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Schinopsis balansae tannin-based flocculant in removing sodium dodecyl benzene sulfonate

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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 *SilvaFLOC* and consists of a chemical modified tannin extract from *Schinopsis balansae*, commonly known as *Quebracho*. A fully detailed study has been carried out. *SilvaFLOC* has been revealed as an efficient product in anionic surfactant removal. Around 80% of SDBS removal has been achieved with *SilvaFLOC* doses of 300 mg L^{-1}. pH has a negative influence on surfactant removal, while the higher initial surfactant concentration the higher q capacity is obtained. Theoretical data adjustment has been carried out according to three different models: Fowler–Frumkin–Guggenheim (FFG), Gu and Zhu (G-Z) and Freundlich (F). Adjustment parameters have been obtained with r^2 levels above 0.96 in all cases. In order to study the interaction between pH and initial surfactant concentration, a design of experiments procedure has been carried out. Optimum pH has been found in 5.8.

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, personal care products, etc., but not only: 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. Attending to last statistical data, more than 12 Mtonnes/year [2] are used, so surfactants can be considerered as a first importance chemical group.

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

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 [5], chemical association [6] or electrochemical removal [7]. However, new removal methods should be researched on 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 [8,9]. 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 vegetal secondary metabolytes [10]: bark, fruits, leaves, etc. Tannin-rich barks come from trees such as *Acacia*, *Castanea*, *Schinopsis*, etc.

However, it is not needed to search for tropical species: *Quercus ilex*, *suber* or *robur* have also tannin-rich bark.

In the case of *Quebracho* tannins, nature of these chemical species have been thoroughly characterized by several researchers [11]. About *Quebracho* composition it can be said that is mainly based on combinations of resorcinol, catechol and pyrogallol building blocks [12]. That structure provides a useful base over which is easy to link several active groups that may enhance the flocculant and coagulant activity [13].

Several references have been found regarding this kind of chemical processes [14,15]. Most of them are patents, including the specific process for TANFLOC (used in the present investigation), which is reported [16]. The scientific literature refers a reaction mechanism that involves three reagents: a tannin mixture, mainly polyphenol tannins whose structure may be similar to flavonoid structures such as resorcinol A and pyrogallol B rings; an aldehyde

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such as formaldehyde and an amino compound, such as ammonia or a primary or secondary amine or amide compound [14]. The three reagents, under certain conditions of pH and temperature (80 °C), may produced the mentioned flocculant agents. Several references are found regarding these kind of chemical processes [17], called *Mannich base* reaction.

Schinopsis balansae, commonly known as *Quebracho*, is a tree that comes from South America. It was considered the first source of tannins until *Acacia mearnsii* de Wild replaced it because its high percentual tannin content and its relatively easy reproduction procedure. However, *Quebracho* is an important feedstock for tannin production [18]. Its content in tannins has been thoroughly determined [19].

SilvaFLOC is a trademark that belongs to Silvateam (Italy). It is a tannin-based product, which is modified by a physico-chemical process presumably similar to those described above, and has a high flocculant power. It is obtaine from *S. balansae* bark and production process is under intelectual patent law. Similar products have been studied as general flocculants previously [20].

According to Silvateam information, *SilvaFLOC* is compound of *Quebracho* tannin extract, 2-aminoethanol, hydrochloric acid and formaldehyde. It is presented as a dark brown liquid with a 16% of solid content. No special requirements are needed in order of handling it and health risks are rather reduced.

After a preliminary screening on surfactant-removal ability of several natural agents, this paper aims to characterize an interesting capacity *SilvaFLOC* seems to present: surfactant removal. Several anionic surfactants have been tested to be removed by *SilvaFLOC*. Among them, we have selected SDBS as an specific target.

2. Materials and methods

2.1. 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 suplied by PANREAC in analytical purity grade.

2.2. Natural coagulant products preparation

Apart from *SilvaFLOC*, nine natural coagulant products were tested in a preliminary screening. They were prepared in the following way:

- *Moringa oleifera seed extract* was obtained as described previously [21–23]. Seeds were obtained from SETROPA (Holland). The extraction process was carried out in the following way: seeds were reduced into powder by a domestic mill. A 1 M NaCl (PANREAC) solution was prepared and 5 g of powder were put into 100 mL of it. The NaCl solution with powder was stirred for 30 min time at room temperature (around 25 °C). No pH modification was needed, as natural pH 7 was achieved. Then, the extract was filtered twice: once through commercial filter paper on Büchner funnel and once again through a fine filtering *millipore* system (0.45 μm glass fiber). The result is a clear, milky-like liquid.
- *Cationic starch* was supplied by CARGILL (USA). It is used as an authorized alimentary supplement. It is presented as powder.
- *Opuntia ficus-indica mucilage* was obtained as described previously [24,25]: pods of *O. ficus-indica* were cut and external layer was removed manually. Internal fraction was milled in a domestic blender (Braun). 200 g of the resultant juice were put into a beaker and it was filled up to 1 L with distilled water. Then it was kept at 60 °C for 24 h. After this period, the mixture was filtered and concentrated by vacuum evaporation to one-third of the initial volume. Then, it was precipitated with ethanol twice, in order to achieve a clean, impurities-free mucilage. The resultant mix of ethanol and mucilage was dried in a heater at 60 °C for 12 h. Final product presents a green, crystal aspect.
- *Other modified tannin* were supplied by TANAC, S.A. (Brazil). Its name is TANFLOC and consists of tannins from *Acacia mearnsii* that have been chemically modified in order to introduce a quaternary nitrogen that confers TANFLOC its cationic character. AQUACHIMICA SETA, S.A. (Brazil) provides two more *A. mearnsii* tannin-based flocculants: AQUAPOL C1 and AQUAPOL S5T. Differences between *SilvaFLOC*, AQUAPOL C1 and S5T and TANFLOC lay on tannin nature (*A. mearnsii* for AQUAPOL and TANFLOC and *Quebracho* for *SilvaFLOC*) and on chemical modification, which is under copyright law. TANFLOC and AQUAPOL C1 are presented as powder, while *SilvaFLOC* and AQUAPOL S5T are presented as a dense solution.
- *Guar and Karaya gum* were supplied by SIGMA. They are presented as powder.
- *Aluminium sulfate* $Al_2(SO_4)_3{\cdot}18H_2O$ was supplied by PANREAC.

2.3. Preliminary screening of the efficiency of SilvaFLOC in removing other anionic surfactants

Eight anionic surfactants were tested with *SilvaFLOC* in order to characterize its behaviour as flocculant agent. They were the following ones:

- Sodium dodecyl benzene sulfonate (SDBS) $C_{18}H_{29}SO_3Na$.
- Sodium dodecyl diphenyl ether disulfonate (SDDED) $C_{35}H_{56}S_2O_7Na_2$.
- Sodium lauryl sulfate (SLS) $C_{12}H_{25}SO_4Na$.
- Sodium triethanolamine lauryl sulfate (TEA-LS) $C_{18}H_{40}NSO_4Na$.
- POE (3.5) sodium lauryl ether sulfate (SLES) $C_{12}H_{25}(OCH_2CH_2)_X OSO_3Na$, where average value of X is 3.5.
- Sodium dioctyl sulfosuccinate (SDSS) $C_{20}HSO_7Na$.
- Sodium lauryl sulfoacetate (SLSA) $C_{14}H_{27}SO_5Na$.
- POE Sodium sulfated nonylphenol (SSN) $C_{17}H_{28}SO_5Na$.

All reagents were suplied by Chem Service Inc. (USA) and they are presented in analytical grade.

2.4. 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 1 h, until equilibrium was achieved. Kinetic studies (data not shown) reported this period was enough for guarantee equilibrium. Then, a sample was collected and it was centrifuged. Surfactant removal were determined by visible spectrophotometry.

2.5. Surfactant analysis

In order to analyse surfactant concentration, a method based on methylene blue-anionic surfactant association was used [26]. 5 mL of clarified sample were 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 were 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