STUDY OF THE BIODEGRADABILITY OF SODIUM SALT FROM THE CONDENSATION PRODUCT OF NAPHTHALENE SULPHONIC ACIDS AND FORMALDEHYDE

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Abstract

The biodegradability of dispersants (naphthalenesulfonate formaldehyde condensates), used with disperse dyes, has been evaluated using different techniques such as chemical oxygen demand (COD), UV-spectroscopic analysis and tonometry. A biomass was used from industrial waste water which was acclimated for six months prior to use. The study has shown that biodegradation involves two steps: first, the cleavage of the CH2 bridges; second, the degradation of the aromatic nuclei. We identified a series of bacteria (Pseudomonas cepacia, Pseudomonas vesicularis, Pseudomonas stutzeri, Pseudomonas pichetti, Shevanella putrefacians, Agrobacterium radiobacter and Aeromonas hydrophila) that proved to biodegrade the dispersant very efficiently.

Key words:

disperse dye, naphthalene sulphonic acid, dispersant, biodegradability, waste water

Introduction

The pollution of water caused by means of chemical products has become one of the major environment problems. The textile industry produces a huge quantity of waste water (waste water of fibre dyeing, fabric printing, carpet dyeing, dispersants and tannery). Modern dye houses use dyes in liquid form instead of powders because of convenient handling properties suitable for automated dispensing. The estimated world-wide use of naphthalenesulfonate formaldehyde condensates as a concrete admixture and as a dye dispersant is about $300X10^6$ kg/year [1]. The composition of the technical mixtures varies to a high degree depending on the reaction used in the production process and the degree of polymerisation.

Liquid dyes are true or colloidal solutions, or aqueous dispersions stabilized with a polymeric dispersant (naphthalenesulphonate formaldehyde condensates) [2, 3]. Aromatic sulphonates are well-studied pollutants for their wide spread occurrence in the environment and for their potential hazard for human and wildlife health [4,5]. Despite this concern about monomeric aromatic sulphonates, only a few researchers [6,7] have investigated the environmental occurrence of naphthalenesulphonate formaldehyde condensates (polymeric dispersant) type compounds.

Mecanism Of Dye Dispersion

Water-insoluble dyes, pigments, and pharmaceutical and agricultural chemicals are dispersed in water by reducing their particles to a size which can be stabilised by a dispersant [8,9]. The dispersant aids wetting of dye particles with water, facilitates breaking of agglomerates [9, 10] and stabilizes the dispersion by forming a steric or an electrostatic barrier by absorption on the surface of the particles.

Dispersants (naphthalenesulphonate formaldehyde condensates) constitute a class of materials that are capable of bringing solid particles into a state of suspension to inhibit or prevent their agglomeration. Dispersants break up the agglomerates or aggregates of dyes, bringing fine dye particles into colloidal solution.

Stable aqueous dispersions of dyes are prepared by grinding the dye in water containing a dispersant and other additives needed to stabilise the dispersion. The dispersant facilitates wetting of the dye

agglomerates by the aqueous medium and stabilises the dispersion by absorption on the surface of the dye particles [11, 12].

The stability of the dispersion to flocculation and sedimentation depends on the attractive and the repulsive forces between the dye particles, which in turn depend on the interactions at the water-dispersant-dye interfaces and the particle size of the dye. An absorbed amphiphilic dispersant lowers the dye-water interfacial tension by rendering the dye particle hydrophilic, and it stabilises the dispersion by steric and electrostatic mechanisms.

The dispersion is a mixture of individual dye particles and aggregates. If a system like this is agitated or otherwise disturbed (as it is pumped, for example), the resultant turbulence causes the particles to collide.

These collisions result in a loss of energy which must be put back into the system by the agitator or pump. If the above system were a liquid dispersed in water, the result of the collision might be coalescence. In some cases, there is a driving force for the particles to stick together. The collisions will not only result in an energy loss but larger aggregates will result. These have a greater probability of further collisions, thus, compounding the problem. Most dispersed phases seem to have this driving force toward aggregation. These forces can be electrical or even a "desire" to get away from the water. Parenthetically the present dye dispersants do not do a good job at breaking up aggregates. An external force (mills, grinders, etc...) is usually needed. One of the functions of a dispersant, however, is to prevent the natural course of re-aggregation [13].

When the above system is treated with a dispersant, a shell is produced around the particles which change the nature of the collisions. In this condition when dye particles collide, the interactions are modified. First of all, because the particles have a hydrophilic surface, the driving force between the particles is reduced. This reduces the tendency toward re-aggregation. Secondly, when particles collide it is their shells that interact. If the force that produces the absorption of the dispersant is less than the total energy of the collision, then the dispersant will shear off. This produces a lubrication effect [13].

Lastly, because of this shell, when this system is at rest, the system does not settle as quickly as the untreated dispersion. When it does settle, it settles as a soft floc which is generally easily re-dispersed.

Regarding the wide use of dispersants in the industry, many studies [14, 15] have shown that the biodegradation rate of this category is the lowest. The biodegradation is the quality of a substance which may be deconstructed due to such microcosms as some bacteria or mushrums.

Biodegradability

The biodegradability of the dispersant is the expression with which the living organisms present in the water cause its degradation. According to the current definitions, there are the following kinds:

- **primary** degradation, when the dispersant loses its surfactant properties and is no longer assayable according to the methods defined by the European norms,

- **total** biodegradation, when the dispersant is completely transformed into CO_2 and biomass water.

A consortium of micro- and macro-organisms called the biomass is able to use the dispersant as food. Consequently the polymerisation degree is reduced. The most commonly identified microorganism is heterotrophic bacteria that include genera such as *Pseudomenas, Achromobacter, Flavobacterium, Alcaligenes, and Zooglea* [10]. These are often associated with filamentous organisms which contribute to biofloculation. The extracellular polymers produced help cells to aggregate and facilitate their attachment to solid support.

The two most frequent methods to determine the rate of biodegradation [11] are the standard AFNOR T 73-260 method referring to the French legislation, and the standard method coming from the European legislation (O.C.D.E).

The AFNOR T 73-260 method consists of comparing the evolution of the solution composition studied with a standard chemical solution (linear dodecylbenzene sulphonate whose biodegradation rate is 82.5%) under the same conditions [11]. The surfactant's titration is carried out after 7 and 10 days, and the rate of biodegradation is determined according to the following formula (1):

$$\mathbf{T}=100-2.5(C_t-C_0) \quad (1)$$

where C_t is the surfactant concentration after 7 or 10 days, and C_0 the initial surfactant concentration.

The T value will be used to calculate the biodegradation rate of the dispersant. This rate is given by equation (2):

$$\mathbf{B}=\frac{0,5T_7+T_{10}}{0,5Tr_7+Tr_{10}} \quad (2)$$

where T_7 = the biodegradation rate of the dispersant after 7 days, T_{10} = the biodegradation rate of the dispersant after 10 days, Tr_7 = the biodegradation rate of the reference after 7 days, Tr_{10}= the biodegradation rate of the reference after 10 days.

The test of the O.C.D.E [12] is the percentage of biodegradation, and is calculated according to formula (3):

$$\mathbf{B_t}=\frac{C_0-C_t}{C_0}\times 100 \quad (3)$$

Bt is the biodegradation observed after a period t starting from the initial C_0 concentration.

Previous work [13, 14] has shown that the biodegradation rate can be linked to the nature of the chemicals, e.g. the length and branching of the alkyl chains, and to the environment (presence of sand or salts). Furthermore, the condensed naphthalene sulphonic acid and formaldehyde dispersants are reported to be difficult to biodegrade. In this article, we report on the biodegradation properties of such dispersants.

The dispersant analysed (Dispergator CC from CIBA) is a synthetic chemical used to homogenise the dispersed dyes in dyeing baths, and it prevents their agglomeration. It is prepared by the addition of concentrated sulphuric acid to melted naphthalene, followed by condensation with formaldehyde, neutralisation with caustic soda, and dilution with water to obtain the final dispersant [15]. The final product is composed of numerous products with different molecular masses. The average molecular weight ranges between 242 and 2000 g. The degree of condensation is not ??-clear. Two to ten aromatic nuclei are linked. It is very difficult to determine their molecular weight [16].

In the dyeing process, this dispersant is used at two stages: some is added to the dyes, and some is added later on to the dyeing bath, especially in the case of polyester dyeing by dispersed dyes. The chemical structure [16] of the dispersant investigated is depicted in Figure 1.

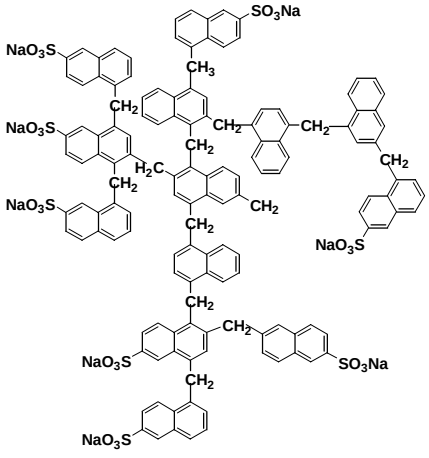

Figure 1. Structure of the dispersant analysed [16]

Experimental Part

The measurement of the average molecular weight (Mn) by tonometry allowed us to determine the rate of biodegradation at the macromolecular level of the chains. A KNAUER vapour-pressure osmometer model N°11.00 was used. The vapour-pressure osmometer was used for determining molecular weights in aqueous media. Therefore the instrument was calibrated with an osmolal calibration solution. For this**,** a first series of measurements of ΔR (equation (4)) was carried out on polyethylene glycol (PEG) with a known average mass (Mn = 400 g/mol) to calculate K.

$$\mathbf{\Delta R/C =} K[1/M_n + A_2C + A_3C^2 + \ldots] \quad (4)$$

R: resistance (signal given from apparatus), C: concentration of analysed product, K: constant determined by calibration, Ai: Viriel constant.

The extrapolation of this calibration curve at the origin gives the value of K/Mn, knowing that $Mn_{(PEG)}$ =400 g/mol; thus the constant value K can be calculated, so K=3020.

To determine the average mass in number of the dispersant before and after biodegradation, a similar series of measurements was carried out as for PEG. We thus established an Mn value of 1680 g/mol for the studied dispersant (before biodegradation). This value indicates that this compound result of the condensation of 7 to 8 monomers (a monomer unit mass is equal to 242 g, Figure 2).

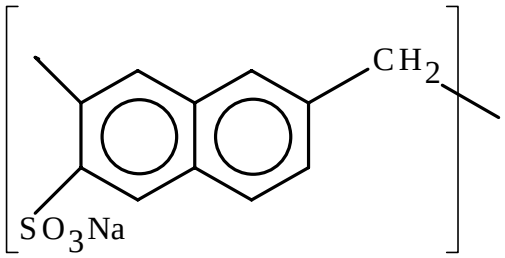

Figure 2. Structure of monomer unit for studied dispersant

Subsequently, the effect of the concentration of the dispersant was studied using two different solutions A and B (5.11 and 10.23 g/l respectively) chosen approximately in order to be as close as possible to the industrial conditions.

Spectroscopic analysis was carried out with a UV-VIS recording spectrophotometer (UV 2401 PC SHIMADZU). The analysis was achieved in water using a quartz cell at 288 nm wavelength.

Infrared analysis was carried out with a SHIMADZU Fourier Transform IR Spectrometer using a resolution of 4 cm^{-1}. The spectrum was an average of 50 scans for each sample. A potassium bromide (KBr) pellet technique was employed. The sample was ground with KBr in order to obtain a finely dispersed mixture, a pellet was pressed, and the spectrum was recorded.

The COD was assayed according to the micro-method by Wolf and Nordmann [17]. The biodegradation test was conducted using the method described by Marcou [12]. A blend of fresh seawater and waste water from the water-treating plant of a dyeing factory were used.

0.1ml of the sample (dispersant tested in the presence of bacterium) was incubated at 30°C for 48 hours to 72 hours on an ordinary nutritive gelose medium.

Gram and oxydase tests were run in order to define the profile of the bacteria; then the biochemical profile of the strains was studied by using the API20NE medium (BIO-Merieux) test, which enabled us to identify each bacterium precisely [18, 19].

All tests were carried out at 25°C under aerobic conditions. Measurements were run at intervals of 1 to 2 days. The COD was measured every 4 to 5 days.

Results And Discussion

After 30 days of treatment, a Mn value of 240 g/mol for solution A and a Mn value of 430 g/mol for solution B were obtained by tonometry. This shows a structural biotransformation of the dispersant into monomers and dimers, which is more pronounced in the case of the less concentrated A solution.

COD evolution over time was presented in Figures 3 and 4. It shows that the biodegradation rate is higher when the concentration is weaker. So, bacteria find their optimal activity in the most diluted medium. In addition, the COD value decreases and becomes stable after 30 days, which can be explained by the reduction of the concentration of the dispersant due to its biodegradation.

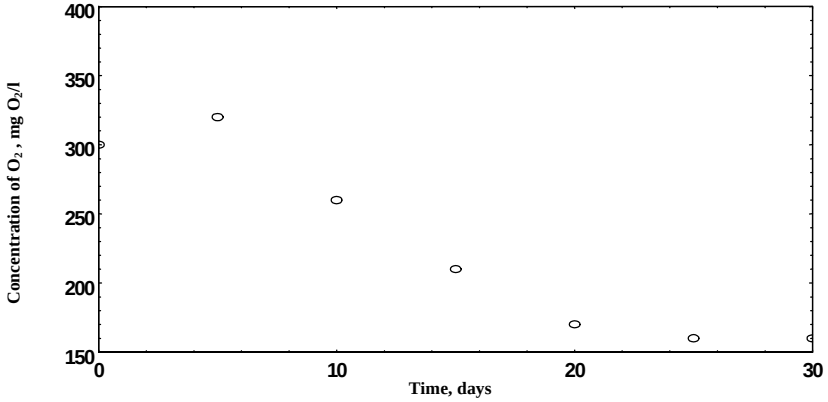

Figure 3. Evolution of COD versus time (concentration 0.102 g/l)

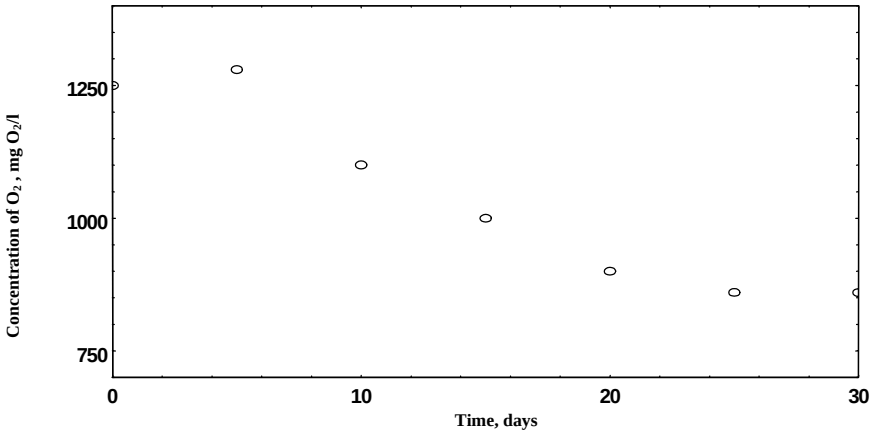

Figure 4. Evolution of COD versus time (concentration 0.511 g/l)

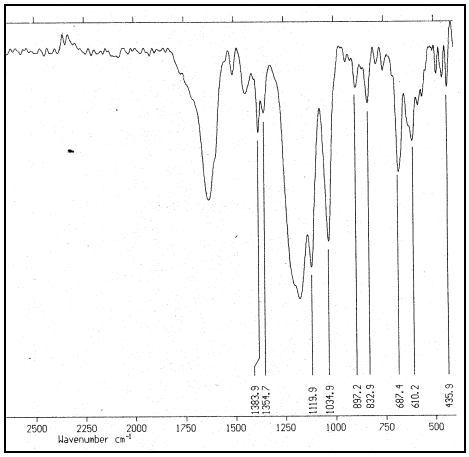

Figure 5a. IR Spectrum of dispersant before biodegradation

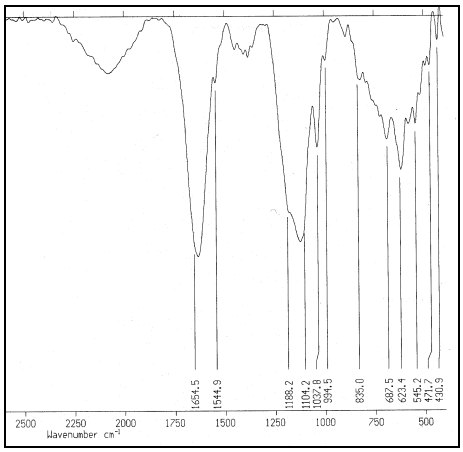

Figure 5b. IR Spectrum of dispersant after biodegradation

Before the biodegradation tests, the IR spectrum shows the following of characteristic bands (see Figure 5a):

- At 1632 cm^{-1}: characteristic band of conjugated bonds of the naphthalene ring.
- Between 1354 cm^{-1} and 1450 cm^{-1}: characteristic band of CH_2 bridge,

After 30 days spent with the biomass at 25°C, the new IR spectrum shows a reduction in the band characteristic of the CH_2 bridges (rupture of CH_2 bridges) and an increase in that of the naphthalene rings, Figure 5b.

Furthermore, the analysis of the curves representing the evolution of absorbance with time for the various concentrations considered shows an increase in the absorption up to the 7th day, followed by a decrease until the 30th day. We confirmed the presence of the same phenomena for all the concentrations measured (0.102 g/L, 0.51g/L, 2.55g/L, 5.11g/L and 10.23 g/L). Figure 6 shows one example for the concentration of 0.102 g/L.

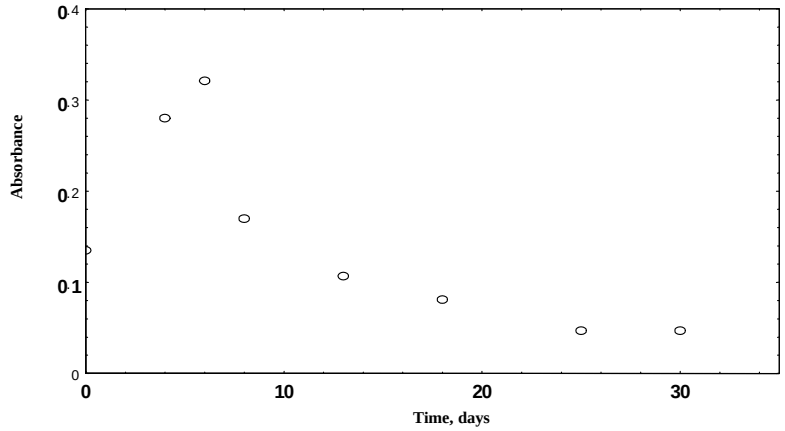

Figure 6. Evolution of the absorbance versus time (concentration 0.102 g/l)

This absorbance increase during the first day can be explained by the cleavage of the methylene bridges, which causes an increase of the number of small-size molecular chains. Indeed, this increase in absorbance is probably due to the increase in the monomer of naphthalene rings. This can be explained by a growth of the optic density, since the UV absorbance of monomer is more intense than that of the polymerised chains [16].

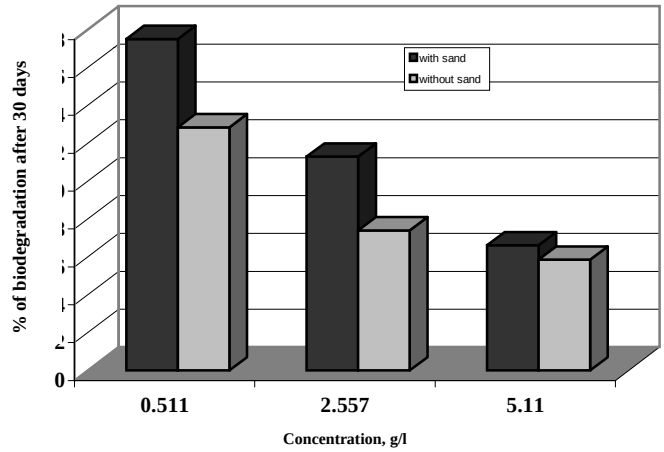

Figure 7. Influence of the presence of sand on the biodegradation

The successive continuous decrease of absorbance is probably due to the biodegradation of the aromatic ring. Indeed, the probable attack of the naphthalene rings by the bacteria leads to the

opening of these cores, hence the reduction in their number. Consequently, the absorbance decreases.

In order to verify the influence of the presence of sand with the biomass [20], recovery experiments were performed for various concentrations of the dispersant. Sand improves bacterial activity, and consequently the biodegradation processing of the dispersant (Figure 7).

The presence of sand improves the bacterial activity. As a consequence, the biodegradation is better assisted in media with sand than in those without sand. In fact, bacteria found in this sand nutritive substrate, and they are protected by the sand against predators and water current.

Bacteria tested for their ability to biodegrade the dispersant were obtained from a polluted medium. Monitoring of the biodegradation of the dispersant was carried out using the physicochemical methods previously described.

As a result, the majority of the active bacteria found present in the various samples, are *bacilli* Gram negative that give a positive response to the oxydase test. These strains belong to the *Pseudomonas*, *Alcaligenes or Aeromonas species.* The species identified are as follows: *Pseudomonas cepacia, Pseudomonas vesicularis, Pseudomonas stutzeri, Pseudomonas pichetti, Shevanella putrefacians, Agrobacterium radiobacter and Aeromonas hydrophila*.

Conclusion

This work describes for the first time the biodegradation of dispersants (various sodium salt of the dinaphtylmethanedisulfonic acid) using various techniques such as chemical oxygen demand (COD), UV-spectroscopic analysis, IR analysis and tonometry. The study of the biodegradation of this dispersant shows that its biodegradation is a two step process : cleavage of of the CH_2 bridges, then degradation of the aromatic nuclei. Furthermore, this work enabled us to identify the bacteria which are most active and which caused, consequently, the degradation of the dispersant in question.

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