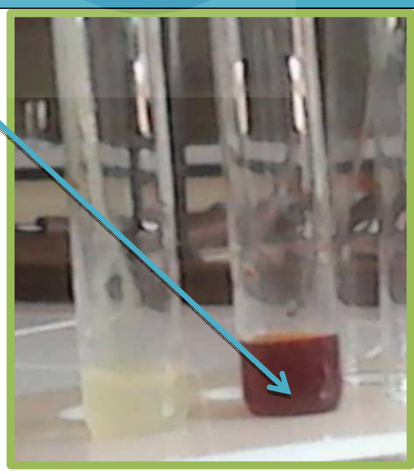
Figure 10: ferric Sulphate before the solubilizations (on the left) and after solubilizations and filtration (on the right)

3.3.2. Qualitative analysis

The analysis is made qualitatively in order to verify the efficiency of the reaction while identifying the presence of the III iron and the ion SO_4^{2} sulphate - in the final environment. The protocol and the result are summarized in the next table :

Table 5 : qualitative Analysis of ferric sulphate

Element to identify	Reactive of analysis	Protocol	Result	Photo of identification
Fe^{3+}	Solution 0,1M of thiocyanate of NH_4SCN ammonium	In a tests tube containing 1 ml of the ferric solution, add some drop of 0.1 M of ammonium thiocyanate,	Red coloration by complexation	

SO_4^{2-}	Nitrate of $Ba(NO_3)_2$ barium Acidic HCl 6M	Add 1ml of acid HCl 6M in 1ml sulphated solution. Then add 10 drops of $Ba(NO_3)_2$.	white precipitate of $BaSO_4$	

3.4. Application of the products gotten for the treatment of drinking waters

3.4.1. Origin and characteristics of raw water

The raw water used for the test of the products gotten has been taken from the river of Andromba, situated in the township of Fenoarivo Alakamisy, district of South Antananarivo.

The geographical coordinates of the point of sampling are the following :

- 18°58 (South latitude);
- 47°24 (East longitude);
- altitude 1318 m.

Illustration 11: satellite Picture of the part of the place of water sampling: (Google Earth), consulted on 23/10/2014, [http://www.gosur.com/map /]

The samplings have been done during the month of September (September 2 and 26, 2014).

The physic and chemical characteristic of the raw water are summarized below in the next table. The analysis has been achieved by the control quality laboratory of the water of the JIRAMA located in Antananarivo.

Table 6 : physic and chemical characteristics of the water of the river of Andromba, collected on 2 and September 26, 2014.

Parameters	Units	Water collected September 2	Water collected September 26	Norm of drinkability
Temperature	°C	24.6	23.9	/
Turbidity	NTU	**266**	**236**	**<5**
pH	/	7.34	7.19	6.5-9.0
Conductivity	(S/cm	57.3	37.5	<3000
Mineral matters	mg/l	40	35	-
TH toughness	mg/l	3.2	2.7	50
Calcic toughness THca	mg/l in CaCO2	1.9	1.5	-
TA/TAC	mg/l	0/2.2	0/1.6	200
M.O	mg/l	2.6	2.44	2.0
NH_4^+	mg/l	0.443	0.235	0.500
Iron	mg/l	1.00	1.00	0.50
Cl^-	mg/l	8.52	8.52	250
SO_4^{2-}	mg/l	3.89	31.39	250
NO_2 -	mg/l	0.036	0.296	0.100
NO_3^-	mg/l	0.571	5.050	50

We noted that only, the turbidity passes widely the norm of drinkability for the two samples.

3.4.2. The Jar-Test

The principle consists in appreciating the quality or the size of the plops formed during the flocculation/coagulation as well as the minimal turbidity after the addition of some quantities of coagulating/flocculating agents on a certain volume of water sample.

We first compared the results of the performance of the products synthesized during this work in relation to the sulphate of alumina, classic product used by the JIRAMA society for the treatment of drinking waters in Madagascar. Indeed, the ferric sulphate (III iron), the green color ferrate (IV iron or V) and the purple color ferrate (VI iron) are all the products that have not been met usually yet at the JIRAMA according to the staff of the laboratory.

All treatments have been achieved according to the usual method of the laboratory.

The results of the Jar-Test of every product are represented in the following graphic :

- **Sulphate of alumina**

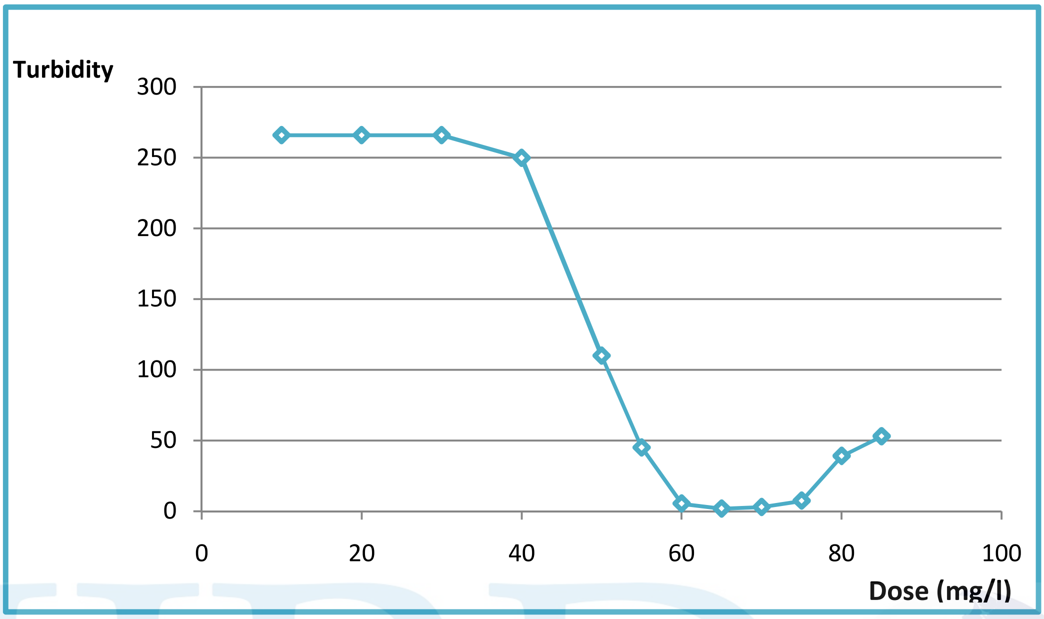


Figure 12 : Curve of determination of the optimum dose of the alumina sulphate

Therefore, the optimum dose of alumina sulphate is localized at 65mg/l.

- **Ferric sulphate**

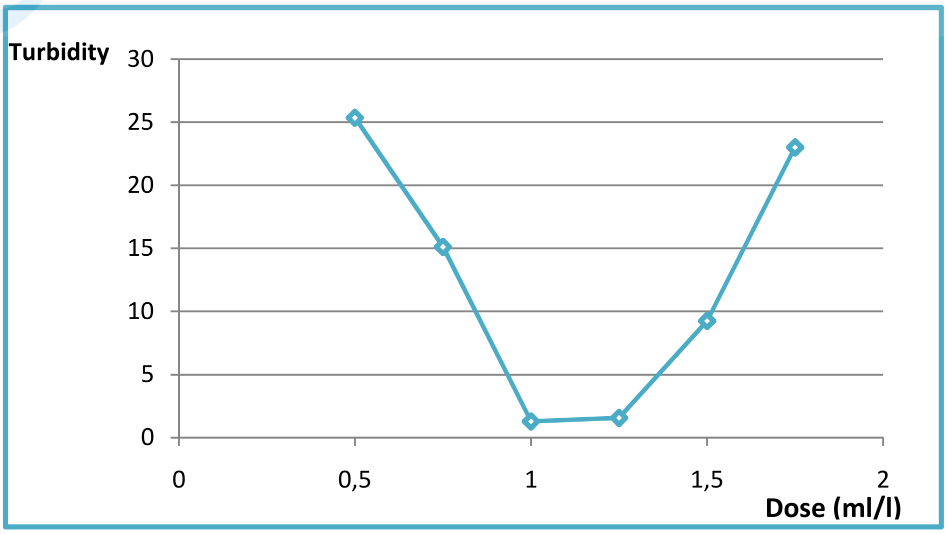


Figure 13 : Curve of determination of the optimum dose of the ferric sulphate

The optimum dose of the ferric sulphate is localized to 1ml for 1 L of water.

- **Ferrate IV or V**

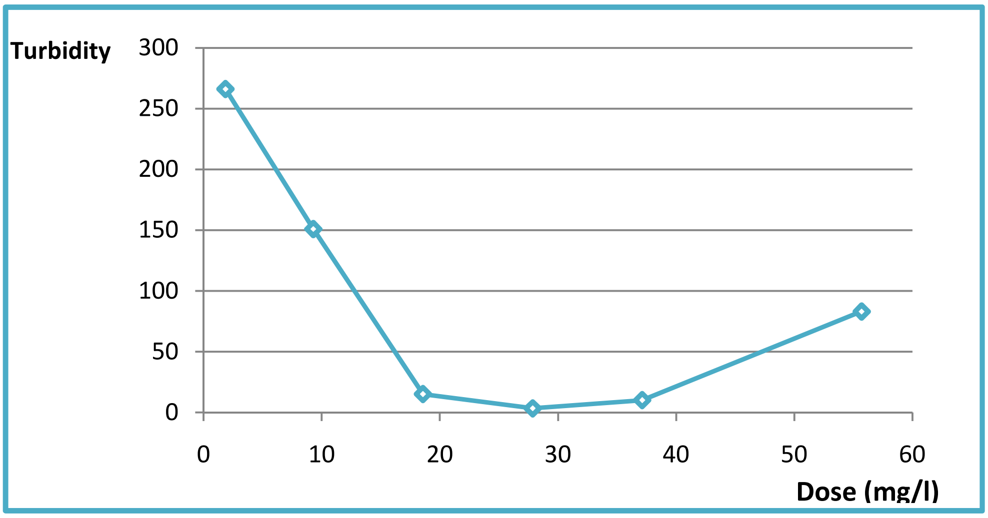


Figure 14 : Curve of determination of the optimum dose of the IV ferrate or V

- **Ferrate VI**

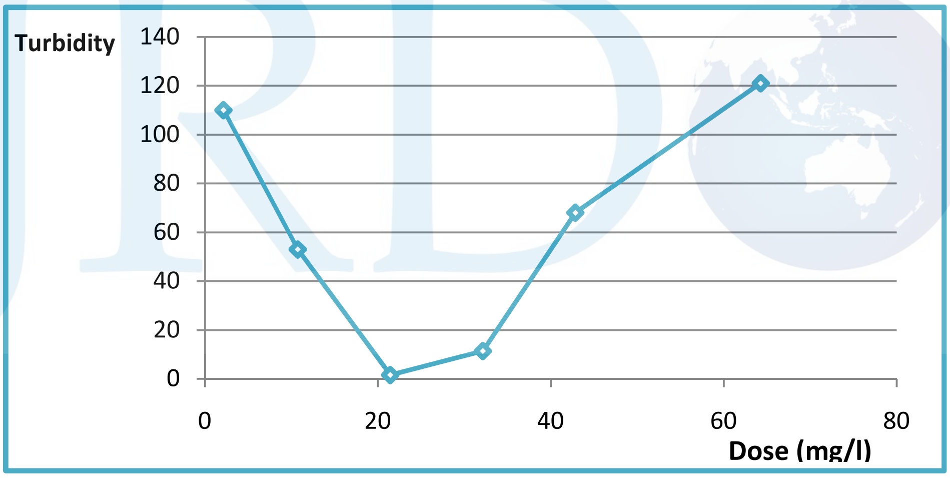


Figure 15 : Curve of determination of the optimum dose of the VI ferrate

The optimal doses of ferrate IV or V and ferrate VI are respectively 27.86 mg/l and 21.43mg/l.

3.4.3. Physic and -chemical characteristics of the treated water

After the tests of clarifications, we did the water analysis that presents the optimal turbidity. The results are reported in the next table:

Table 7: Result of physic and chemical analysis of the treated, water taken away on September 02, 2014

Parameters	Units	Norm to respect	Alumina sulphate	Sulphate Ferric	Ferrate IV or V	Ferrate VI
Temperature	°C	/	24.4	24.2	23.8	24.3
Turbidity	NTU	<5	1.80	1.28	3.50	1.57
pH	-	6.5-9.0	8.31	8.33	8.51	8.30
Conductivity	(S/cm	<3000	1366	2860	2860	1400
M.M	mg/l	/	1155	2648	2120	945
TH toughness	mg/l	50	3.8	2.0	3.5	3.2
Calcic toughness THca	mg/l in $CaCO_2$	-	1.7	1.4	0.6	1.8
TA/TAC	mg/l	200	29.4/47	12/14.0	22.4/34.6	3.0/10.3
M.O	mg/l	2.0	2.5	2.0	2.3	1.9
NH_4^+	mg/l	0.50	2.534	2.529	2.524	0.00
Iron	mg/l	0.50	0.60	0.60	0.40	0.36
Cl -	mg/l	250	55.38	28,4	121.41	18.10
SO_4^{2-}	mg/l	250	459.12	897.45	305.40	146.89
NO_2^-	mg/l	0.10	0.131	0.447	2.360	0.135
NO_3^-	mg/l	50	27.271	141.70	63.690	14.230

The gotten results show that the ferric sulphate is the most performing; we got the lowest turbidity with this product. During the tests of treatment, it is with this product that we got the biggest plop. Visually, waters are all limpid except the one treated with the IV ferrate or V that have a yellow color trace.

We also saw in the result of the flocculation tests, the strong presence of ammonia, nitrite, nitrate and sulphate in water. These values pass the widely of the authorized norm especially for the sulphate of alumina, the ferric sulphate and the IV ferrate or V. We noted that the value of these parameters increased during the treatment. The contribution is due to the use of ammonia as agent of rectification of the pH, for the sulphate of alumina and the ferric sulphate. The rectification of the pH is necessary because the plops only form themselves from the pH = 7 to 8.

For the one of the IV ferrate or V, the contribution is due to the insufficiency of the temperature during the synthesis of the product, the KNO_3 decomposed itself in KNO_2 instead of K_2O.

It is for these reasons that we did the second test of treatment. The taking of sample has been made on September 26 2014. We used lime for the correction of the pH. The optimum dose determined to have optimal plops size is the following :

Table 8: Dose of the lime and pH of flocculation

Type of product	Ferric sulphate	Sulphate of alumina
Rate of lime (g/l)	10	2
pH	11 à 12	8 à 9

The result of the analysis of the treated water is represented below in the next table:

Table 9: Result of physic and chemical analysis of the treated water, taken away on September 26, 2014,

Parameters	Units	Norm to respect	Sulphate of alumina	Ferric sulphate.	Ferrate IV or V (with lime)	Ferrate IV or V (without Lime)	Ferrate VI
Temperature	°C	/	23.6	23.9	23.6	23.5	23.7
Turbidity	NTU	<5	1.92	1.30	2.15	2.57	1.61
pH	/	6.5-9.0	7.19	7.05	8.12	8.54	8.17
Conductivity	(S/cm	<3000	848	1009	541	728	567.3
Mineral materials	mg/l	/	728	953	486	656	449.2
TH toughness	mg/l	50	45	27	19	5.0	3.7
THca toughness	mg/l in CaCO2	/	4.5	9.1	5.7	1.5	1.7
TA/TAC	mg/l	200	0/2.6	0/1.7	0/6.1	3/15.7	0/1.8
M.O	mg/l	2.0	2.0	1.3	2.6	1.9	0.9
NH_4^+	mg/l	0.50	0.020	0.013	0.038	0.021	0.016
Iron	mg/l	0.50	0.10	0.05	0.12	0.12	0.023
Cl^-	mg/l	250	125.1	9.23	5.68	6.39	5.68
SO_4^{2-}	mg/l	250	159.36	169.05	14.6	9.35	7.18
NO_2^-	mg/l	0.10	0.026	0.049	2.332	2.350	0.039
NO_3^-	mg/l	50	3.552	15.05	78.14	97.854	2.235

After replacement of the ammonia water by the lime, the nitrite and nitrate parameters of the water treated by the IV ferrate or V persists again. It is difficult to eliminate them because it is the reagent coagulant used itself that brings these elements in the treated water. Its presences in water have never been accepted; they can provoke serious consequences on the human health. In addition, visually the water treated by the IV ferrate or V presents a yellow color trace that is not at all pleasant to see. Therefore, the IV or V iron is not appropriate for the treatment of the drinking waters.

For the other products, the parameter has improved in relation to the first test of treatment. Water treated with the sulphate of alumina and the ferric sulphate presents a pretty big value in SO_4^{2-}. However, they are still substandard; it can be explained by the presence of sulphate in the outgoing reagent.

Some parameters (as the conductivity, the mineral matters, etc.) increased in relation to the outgoing content by the effect of the reagent added during the treatment. But these values always respect the norm; thus they not cause any risk for the human health.

From a physic and chemical viewpoint, the ferrate and the ferric sulphate gave good results that can compete the sulphate of alumina, classic product used currently by the JIRAMA society for the treatment of drinking waters.

The dose of the reagents used during the treatment is given in the next table :

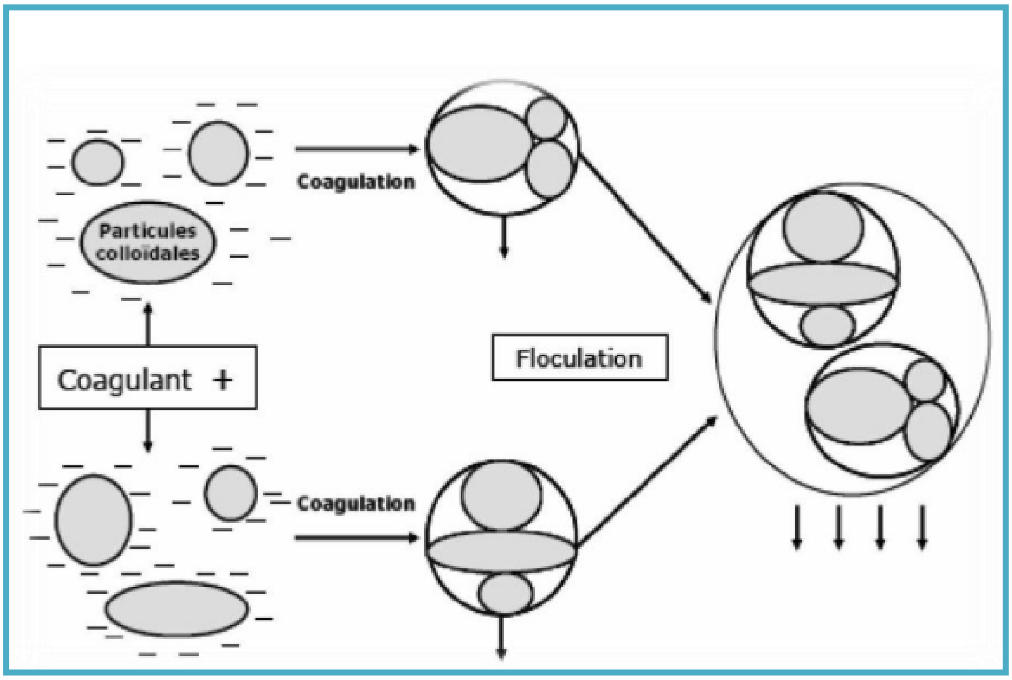
Table 10: Summary of the dose of the reagents at the time of the treatment of waters

Type of product	Sulphate of alumina.	Ferric sulphate	Ferrate of potassium
Dose	60 mg/l	1 ml/l	21.43mg/l
Accompanied lime dose	5ml (2g/l)	2ml (10g/l)	without

According to this picture, 1 ml of ferric sulphate was sufficient to clarify 1 liter of water, against 60 mg/l for the sulphate of alumina, even though the ferric sulphate needs dose of lime milk a lot more concentrated than the one of the alumina sulphate.

It is identical for the ferrate, the dose added to clarify 1 liter of water is lower to the one of the alumina sulphate. In addition, lime is useless for the ferrate except if the rate of iron in water is very high. Thus, it is used to decrease the rate of iron in water.

We saw previously in the physic and chemical analysis result that the ferrate and the ferric sulphate can compete the sulphate of alumina in the treatment of waters. They even show some asset on the level of some parameters, especially on the level of the organic matters; it is explained by the fact that these two products are capable to produce bigger plops than the sulphate of alumina. It is also marked on turbidity level. The system of formation of the plops happens as the next diagram shows:



Source : (Cabana 2011)

Figure 16: System of coagulation/flocculation

Therefore according to this diagram, it is the ferric sulphate that manages to more cohead the colloidal particles in water, then the ferrate in relation to the sulphate of alumina.

3.4.4. Result of the bacteriological analysis of the treated water

For the bacteriological treatment of waters, we did 4 types of treatments:

– treated water with the sulphate of alumina without hypochlorite ;
– treated water with the sulphate of alumina added of hypochlorite ;
– treated water with the ferric sulphate without hypochlorite ;
– water treated with only ferrate.

The results of the analyses are given in the next table :

Table 11: Result of the bacteriological analysis of the treated waters

Type of product	Norm	Raw water	Sulphate of alumina		Ferric sulphate	Ferrate
			without hypochlorite	with hypochlorite		
Total coliformeses at 37°C/100m	0/100ml	$1.5.10^2$	1.10^1	<1	8	4
Escherichia coli at 44°C/20 ml	0/100ml	2.10^2	1.10^1	<1	<1	<1
Streptococci fecal /100mls	0/100ml	2.10^2	1.10^2	<1	6	<1
Anaerobe sulfito-réducteur/20ml	< 2/20ml	in	in	<1	<1	<1

According to the result presented above in the table, the sulphate of alumina permits to eliminate nearly 40% of the vestigial germs in water, the ferric sulphate manages to eliminate into 70% of the germs but the ferrate nearly eliminated all, up to 99% of the germs. Thus, this result proved the advantage of the ferrate in the treatment of the drinking waters that doesn't require hypochlorite to disinfect water.

Concerning the ferric sulphate, the result is well interesting because it doesn't need a lot of hypochlorite to disinfect water. It can be explained by the fact of its very acidic state compared with the sulphate of alumina that can kill a part of the pathogenic germs at the time of its addition in water to treat and by its power to form big plops in relation to the two other reagents that allows it to eliminate by adsorption most pathogenic germs with matters in suspension.

The reaction of the ferrate (VI) with the treated water shows that:

- the ferric hydroxide formation generates an episode of trapping and coagulation/flocculation,
- the reaction generates a clearing of oxygen that confers oxidizing properties,
- the decomposition of the ion ferrate produces an auspicious basic environment to the precipitation of the heavy metals.

CONCLUSION

While referring on the bibliographic data that we collected, the results of the works that we did in the laboratory allowed us to deduct that the ferrate and the ferric sulphate synthesized from the ore of iron as the pyrites can be used in the treatment of waters.

The synthesis of the ferric sulphate from the ore of iron (pyrites) found in the district of Mampikony, region of Sofia is a simple process but demands a lot of precautions. A quarter of an hour is sufficient to get the ferric sulphate. The application of this latter in the treatment of waters (water of the river of Andromba) is very practicable because it nearly reduces 99% of the water turbidity while eliminating the totality of the organic matters and matters in suspension in water by the precipitation of big plops. It also manages to eliminate about 70 to 80% of the pathogenic germs in water.

During the synthesis of the potassium ferrate, we got a type of product (colored in turquoise blue) that we have the named IV ferrate or V, because after qualitative analysis, we could note that its state of oxidization increased but not until the VI state, it is due the insufficiency of the temperature (<800°C) and of the reaction time. Otherwise, this product can be accompanied by nitrite like by-product by the insufficiency of the decomposition of the KNO_3 in K_2O. Its application in the treatment of waters is then non acceptable because the presence of the nitrite in water has ominous effects on the human health.

After several tests to the laboratory, we succeeded in synthesizing the VI ferrate of potassium to a temperature superior or equal to 800°C. The reaction of synthesis is total after three hours. The VI ferrate of potassium is colored in black-purplish; its stability is weak because in contact with air, it decomposes itself very quickly. Its application on the treatment of waters is satisfactory to the norms of drinkability. Not only it plays the powerful coagulant role while hurling down matters in suspension but it also plays the powerful disinfectant role while destroying the totality of the pathogenic micro-organisms in water.

The comparison done on the three products (ferrate of potassium, ferric sulphate and sulphate of alumina,) showed the advantage and the efficiency of the ferrate in the treatment of waters in relation to the ferric sulphate and the sulphate of alumina. These last two products need the accompaniment of other products (the hypochlorite and the lime) to return the drinking water while the ferrate reacts only to manage to fill the conditions of physic, chemical and bacteriological drinkability by itself demanded by the norm. In addition, the quantity of added ferrate to treat 1 liter of raw water is lower to the one of the alumina sulphate. But, it is not necessary to deny that ferrates showed problems related to their stability and difficulties related to the methods of preparation, to the output and to the reduction of the production cost.

However, the ferric sulfate brings more advantage concerning the dejection of the colloidal materials in the water by cohering them to form big plops. In addition, it presents the particular advantages on the production cost because its preparation is simple, do require neither an elevated temperature nor reagents difficult to find.

Thus, our project to propose two types of reagents, of which each presents these particular advantages, can be well placed to replace the sulphate of alumina, that already took several decades of place in the treatment of waters in Madagascar. This project can then as served a continuation of possible application on an industrial scale.

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