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Removal of direct Yellow 27 dye using animal fat and vegetable oil-based surfactant

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ABSTRACT

The textile industry uses large amounts of water in its processes. Such water ends up contaminated by a number of substances, including dyes, creating an environmental challenge. The present study aims at removing dye by applying the precipitation process using a sodium soap (anionic surfactant), derived from animal fat and vegetable oil, promoting dye decontamination using biodegradable materials. Sodium soap, in the presence of calcium ions, forms another insoluble surfactant. This new surfactant, under stirring, aggregates and forms hydrophobic flocs that are capable of adsorbing organic materials dissolved in aqueous solutions, including dyes. Dye removal was assessed considering the influence of initial surfactant concentration, temperature, pH, presence of electrolyte, equilibrium time, and stirring rate. Dye removal efficiency reached 97.6%.

1. Introduction

The textile industry is one of the largest polluters worldwide due, primarily, to the high water consumption and the elevated volume of colored wastewater production. Dye bath wastewaters can interfere in the penetration of solar radiation in aquatic systems, thereby disturbing biological processes [1,2]. In the dyeing process, it is usual to add chemicals such as dyes with trace amounts of heavy metals (such as chromium, cadmium, and zinc), acids, alkali, nitrate and sulfate salts, surfactants, and formaldehyde to improve dye fixation [3,4]. Therefore, adequate water treatment is important before discharging this wastewater into the environment.

Synthetic dyes bring considerable industrial interest, since they are relatively stable compounds, with widespread applications in the dyeing processes of textile companies. However, these dyes are difficult to remove in wastewater treatment plants, whether by physical, chemical, biological, or a combination of these processes [4]. Dyes have complex structures. Direct dyes are anionic water-soluble dyes and, when in the presence of electrolytes in aqueous solutions, exhibit a considerable affinity for cellulose fibers [5]. Nowadays, several technologies are being used to produce better fade-resistant fabrics, and increase the variety of shades available [6].

Several studies have been made in order to develop new ways to treat textile wastewaters, including techniques such as: coagulation–flocculation [7–9]; advanced oxidation processes [10–14]; adsorption [15–17]; membrane filtration [18–20]; and biological processes [21–23]. Although a number of textile wastewater treatment processes are under development, they exhibit several disadvantages [8]: processes involving the application of oxidizing agents, such as ozone, Fenton's reagents, and photochemical sonolysis, are costly and difficult to handle, produce large amounts of sludge, and form byproducts and large amounts of dissolved oxygen. Biological processes, despite being rendered environmentally friendly, are slow, require adequate nutrient levels, and have a restricted working temperature range.

Surfactants are amphiphilic molecules composed of at least two parts, one of them polar or hydrophilic (head group) and the other one nonpolar or hydrophobic (tail). Surfactant monomers act as typical electrolyte when they are present in diluted solutions, accumulating at interfaces and reducing the interface tension. When the surfactant concentration is increased, colloidal organized aggregates called micelles are formed by self-association of a large number of monomers. The critical micelle concentration (c.m.c.) is the concentration at which micellization starts [24].

The carboxylate soaps can interact with calcium ions (Ca^{2+}) forming salts of low water solubility and precipitating as scummy

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Table 1
Mean composition (wt.%) in fatty acids in the animal fat and coconut oil.

Acid, carbon number	Coconut oil (wt.%)	Animal fat (wt.%)
Capric, C10	6	–
Lauric, C12	47	–
Myristic, C14	18	5
Palmitic, C16	9	29
Stearic, C18	3	25
Oleic, C18=	6	36
Linoleic, C18,2=	2	1.5
Palmitoleic, C16=	6	3

deposits [25] that can aggregate to form flocs when submitted to stirring. This interaction can be described by a solubility product relationship between the free or unassociated species involved [26]. The flocs end up exhibiting significant decontamination potential for organic compounds, because they exhibit the hydrophobic character of the non-polar tail of the surfactant. Depending on their weight, they will decant or remain suspended in the medium, being separated by filtration.

The use of surfactants to treat dye-bearing wastewaters is the object of study of our research group [27,28]. The treatment proposed in this research is based on the use of carboxylate surfactants, which have the advantage of being low-cost, biodegradable, and low-toxicity products. Another advantage is the use of low surfactant concentrations. Experiments were conducted to remove the Direct Yellow 27 dye by flocculation, assessing the influence of surfactant concentration, stirring rate, equilibrium time, electrolytes concentration, pH, and temperature on removal efficiency.

2. Materials and methods

2.1. Materials

The surfactant used was synthesized in the laboratory from animal fat and coconut oil with a mass percentage of 95% and 5%, respectively. Table 1 presents the mean composition of fatty acids present in animal fat and coconut oil. The surfactant obtained was a mixture of surfactants, commercially known as base soap (SB), including sodium dodecanoate and sodium hexadecanoate. The mean molecular mass of the obtained surfactant was 289 g/mol and its critical micelle concentration (c.m.c.) was 0.0063 M (1820 ppm) [29]. Sodium dodecanoate and sodium hexadecanoate were also used as surfactants, both synthesized in the laboratory. Direct Yellow 27 (DY27 – Ciba-Geigy; molar mass = 662.62 g/mol; λ_{max} = 393 nm; empirical formula: $C_{25}H_{20}N_4Na_2O_9S_3$; CAS number: 10190-68-8) was used as dye to prepare the synthetic wastewater. Fig. 1 presents the chemical structure of DY27. Calcium chloride (CRQ) was used to obtain the calcium solution to perform flocculation. In the experiments that assessed the effect of pH, this was adjusted using hydrochloric acid (Vetec) and sodium hydroxide (NEON) solutions. NaCl (Anidrol) was used in the experiments to evaluate the presence of electrolytes in the dye removal process. All reagents were of analytical grade. Aqueous solutions were prepared using distilled water.

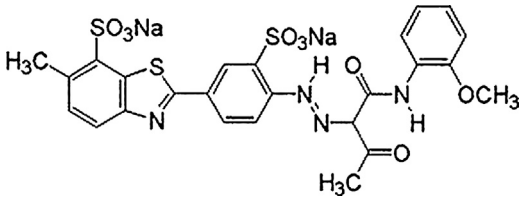

Fig. 1. Chemical structure of Direct Yellow 27 (DY27).

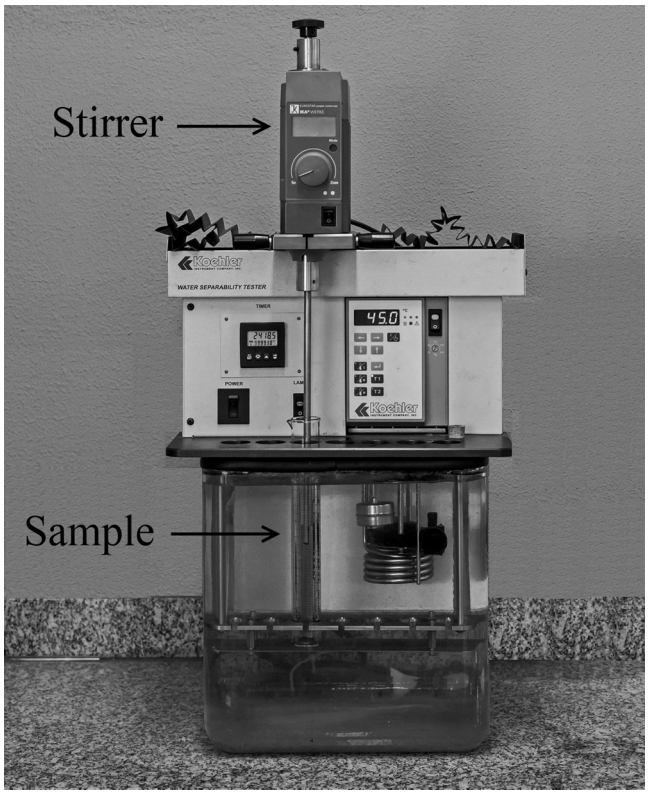

Fig. 2. Photograph of the experimental setup used to perform dye removal experiments.

2.2. Methods

2.2.1. Dye extraction experiments

Initially, stock solutions of dye and calcium were prepared with 1000 and 2000 ppm, respectively. In all experiments the concentration of DY27 was maintained at 100 ppm, which corresponds to a higher concentration than that found in textile wastewaters containing direct dyes [30]. In 100-mL test tubes, the dye solution was added and, soon after, SB was weighed and dissolved according to the required concentration (220, 260, 290, 330, 360, 390, 520, and 650 ppm – all lower than the c.m.c. value). The calcium solution was added in a concentration corresponding to half the SB concentration. The tests were conducted in a thermostatic bath (Koehler Instrument Company, Inc., USA) combined with a stirring system (EUROSTAR Power control-visc KIKA®-WERKE) (Fig. 2), at constant temperature (30, 40, 50, 60, and 70 °C), 100 rpm stirring rate during 3 min, then 50 rpm for 2 min [31,32]. After stirring, the samples were allowed to rest for 5 min and, then, filtered using a 0.7 μm glass fiber membrane (AP40, Millipore). The filtrate was analyzed in a molecular absorption spectrophotometer (Varian Analytical Instruments, Cary 50 Conc USA) and in an atomic absorption spectrophotometer (Varian, AA240) to determine final dye and residual calcium concentrations, respectively. Dye removal efficiency was calculated by using Eq. (1):

$$\%\text{Efficiency} = \frac{C_{\text{DY27 initial}} - C_{\text{DY dilute}}}{C_{\text{DY27 initial}}} \times 100 \quad (1)$$

where, $C_{\text{DY27 initial}}$ is the initial concentration of dye and $C_{\text{DY27 dilute}}$ is the concentration of DY27 in the dilute phase, after floc separation.

2.2.2. Effect of pH on dye removal efficiency

In experiments to evaluate the effect of pH, the solution containing SB was restricted to only three concentrations (390, 520, and