IMPROVEMENT OF TREATMENT BY FLOCCULATION AND DISCOLORATION OF WASTEWATER BY THE CHITOSAN OF MADAGASCAR CRUSTACES

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ABSTRACT

This work presents the studies carried out on the physico-chemical and biological treatment of wastewater from the textile industries in Antsirabe, Vakinankaratra, Madagascar.
Laboratory work has been done to verify and test the treatment using alumina sulphate, calcium hypochlorite and chitosan.
This study showed the effectiveness of chitosan, a natural flocculant in the crustacean exoskeletons of Madagascar, for the discoloration of wastewater from the textile industries and the improvement of the values of pollution indicator parameters, such as the turbidity reduced by 125 UTN at 1.2 UTN, the content of suspended matter from 1075 mg.L^{-1} to 54.7 mg.L^{-1}, the biological oxygen demand in 5 days from 333 mg of O_2.L^{-1} to 10 mg of O_2.L^{-1}, and the chemical oxygen demand from 601 mg of O_2.L^{-1} to 24.69 mg of O_2.L^{-1}

Keywords: *Treatment, wastewater, textile, crustacean, chitosan, Madagascar.*

1. INTRODUCTION

Environmental problems have been one of the major concerns of all governments and international institutions for several decades.
Indeed, the world population, which has exceeded six billion and which continues to increase, needs more and more resources and services, the production of which often generates more and more waste. This waste is indisputable evidence of the continuation and extension of environmental degradation [1].
Among the various forms of environmental destruction, that caused by industrial pollution presents the most danger to humanity [2].
Industries are sources of income, they create jobs. However, they have harmful consequences on the environment; they contribute to the development of pollution of natural resources. Solid, liquid and gaseous industrial discharges constitute an increasing danger for the natural environment. Some cause changes in the surrounding environment due to their charges which are sometimes toxic. Liquid discharges are the most polluting [3].
Water, which is the natural resource essential for life, is only available in limited quantities [4], so care must be taken to preserve the spillage without treatment of industrial liquid discharges into a receiving environment such as the river or river for a source of environmental pollution.
The summit of the member states of the United Nations organization on sustainable development is an opportunity to put the world back on the path to sustainable, inclusive and resilient development [5]. The program on sustainable development includes a set of 17 global goals to end poverty, fight inequality and injustice, and tackle climate change by 2030.
In Madagascar, over the past ten years, industrialization has undergone a great evolution.
Currently, the Vakinakaratra region is particularly marked by industrial activity which constitutes one of the important economic functions.

Moreover, the Madagascan government requires that all industrial wastewater must be qualitatively characterized in order to assess the degree of pollution that it can cause. The discharge of industrial liquid discharges is decreed by the Malagasy law n° 2003/464 / of April 15, 2003 [6].
The general objective of our study is to discolour wastewater so that it can be reused after physico-chemical and biological treatment of wastewater.
Thus, treatment trials have been made using alumina sulfate, calcium hypochlorite and chitosan.
Chitosan is a linear polycationic biopolymer with a molecular weight high, industrial chitosan have a molar mass of the order of 200,000 $g.mol^{-1}$, it is one of the coagulating and flocculating agents which have an advantageous property in terms of adsorption of the organic compound and of heavy metals, chitosan is available as solutions, granules, and powder [16].
The production of this product in Madagascar is feasible, because it is obtained from the crustacean exoskeleton (crab, shrimp ...)

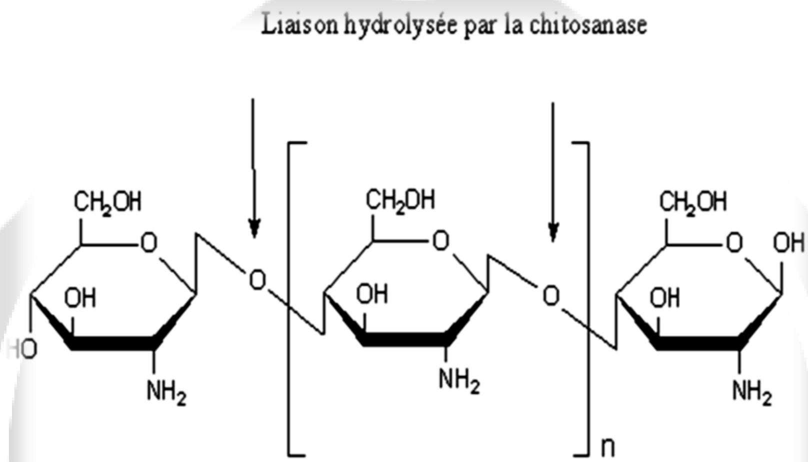

Fig-1 : Structure molecular of chitosan

Since chitosan is insoluble in water, in concentrated or diluted alkaline solutions and in the most common organic solvent [18]. This quasi-insolubility is explained by three main reasons : the large molar mass of each of the polymer chains, the formation of hydrogen bond between the different functional groups carried by each of the units and the folding of the chains [19] but it is soluble in most organic acid solutions, the most commonly used solution is acetic acid, where you can dissolve 10g of chitosan powder in 1 liter of acetic acid.

2. METHODOLOGY

2.1. Choice of parameters

The choice of pollution indicator parameters [8] analyzed was made from a list fixed by Decree n° 2003 / 464 / of April 15, 2003 of the Malagasy Ministry of the Environment [3].

Table-1: Choice of parameters

Parameters	Analyzed element	Goal
Organoleptic and Physical	Colour	Determines the presence of matter organic or mineral
	Smell	Evidence of increased biological activity by the presence of excess material organic decaying or by the presence of chemicals
	Temperature	The increase in temperature of environments disrupts aquatic life and can intensify the smell and flavor
	pH	Determines the acidity or alkalinity of water to provide adequate treatment
	Conductivity	Evaluate the mineralization of water, the reuse depends on the rate of minerals dissolved and ion content.
	Turbidity	Measure the presence of particles in the water
	Suspended matter	Confirms visual information
Chemical	Oil and grease	Provide adequate water treatment Worn
	Chloride	Ion toxic to plants and the aquatic organism
	Sulphate	Ion toxic
	Nitrate	Nitrate has a capacity to transform into nitrite

	Nitrite	Very toxic to fish and often mortal
	Iron	This metal can be harmful to plants Aquatic
Biologic	Biological oxygen demand in 5 days	Know the oxygen consumption relating to the phenomenon of self-purification and the destruction of organic matter
	Chemical oxygen demand	Know the organic charge rates present in waters

The methods of analysis of the parameters used are presented in table 2.

Table-2: Methods of analysis used

PARAMETERS	UNIT	METHOD	AFNOR STANDARD
ORGANOLEPTIC AND PHYSICAL FACTOR			
Color		Visual	-
Odour		Sensory analyzes (smell)	-
Temperature	^{0}C	Electrometry-Thermometer	-
pH		Electrometry-pH meter	pHmeter- Beckman century ss-1(NFT 90 008)
Conductivity	$Us.cm^{-1}$	Electrometry-Conductivity meter	Conductimeter- Tacussel CD7N (NFT 90 031)
Turbidity	UTN	Electrometry-Turbidimeter	Turbidimeter- HF Instruments DRT 100B (NFT 90 033)
	$mg.L^{-1}$	Membrane filtration	Filtration (NFT 90 105)

Suspended matter			
CHEMICAL FACTOR			
Oil and grease	mg.L^{-1}	Gravimetric method	-
Chloride	mg.L^{-1}	Ion spectroscopy	-
Sulphate	mg.L^{-1}	Ion spectroscopy	-
Nitrate	mg.L^{-1}	Ion spectroscopy	-
Nitrite	mg.L^{-1}	Ion spectroscopy	-
Iron	mg.L^{-1}	Spectrophotometer	-
BIOLOGICAL FACTOR			
Biological oxygen demand in 5 days	mg d'O_2 .L^{-1}	Manométric	Respirometry
Chemical oxygen demand	mg d'O2 .L^{-1}	ISO 6060	Acid, $K_2Cr_2O_7$ (NFT 90 101)

Coagulation - flocculation

Coagulation is an operation which consists in destabilizing the suspensions to facilitate their agglomeration by the addition of a chemical reagent, the coagulant

The most used coagulation reagents are based on aluminum or iron salts. It is also possible to use cationic polyelectrolytes which are synthetic organic coagulants directly neutralizing negative colloids.

The flocculation allows the agglomeration of these neutralized particles into micro-flocs, then into bulky and decantable flakes, the flocs. Adding another reagent, the flocculant or flocculation aid, can improve this flocculation.

The flocculants can be silica mineral polymers (activated), natural polymers (starch, etc.), or synthetic polymers [14].

Flocculation tests

-Alumina sulphate, it is a metal salt of formula Al2 (SO4) 3 which is the most used coagulant / flocculant, its reaction involved in water is:

$$Al_2 (SO4)_3 + 6\ HCO_3 \leftrightarrows 2\ Al\ (OH)_3 + 3\ SO_4^{2-} + 6\ CO_2$$

-Calcium hypochlorite, It is an oxidizing agent which ensures the disinfection of the pathogenic germ and ensures chemical precipitation, here is the reaction involved :

$$Ca\ (ClO)_2 + 2H_2O \leftrightarrows 2ClO^- + Ca^{2+} + 2\ H_2O$$

-Chitosan,

For wastewater, we had carried out six noted samplings: B1, B2, B3, B4, B5, B6 and we had fixed the pH at.
For each sample, the quantity used is 1 liter while for the appearance of the flock:
1: means no flock,
2: means small flock,
3: means medium flock,
and 4: means large flock.
In order to determine the quantity of flocculants for an effective treatment, we carry out flocculation tests.
Tables 3 and 4 show the color development and the turbidity of the wastewater

Table-3: Treatment test with calcium hypochlorite and alumina sulphate

Beakers	B1	B2	B3	**B4**	B5	B6
pH fixed (optimal)	6.5	6.5	6.5	**6.5**	6.5	6.5
$Ca(ClO)_2$ dose ($mg.L^{-1}$)	350	350	350	**350**	350	350
Amount of active chlorine ($mg.L^{-1}$)	245	245	245	**245**	245	245
Chlorine quantity (mL)	35	35	35	**35**	35	35
Alumina sulphate dose ($mg.L^{-1}$)	100	200	300	**350**	400	500
Alumina sulphate dose (mL)	10	20	30	**35**	40	50
floc aspect	2	2	3	**4**	3	2
Decanted water color	brown claire	brown claire	colorless	**colorless**	colorless	colorless
Turbidity (UTN)	70.7	53.4	8.70	**1.94**	1.38	1.05

Table-4: Treatment test using chitosan alone and chitosan and alumina sulphate

Beakers	B1	**B2**	B3	B4	**B5**	B6
pH fixed (optimal)	6.5	6.5	6.5	6.5	6.5	6.5
Chitosan dose (mg.L-1)	100	110	120	100	110	120
Chitosan quantity (mL)	10	11	12	10	11	12
Alumina sulphate dose (mg.L-1)				250	300	350
Alumina sulphate quantity (mL)				25	30	35
Floc aspect	4	4	4	4	4	4
Decanted water color	brown	colorless	colorless	grey	colorless	colorless
Turbidity (UTN)	1.48	1.22	1.51	3.36	5.35	9.99

3. RESULTS AND DISCUSSIONS

3.1. Results of analyzes before and after treatment with flocculation

From the optimal quantities determined for each flocculant by the flocculation tests, we carried out analyzes in order to characterize the wastewater before and after treatments.

Table-5: Result of the wastewater analyzes before treatment

PARAMETERS	**UNIT**	**RESULTS**			
		ECH 1	**ECH 2**	**ECH 3**	**AVERAGE**
ORGANOLEPTIC AND PHYSICAL FACTOR					
Color		Dark blue	Light Blue	Dark Blue	
Odour		Odorless	Odorless	Odorless	
Temperature	^{0}C	28	27.5	29.5	28.4
pH		9.17	9.20	9.13	9.16

Conductivity	Us/cm	887	892	885	888
Turbidity	UTN	128	130	127	128
Suspended matter	$mg.L^{-1}$	1075	1070	1079	1074
CHEMICAL FACTOR					
Oil and grease	$mg.L^{-1}$	0.1168	0.1167	0.1169	0.1168
Chloride	$mg.L^{-1}$	29.99	28.55	29.65	29.39
Sulphate	$mg.L^{-1}$	46.05	46.02	46.06	46.04
Nitrate	$mg.L^{-1}$	22	20.5	23	21.83
Nitrite	$mg.L^{-1}$	0	0	0	0
Iron	$mg.L^{-1}$	5.82	5.75	5.88	5.81
BIOLOGICAL FACTOR					
Chemical oxygen demand	mg d’$O_2.L^{-1}$	601	575	627	601
Biological oxygen demand in 5 days	mg d’$O_2.L^{-1}$	330	321	349	333

Table-6: Result of analyzes after treatment according to the flocculants used

PARAMETERS	**UNIT**	**Results after treatment with**			**REJECTION STANDARD**	
		Alumina sulphate + Hypochlorite	**Chitosan**	**Chitosan +Alumina sulphate**	**Malagasy**	**OMS**
ORGANOLEPTIC ET PHYSICAL FACTOR						
Color		colorless	colorless	colorless	colorless	colorless
Odour		**Bad smell**	odourless	odourless	odourless	odourless
Temperature	^{0}C	27.50	29.00	27.26	<30	<30
pH		7.75	6.25	6.75	6-9	6.5 - 9.5
Conductivity	$\mu s.cm^{-1}$	1240	900	920	200	
Turbidity	NTU	4.00	1.40	5.90	25	
Suspended matter	$mg.L^{-1}$	47.23	54.07	43.21	60	20 - 30
CHEMICAL FACTOR						
Oil and grease	$mg.L^{-1}$	0.00	0.00	0.00	10	
Chloride	$mg.L^{-1}$	256.80	32.18	20.90	250	
Sulphate	$mg.L^{-1}$	244.00	87.72	239.20	250	

Nitrate	$mg.L^{-1}$	3.49	6.09	0.00	20	
Nitrite	$mg.L^{-1}$	0.00	0.00	0.00	0.2	
Total iron	$mg.L^{-1}$	2.37	1.75	1.25	10	<15
BIOLOGIC FACTOR						
Chemical oxygen demand	mg d'O_2. L^{-1}	36.54	24.69	23.78	150	
Biological oxygen demand in 5 days	mg d'O_2. L^{-1}	13.00	10.00	14.00	50	30 à 40

3.2. Discussions

These results show that the mixture of flocculants with the calcium hypochlorite solution and the alumina sulfate is effective on discoloration but causes a pungent odor emanation, this may be due to the reaction of hypochlorite with existing molecules. in wastewater.

Thus, calcium hypoclhorite has been replaced by chitosan to have the alumina sulfate-chitosan mixture, and it can be seen that for a concentration of chitosan between 100 to 120 $mg.L^{-1}$, the color of the water after decantation becomes colorless, and the other physico-chemical and biological parameters comply with the wastewater discharge standard, with a reduction in pH values, turbidity, suspended matter, chloride, Nitrate, iron, biological oxygen demand, and chemical demand in oxygen.

For chitosan alone, at a concentration between 100 - 120 $mg.L^{-1}$. This natural flocculant succeeds in removing the color of the used water after decanting without leaving an unpleasant odor, the turbidity decreases markedly to around 1.20 NTU and the physico-chemical and biological parameters comply well with the standard for rejection, with a reduction in the values of turbidity, suspended matter, nitrate, iron, biological oxygen demand, and chemical oxygen demand.

4. CONCLUSIONS

Madagascar has several texts relating to the environment. Industrial investors are particularly concerned by the texts on MECIE according to which, public or private investment projects must be the subject of an impact study. A project must demonstrate that it respects the environment.

Thus the establishment of a treatment unit suitable for the types of effluents is essential for the environment.

The design of such a unit is based on knowledge of the type of effluent. Indeed, for water with a dominant mineral character, physicochemical treatment systems are more appropriate, while for biodegradable effluents, biological treatments will be more suitable.

When designing this treatment unit, the choice of facilities was based on the characterization of the effluents from information provided by the promoters and data from the designers' experiences. The treatment method is of physico-chemical type combined with biological treatment.
As part of this study, after characterizing the wastewater from the textile industries of the Vakinakaratra region, we carried out treatment tests in the laboratory to determine a suitable treatment for the wastewater of textile companies. Raw water analyzes were therefore carried out to be able to characterize the effluents and thus justify the choice of treatment. Analyzes of treated wastewater in the laboratory were also carried out to assess the depollution caused by each treatment operation, the results show that: • calcium hypochlorite with alumina sulphate succeeds in discolouring wastewater with the reduction of pollution indicator values; but the use of these products gives off a slightly pungent odor. Chitosan alone or chitosan combined with alumina sulphate, discolour the wastewater by reducing the values of the pollution indicator parameters up to -85% and comply with the discharge standard. Thus, the use of chitosan, remains the most interesting method for discoloration and deodorizing of wastewater, in addition to the reduction of the values of turbidity, suspended matter, Nitrate, Iron, biological oxygen demand, and demand chemical oxygen. It should be noted that this method with chitosan replaces the use of synthetic chemical flocculants with a natural flocculant.

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