Chemical Engineering Journal 153 (2009) 56–61

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Removal of sodium dodecyl benzene sulfonate from water by means of a new tannin-based coagulant: Optimisation studies through design of experiments

J. Beltrán-Heredia [1], J. Sánchez-Martín *, C. Solera-Hernández

Universidad de Extremadura, Department of Chemical Engineering and Physical Chemistry, Avda. de Elvas, s/n, 06071 Badajoz, Spain

ARTICLE INFO

Article history:
Received 18 March 2009
Received in revised form 20 May 2009
Accepted 3 June 2009

Keywords:
Anionic surfactants
Natural flocculation agents
Sodium dodecyl benzene sulfonate
Tannins

ABSTRACT

A new tannin-based coagulant and flocculant agent has been tested on the removal of sodium dodecyl benzene sulfonate (SDBS), a dangerous and pollutant anionic surfactant. It is called *Tanfloc* and consists of a chemically modified tannin extract from *Acacia mearnsii de Wild*. In order to study the interaction between pH and initial surfactant concentration (ISC), a design of experiments procedure has been carried out. The influence of these two variables has been evaluated. Increasing pH level leads to a loss of efficiency in surfactant removal, while increasing ISC allows the system to enhance the efficiency of the removal process. ANOVA test reported significativity for four of the five involved variables and the influence of pH was similar to the influence of ISC. An optimum q of 0.96 mg mg^{-1} was found at pH 4.9 and ISC equal to 103.2 mg L^{-1}.

1. Introduction

Surfactants have become a very important group of compounds in modern life. They are present in a large variety of usual and normal products like soaps, detergents, pharmaceuticals or personal care products. They are used in chemical industry, "hi-tech" devices, paints, leather [1]. As it can be appreciated, surfactants have achieved a main position in human activity. More than 12 M tonnes per year [2] are produced, according to the latest statistical data, so surfactants can be considered as a first importance chemical group.

Surfactants dumping into the environment represent a harmful and noxious practice [3]. They may be useful and needed compounds, but they are also considered dangerous and undesirable substances because of their impact on water fauna and vegetal life [4]. The main aspects in which surfactants modify on environmental equilibrium involve [5] groundwater and lakes pollution, pharmaceutical products binding (so pollution activity of these kinds of chemical compounds is considerably increased), animal and human toxicity and biopersistence [6].

Due to these reasons, removing surfactants from water flows has become a priority of a large number of researchers. Nowadays, surfactants can be removed by several mechanisms, most of them imply adsorption on activated carbon [7] or onto other materials [8], biological degradation [9,10], chemical oxidation [11–15] or electrochemical removal [16]. Recuperation of these products is also a challenge and a scope of several investigations [17]. However, new removal methods should be researched because surfactants and tensioactives impact is high enough. Specifically, the risk of bioaccumulation of sulfonated surfactants, such as sodium dodecyl benzene sulfonate (SDBS), has been fully characterized [18,19]. Taking these risks into account, the investigation we have developed has been focused on this surfactant.

Under *tannins* denomination there are lots of chemical families. Tannins have been used traditionally for tanning animal skins, but it is possible to find several products that are distributed as flocculants. Tannins come from secondary vegetal metabolites [20] that are present in bark, fruits or leaves. Tannin-rich barks come from trees such as *Acacia*, *Castanea* or *Schinopsis*. However, it is not needed to search for tropical species: *Quercus ilex*, *suber* or *robur* have also tannin-rich bark.

Tanfloc is a trademark that belongs to TANAC (Brazil). It is a tannin-based product, which is modified by a physico-chemical process, and has a high flocculant power. Some previous papers have researched on this particular coagulation agent [21]. It is obtained from *Acacia mearnsii de Wild* bark. This tree is very common in Brazil and it has a high concentration of tannins. Production process is under intellectual patent law, but similar procedures are widely reported as Mannich base reaction [22]. Specific industrial process for *Tanfloc* is referred by US patent number 6,478,986 B1 [23]. It involves tannin polymerization by the addition of formaldehyde (37%), ammonium chloride and commercial hydrochloric acid. The product so obtained under certain temperature conditions has a viscous appearance with 36% of active material.

* Corresponding author.
E-mail addresses: jbelther@unex.es (J. Beltrán-Heredia), jsanmar@unex.es (J. Sánchez-Martín), csolerah@alumnos.unex.es (C. Solera-Hernández).
[1] Tel.: +34 924289300x9033; fax: +34 924289 385.

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.06.012

Several references have been found regarding these kinds of chemical processes [24–26]. Most of them are patents, including the specific process for *Tanfloc*, which is reported [23]. The scientific literature refers a reaction mechanism that involves a tannin mixture, mainly polyphenol tannins whose structure may be similar to flavonoid structures such as resorcinol A and pyrogallol B rings.

Similar products have been studied as general flocculants previously [21]. *Tanfloc* has been tested as flocculant in wastewater [27,28] and its results are promising.

Environmental aspects are considered a primary target to work on, but usually economical and availability criteria are not taken into account when a technical solution is proposed for remediation processes such as surfactants removal. This investigation focus its interest in advancing in surfactant removal by means of a new process that is (a) cheaper than others such as electrocoagulation; (b) based on a natural product, so its biodegradability is higher than other coagulants; and (c) using a coagulant agent that has no need of pH adjustment, so its usage is easier than others. Taking care of environmental subjects may include these and other considerations that make the possibility of becoming clean a universal chance.

SDBS long molecule (Fig. 1) presents a benzene ring and a large linear chain on one side; and a sulfonate negative-charged group on the other side. This charged group and the large organic chain make SDBS a rather-expected molecule to be removed by a cationic coagulant agent, such as *Tanfloc*. pH and initial surfactant concentration (ISC) are presumed to be very important variables that might affect surfactant removal percentage in a severe way. To point out the relative influence of these variables and their interaction and to optimize the surfactant removal process by a design of experiments is the aim of this investigation.

2. Materials and methods

2.1. Sodium dodecyl benzene sulfonate

Surfactant was provided by FLUKA (CAS number 25155-30-0). Sodium dodecyl benzene sulfonate ($C_{18}H_{29}SO_3Na$) has a molecular weight equal to 348.48 g mol^{-1} and it was supplied in analytical grade as powder.

2.2. Buffered solution

All assays were done in a pH-stable medium. A pH 7-buffered solution was prepared by mixing 1.2 g of NaH_2PO_4 and 0.885 g of Na_2HPO_4 in 1-L flask. Assays with different pH were carried out by adjusting this buffered solution to the specific pH by using HCl 0.5 M and NaOH 0.5 M. All reagents were supplied by PANREAC in analytical purity grade.

2.3. General surfactant removal assay

500 mg L^{-1} surfactant stock solution was prepared. Different volumes of this stock solution were put into recipients, and controlled quantity of coagulant was added. Final volume was reached with pH 7 buffered solution. A soft blade-stirring agitation was applied for 2 h, until equilibrium was achieved. Kinetic studies of our specific research (Fig. 2) and previous studies carried out [29]

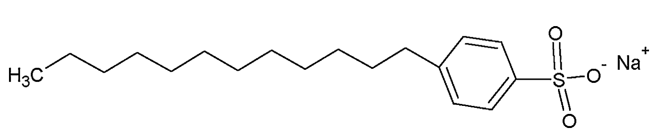

Fig. 1. Structure of sodium dodecyl benzene sulfonate molecule.

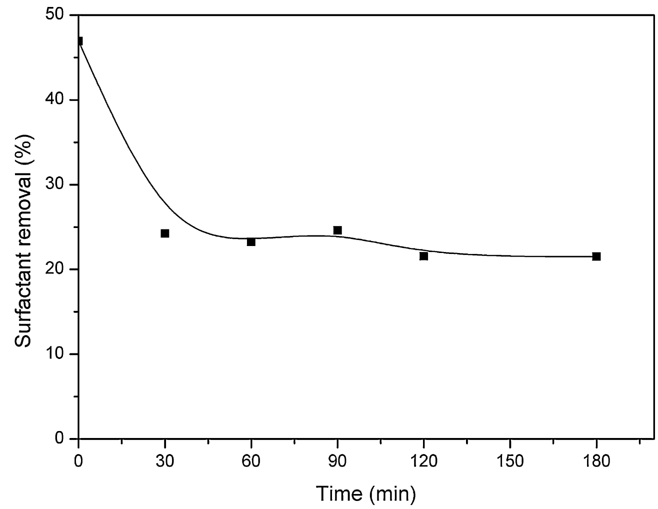

Fig. 2. Kinetic evolution on surfactant removal.

reported this period was enough for guarantee equilibrium. Then, a sample was collected and it was centrifuged. Surfactant removal was determined by visible spectrophotometry.

2.4. Surfactant analysis

In order to analyse surfactant concentration, a method based on methylene blue–anionic surfactant association was used [30]. 5 mL of clarified sample was put into a separation funnel. 25 mL of trichloromethane (PANREAC) and 25 mL of methylene blue solution (PANREAC) were added and funnel was shaken vigorously. Organic fraction was taken out and put into another separation funnel, in which 50 mL of cleaning solution was added. Funnel was shaken again, and the resultant organic fraction was put into a 25-mL flask. It was filled up to the mark with trichloromethane and methylene blue concentration was determined by visible spectrophotometry at 652 nm, with zero made with pure trichloromethane by using a HEλIOS spectrophotometer.

2.5. Mathematical and statistical procedures

Section 3.2 was statistically analyzed by using *StatGraphics Plus for Windows 5.1*. A factorial central composite orthogonal and rotatable design was used with 8 replicates of central point, so the total number of experiments was 16.

3. Results and discussion

3.1. Preliminary evaluation of Tanfloc dosage

Experimental series were made in order to determine flocculant dosage influence on surfactant removal. A fixed dose of 50 mg L^{-1} of surfactant was evaluated to be removed with different doses of *Tanfloc*. As it can be appreciated in Fig. 3, final surfactant concentration tends to decrease as *Tanfloc* dose increases. However, it is observed that process effectiveness arrives to a maximum, and higher doses of extract does not achieve lower surfactant concentrations. There is a residual surfactant concentration that is not possible to remove through this flocculation process and seems to be about 10 mg L^{-1}. This can be due to the existence of an 'equilibrium surfactant concentration' which is highly difficult to remove, as it has been reported previously [31].