Entry to the Stockholm Junior Water Prize

France 2010

Presented by Justine AHISAI, Hélène WALACH and Maxime BLETTNER, chemistry students in the penultimate year at Louis Vincent High School, Metz.

BATIKECO

Development and production of an effluent treatment device for dyeing workshops, for the use of artisans in YAKO, BURKINA FASO

Teachers of chemistry and chemical engineering: Edith ANTONOT, Brigitte MARTEAU, Aurélie REUMAUX and Roger VOGEL.

1. Summary

Louis Vincent High School has been in a partnership with the Yako High School, Burkina Faso, for 15 years. This partnership has enabled us to put in place various items of equipment (computer room, infirmary, physical sciences lab, etc.) during annual visits to Yako by our students and teachers.
This year, eight students in the penultimate year took up the challenge laid down by our teachers in the context of a scientific workshop: to develop a treatment system for effluents from batik dyeing workshops.
The **used dye baths (about 10 to 30 m^3 per year in the case of the local dyers' association of Nug Tuuma)** are currently poured onto the ground and constitute a potential pollution hazard for the table water in a region (the Sahel) where water is precious.
The treatment process chosen must be **low-cost, easy for non-chemists to use and result in the formation of colourless, non-toxic products**. Once the method has been chosen, we will produce a treatment device for the used baths, which will be tested at the start of the next academic year; then we (workshop students and teachers) will install it in February 2011 in Yako and we will explain to the artisans how to use it.
It will then remain available for them to use. Afterwards, students from Yako High School, or from our high school (on annual visits) will provide maintenance to ensure correct functioning.

2. Contents

3. List of abbreviations and acronyms

AOP: Advanced Oxidation Processes.

TOC: Total Organic Carbon (gives the organic matter content of the effluent)

PI: permanganate index. This index measures the mass of dioxygen which will be consumed per litre of solution.

g: gram kg: kilogram mL: millilitre

ICP: Inductively Coupled Plasma.

Bibliographic references (1) to (4) can be found at the end of this document.

4. Acknowledgements

We would like to thank:

- The Principal of Louis Vincent High School, Mr. GARCIA, the Lab Manager Mme CHALEIX and the team of teachers of physics and chemistry, chemical engineering, and English who have helped us prepare for this competition.
- Mr. Hamidou RABDO, an artisan dyer from Yako, president of the association NUG–TUUMA, who supplied us with samples of batik pigment.
- The AHLSTROM company, who supplied titanium dioxide on a non-woven support.
- Mr. MADEIRA of the Belgian company AFRIKOLOR and Mr. OUÉDRAOGO, a textile engineer with UNITEX in Ouagadougou, who gave us the benefit of their assistance and advice.
- The CEDILOR and ARCELOR companies and the University of METZ (in particular Mr. KIRSCH), who carried out analyses of pigments and effluents for us.

This project has been made possible by the generous financial assistance of:

- The City of METZ
- The UIC (Union des Industries Chimiques) and the ARKEMA company
- The Association des Olympiades Nationales de la Chimie
- The VEOLIA foundation

Formalities are still underway at the moment.

5. The students

From left to right:

Hélène Walach (17), swims and rides, plays the guitar and the piano, and would like to work in the field of international solidarity as a nurse.

Justine Ahisai (17) enjoys judo and music.

Maxime Blettner (19) enjoys mountain biking.

6. BATIKECO: Development and production of an effluent treatment system for dyeing workshops, for the use of artisans in YAKO, BURKINA FASO

6.1. Introduction

Our high school has been in a partnership with the Yako High School, Burkina Faso, for 15 years.

Every year, solidarity events in our high school (tombola, sale of T-shirts, etc.) enable us to provide school equipment (exercise books and pencils) and even study grants to students in Yako.

In addition, over several years, teachers and students have gone on field strips during their February holidays and installed in Yako High School, a physical sciences laboratory, an infirmary, a computer room and a multi-sports surface.

These operations have been carried out with the logistic assistance of the Mersens company.

Mme. Marteau, during the installation of the physical sciences laboratory.

Our Batikeco project is original in that, for the first time, the students are actively involved in the partnership and take part in the framework of a scientific workshop that has concrete results in the field.

The effluent-treatment device for batik-dyeing workshops that we will put in place in February 2011 will benefit the local artisans. Its installation will provide an opportunity for dialogue with the teachers and students in Yako. It will be an opportunity for us to demonstrate how chemistry can help in the context of sustainable development.

6.2. Specifications

One of the craft specialities of Yako is manufacturing batik cloth. As we shall see, this manufacture is a source of pollution.

To obtain batik cloth, the textiles are immersed in a sequence of baths prepared from yellow, red, blue and black pigments. The parts of the cloth which are not to be dyed are protected with wax.

This technique involves the use of baths containing toxic pigments. The used baths (about 10 to 30 m^3 per year for the local craft people's association) are poured onto the ground and constitute a potential pollution hazard for the table water in a region (the Sahel) where water is precious. In some areas of Yako, people pump their water from wells or boreholes fitted with manual pumps, and are, as a result, provided with untreated water. (The boreholes of the National Water and Treatment Authority, which feed into a water tower, are the only source of pre-treated water, which is piped to some areas or sold at water distribution points.)



Burkina Faso is a poor country and artisans cannot afford to treat the effluent from their dyeing workshops.

We are planning to install this treatment facility and to provide follow-up, partly through our annual visits and partly by training members of the artisans' association.

The objective of the project is, then, to develop a procedure that addresses the following constraints:

- **It must significantly reduce the pollution caused by these effluents.**
- **It must be easy for non-chemists to use.**
- **It must be low-cost: it must use a minimum of consumable products and, on the contrary, use local resources such as solar energy. This is an essential condition if the artisans are to be able use it, since they cannot afford to purchase costly reagents.**

We envisaged the following action plan:

- In the initial stage, we compared different techniques of treating coloured effluent, in order to choose the most appropriate.
- Then we will have the prototype built, which we will then test and install during a field trip to Yako in February 2011: it will then be presented to the students in Yako and to the artisans. We will explain how to use it and will then put the apparatus into service.

6.3. Treatment methods for dyeing-workshop effluents

We have yellow, blue, red and black pigments used by the artisans of the Nug-Tuuma association.

Mr Hamidou Rabdo also described for us the composition of these dye baths: each litre of water requires about 8 g of pigment, 8 g of sodium hydroxide and 12 g of sodium dithionite, also known as sodium hydrosulphite, a reducing agent.

In an article published in the periodical Actualité Chimique (1), we learned of the environmental risks posed by the waste product from textile colorant baths, the different types of synthetic colorants and the treatment methods for these used baths.

From the methods which may be used to treat these effluents, we have selected the following:

- **action of an oxidant such as sodium hypochlorite (chlorine bleach)**, but its use by non-chemists is not without risk and there is also the danger that colourless but toxic organochloric compounds may form.
- **use of an adsorbent to fix the colorants,** but this would require purchasing adsorbent and dealing with the residues formed.
- **Advanced Oxidation Processes (OAP)** (2) (Fenton's reagent, photocatalysis in the presence of titanium dioxide) based on the production in situ of **hydroxyl radicals** $\mathbf{HO^{\bullet}}$ and their subsequent oxidising action on the pollutants. This leads to **mineralisation** of the pollutants. In the light of our specifications, this would appear to be the ideal solution.

As the basic nature of the environment makes the use of Fenton's reagent impossible, it was most logical to choose photocatalysis in the presence of titanium dioxide.

Given the composition of the baths, we also had to consider the following:

- how to lower the pH of the effluents before release,
- how to significantly reduce the content of reducing agents in the effluents. (They could reduce the dioxygen content of the water table.)

6.4. First method used: photocatalysis in the presence of titanium dioxide

As the artisan does not know the nature of the pigments used, we first verified that the pigments were oxidizible (Annexe (I): oxidizability results with permanganate). We then compared two techniques of oxidization: the action of sodium hypochlorite and the photocatalysis in the presence of titanium dioxide on batik pigment solutions as well as solutions containing dye references. (Annexe (II): methylene blue, an azo colorant (Congo red), an anthraquinone type colorant (alizarin red) and a colorant of triphenylmethane type (gentian violet)).

Our objective was to discover whether or not batik pigments had similar behaviour to known colorants, and therefore a similar structure.

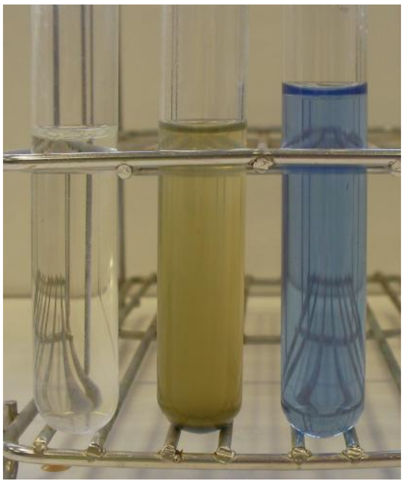
These first tests in test tubes showed that the batik pigments appear to be partially decolorized by sodium hypochlorite (as did most of the reference colours chosen) but that they did not show any visible decolorization by photocatalysis.

Preliminary laboratory tests

We then prepared solutions of equivalent composition to the used yellow, blue, red or black batik colouring baths and carried out photocatalysis experiments in the presence of titanium dioxide in powder form or on a non-woven support.

For these, we used **boxes prefabricated by the high school staff**, which enabled us to submit them to intense UV illumination, mimicking sunlight conditions in Burkina Faso.

The photocatalysis tests demonstrated that batik pigments were adsorbed onto the titanium dioxide, (as powder or as non-woven support) but did not lose its colours in laboratory test conditions. In July 2010, one of our teachers, Mme. Marteau, will travel to Yako and will be able to carry out photocatalysis tests in actual Burkina Faso sunlight conditions.



Tests on blue batik pigment
Sodium hypochlorite TiO$_2$ Control

Photocatalysis with powdered TiO$_2$
Batik blue Batik black

Box produced in Metz High School

Photocatalysis tests with TiO$_2$ on non-woven support

We then considered adding electrolysis in a chloride medium to this photocatalysis device, using a variety of electrode materials. This procedure would enable us to create in situ a sodium hypochlorite solution, capable of breaking down the colorants (3) as follows:

- chlorine obtained at the anode $2\ Cl^- = Cl_2 + 2\ e^-$
- then formation of sodium hypochlorite in situ $Cl_2 + 2\ HO^- = ClO^- + Cl^- + H_2O$
- decolorization of the pigment by the sodium hypochlorite formed

We did not observe the expected decolorization but, on the other hand, **the use of an aluminium anode led to the formation of aluminium hydroxide on which the pigments were adsorbed.**

For this reason, we finally decided to favour the use of an adsorbent to fix the pigments.

6.5. Method selected: use of an adsorbent

We had contemplated using an electro-coagulation procedure which would have made use of electrodes in aluminium, a material which is available cheaply as salvage in Yako, but this method is not feasible as it would require a preliminary lowering of the pH of the effluents, which is too costly. In fact, in a strongly alkaline environment, aluminium hydroxide is transformed into soluble aluminate ions and consequently the method is no longer valid.

$$Al(OH)_3(s) + HO^-(aq) = Al(HO)_4^-(aq)$$

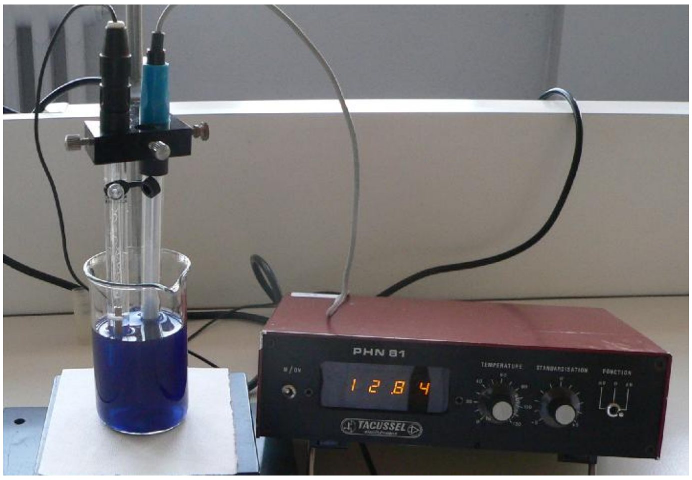
Various coagulants were tested. The coagulant finally selected is **magnesium sulphate heptahydrate** as it has several advantages:

- It is **not ecotoxic.**
- It is **inexpensive** and **available in Burkina Faso** (the SCAB company sells it at a price of 500,000 CFA or 762 euros per tonne.
- It enables **a reduction in the pH** of solutions by removing hydroxide ions through **precipitation of magnesium hydroxide upon which the batik pigments are adsorbed.**

$$Mg^{2+}(aq) + 2\ HO^-(aq) = Mg(OH)_2(s)$$

- **The pigments fixed on the magnesium hydroxide** can afterwards be filtered out onto sand.

Starting with 100 mL of used dye bath (where the pigment content is 6 times lower than in the initial bath), we note the speed of decantation (1 hour), the lowering of the pH of the solution, and the decolorization of the filtrate after filtering through sand.

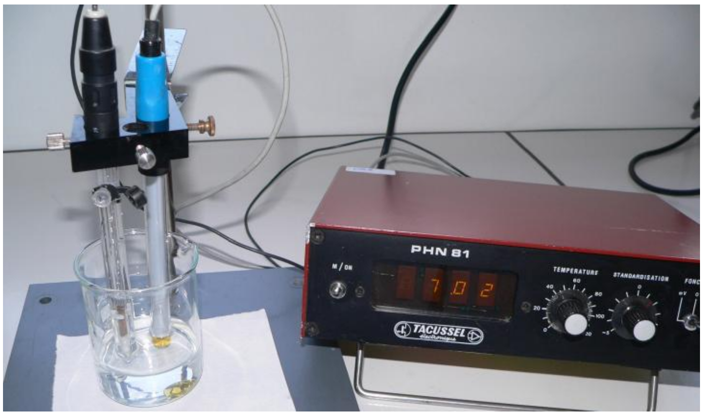


Measuring the pH of the used dye bath : ***pH= 12.84***

Adding magnesium sulphate

One hour later

During filtration

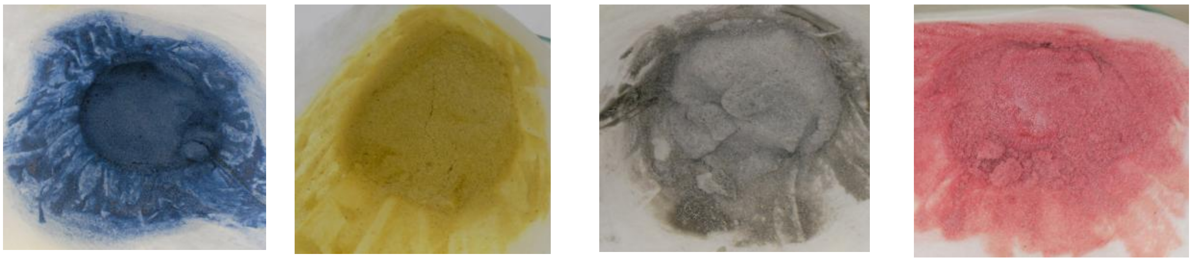


Measuring the pH of the filtrate ***pH = 7.02***

Analyses carried out by the Cédilor company (Annexe (III)) have demonstrated:

- that the pigments do not contain toxic metals (analysis by X-ray fluorescence). As a result, it is possible to imagine these coloured sands being used by Burkina Faso artists to create artistic objects (small flasks, cards, etc.) or else being used in the manufacture of breeze blocks or to add colour to plastic materials.

- that the filtrates have a low content of metallic elements and a very low TOC.



Appearance of coloured sands after filtration through Fontainebleau sand

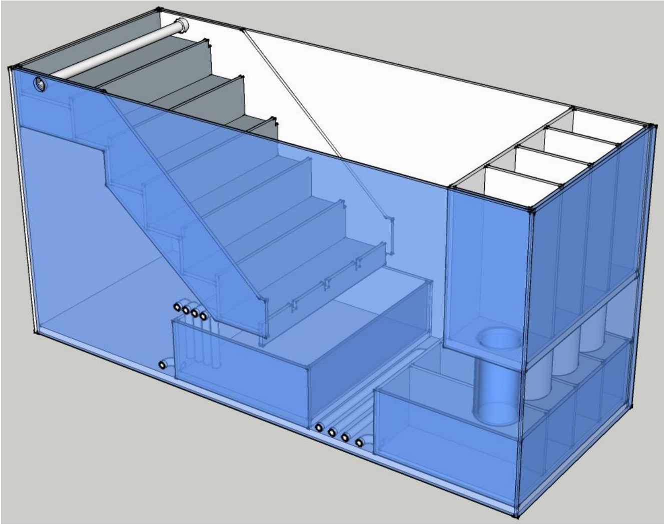
In order to be certain that the filtrates can be disposed of safely into the ground, we must make sure that they do not have too high a content of reducing agent (from the initial sodium dithionite). For this purpose, **a simple aeration of the effluents should suffice**.

In fact, when subjected to the action of oxygen in the air, dithionite ions $S_2O_4^{2-}$ are oxidized to sulphite ions SO_3^{2-} which can in turn be oxidized to sulphate ions SO_4^{2-}, which can be disposed of into the ground. We have confirmed this by measuring the sulphite content of a solution initially containing about 0.3 g/l of sodium dithionite (dye bath diluted to 1/40th): the sulphite content falls from 50 to 20 mg/l in two weeks, and then to only 6 mg/l a month later.

6.6. Model of the selected device

We have considered building a pilot (H= 40 cm, L = 60 cm, W = 30 cm) which will include:

- possibly the part figuring on the left of the diagram: A TFFBR (Thin Film Fixed Bed Reactor), the steps covered with titanium dioxide on a non-woven support: this part will be retained if the photocatalysis tests carried out in the field in July show a decolorization of the baths in Burkina Faso sunlight conditions. Otherwise, we can either abandon it or keep this reagent without using the photocatalyser, and simply aerate the effluents to encourage elimination of sulphite ions through oxidation.
- the part appearing on the right of the diagram: four vats enabling separate filtration through sand of each of the pigments previously fixed onto magnesium hydroxide.



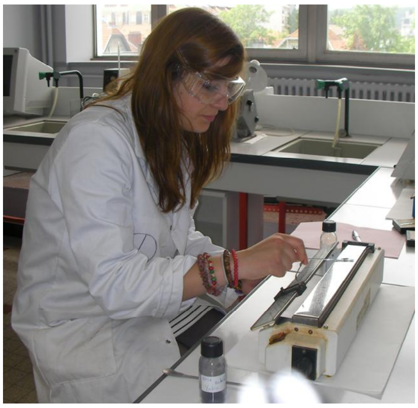
A pump can be added to either empty the tanks or bring the fluids to the top of the steps. (The cost of the entire device has been estimated at about 8000 euros; if we limit ourselves to the filtration vats, the cost is much lower, in the region of 1000 euros.)

The device will most probably be constructed by the Frans-Bonhomme company (we have asked for an estimate).

6.7 Outlook

We are first trying to gain more knowledge of the chemical nature of the pigments:

- by asking the artisans for information.
- by carrying out laboratory tests: measurements of fusion temperature on a Koffler bench have demonstrated that the pigments did not melt on the bench, which would be consistent with the presence in the structure of the pigments of sodium carboxylates (thus ensuring a degree of solubility in water).



- by carrying out analyses such as mass spectrometry which demonstrates that some pigments are a mixture of three substances. We will soon have the carbon, oxygen and sulphur contents of these pigments.

- by cross checking the above results with information Mr. Ouédraogo of the Unitex company will be able to obtain for us. In fact, Unitex is the only company selling dyeing-bath colorants in Burkina Faso, Afrikolor-branded reagents and also water pigments from the local market.

We have applied for the International Year of Chemistry 2011 label for our project.

We are also hoping to make the local artisans' association aware of the health and environment risks (the only measure currently taken is wearing gloves when handling the baths). In fact, if we consider that the Nug Tuuma provincial artisans' association has 56 members including dyers and that the volumes of waste can run to 10 to 30 m^3 per year, that comes to a current annual consumption of:

- 80 to 240 kg of pigment
- 80 to 240 kg of sodium hydroxide
- 120 to 360 kg of sodium dithionite

Taking into account that a part of the sodium hydroxide is consumed in the transformation of the dithionite into sulphite, **to treat 10 litres of used dye fluid by coagulation requires 101 g of magnesium sulphate heptahydrate (at a cost of 51 CFA francs or 0.077 euros)**. **The cost of treating one year's effluents (30 m^3) would therefore be 153,000 CFA francs or 231 euros.**

The average income of a family of 9 persons in the Yako region is 145,000 CFA francs per year i.e 2 euros per person per month.

Even if using the coloured sands in craft products can bring down the cost of treatment for the association, this cost is still considerable for the artisans!

In the framework of our partnership with Yako, we can finance the first year of treatment in full, and the following years up to50%, then30%, etc.

Our objective is that the association should, in the long-term, be able to finance the cost of reprocessing on its own.

To that end, we encourage local initiatives which favour sustainable development: for example, the Nug Tuuma association wants to develop a range of clothes wholly produced in Burkina Faso. (Burkina Faso is a cotton producer but the cloth is often dyed in the

Netherlands). It would be a good idea for the Nug Tuuma association to make contact with the Equiterre association which organises annual ethical fashion shows (http://www.equiterre.com) which could help to promote their work.

We have also noted with interest that the Unitex company promotes exhaust-dyeing training sessions in order to optimise the quantities of reagents needed.

These are interesting lines of thought to follow up in future years.

Finally, the use of magnesium salts to treat effluents (4) has the additional advantage that it appears also to be well adapted to treating baths for tanning leather—a craft which is also well developed in Burkina Faso.

This opens up new avenues for exploration in future years…

7. Bibliography

(1) L'Actualité Chimique No. 277-278 (August–September 2004 pages 57 to 69)

(2) Selected extracts from the thesis of Raphaël Huchon (December 2006 – Lyon): "Activité catalytique de catalyseurs déposés sur différents supports"

(3) Degradation of dye effluent (Pure Appl. Chem, Vol 73, No. 12, pp 1957–1968, 2001)

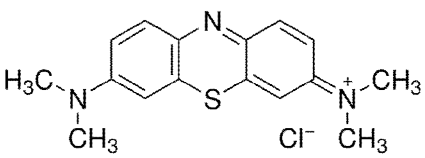
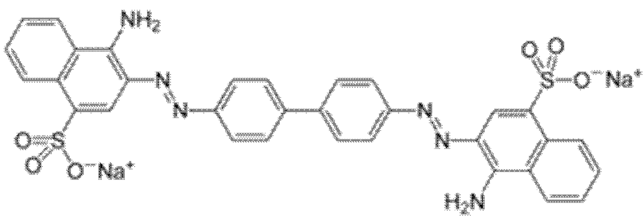
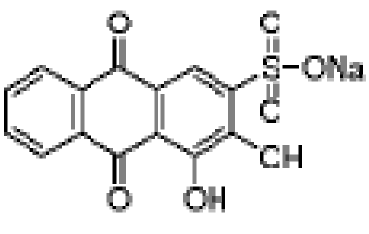
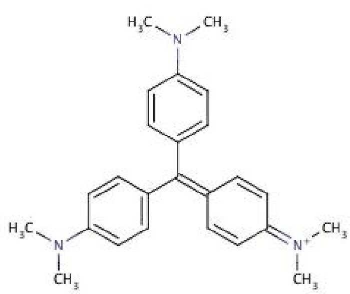
(4) High pH-magnesium coagulation-flocculation in waste-water treatment (by L. Semerjian and G. M. Ayoub (Advances in Environmental Research 7 (2003)

8. Annexes

Annexe (I): Permanganate index

Type of solution	Batik black	Batik blue	Batik yellow	Batik Red
PI in mg O_2/l	867	796	537	713
Comment on the appearance of the solution after dosing	Decoloured	Decoloured	Pale yellow	Pinkish

Annexe (II): Structure of reference dyes

 *Methylene blue*	 *Congo Red*
 *Alizarin red*	 *Gentian violet*

Annexe (III): Results of analyses carried out by the Cédilor company

Measurements of TC (total carbon) and TOC (total organic carbon) were carried out on a TOC infra-red absorption meter.

Elementary analyses were carried out by ICP for filtrates and by X-ray fluorescence.

Pigments

	Blue pigment	Yellow pigment	Black pigment	Red pigment
Carbon content in an aqueous solution at 100 mg/l of pigment	52 mg	53 mg	33 mg	56 mg
Main elements present with an atomic number higher than 11 (percentage mass)	S(1.23) Fe(0.19)	S(2.30) Fe(0.27)	S(3.36) Fe(0.38)	S(1.74) Ca(0.13) Cl(0.12)

Filtrates after treatment of used bath with magnesium sulphate

	Filtrate after treatment of blue batik bath	Filtrate after treatment of yellow batik bath	Filtrate after treatment of black batik bath	Filtrate after treatment of red batik bath
TC/mg.l^{-1}	100	70	105	25
TOC/mg.l^{-1}	15	2	60	2
Fe, Cr, V, Mn, Co , Ni, Cu , Zn, Mo, Cd, Sn	Maximum content 0.08 mg.l^{-1}			