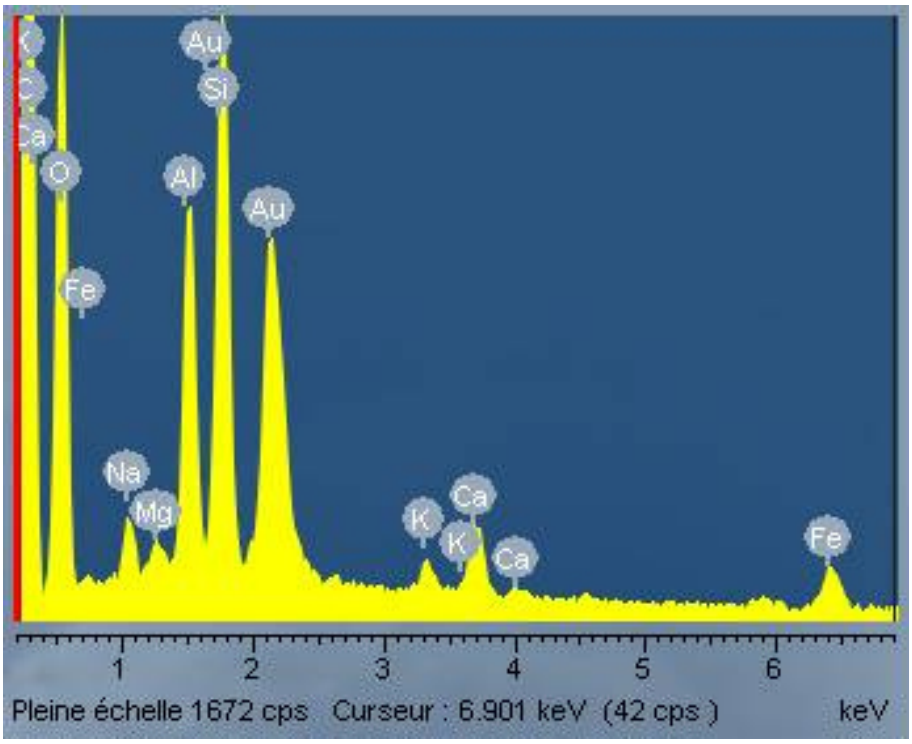


Figure 6. Dose of aluminum sulphate 40 mg + 3 mg bentonite

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.

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

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		

2. DISCUSSION OF RESULTS

We considered only the monitoring of residual aluminium.

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. Station treated water 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 produce the aluminum hydroxide which precipitates and becomes part of the floc. This aluminum is therefore part of the sludge generated by the treatment process. It is

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

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

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

CONCLUSION

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

work in optimum conditions can lead to a minimum aluminum concentration in drinking water. In loaded water, an adjuvant of the coagulation-flocculation can help to reduce the residual of aluminum, as is the case with natural bentonite. The Favorable conditions for hydrolysis of aluminum (pH, t °, agitation and water time stay) allow the formation of the Al_{13} polycation responsible for a good flocculation and reduced residual aluminum including its harmfulness described in several studies. The tests have shown that if one respects the conditions of hydrolysis of aluminum (Table II), we acheive an acceptable level of residual aluminum.

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