U.Porto Journal of Engineering, 8:4 (2022) 13-25
ISSN 2183-6493
DOI: 10.24840/2183-6493_008.004_0003

Received: 30 October, 2021
Accepted: 15 May, 2022
Published: 8 July, 2022

Decolorization of a Simulated Reactive Textile Dyeing Effluent using a Plant-derived Coagulant

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Abstract

The ability of a commercial tannin-based coagulant on the decolorization of a simulated textile effluent containing a reactive dye was studied in batch mode. For comparison, two conventional chemical coagulants (aluminum sulfate and *Rifloc 6548*-organic coagulant) were also tested. Preliminary assays suggested a higher performance of Tanfloc SG and *Rifloc* coagulants over the metal salt. Optimization assays conducted for *Tanfloc SG*, indicated a maximum color removal of 86.4%, recorded at a coagulant dosage of 240 mg/L and at pH 7. A decolorization efficiency of 42.4% was found for the optimized dosage of 144 mg/L at pH 9. At this condition, the treatment cost using *Tanfloc* was estimated as 0.21 EUR/m^3, around twice the *Rifloc* when used at 96 mg/L, generating 81% of treatment efficiency. *Rifloc* outperformed *Tanfloc*, and its use also seemed to be more economical but may have negative impacts on the environment. However, *Tanfloc* still showed promising results and presented a better performance in terms of sedimentation velocity and floc size.

Author Keywords. Coagulation, Tannin, Dyeing, Natural Coagulant.

Type: Research Article
Open Access Peer Reviewed

1. Introduction

Coagulation/Flocculation is one of the most important treatment processes for removing impurities in water and wastewater treatment, playing an essential role in providing clean water for human consumption and in the safe discharges of water resources (Ang and Mohammad 2020). In the coagulation step, the destabilization of suspensions or solutions occurs through the addition of coagulants under rapid mixing (Bratby 2016). Particle destabilization, in this step, is typically explained by four mechanisms that can co-occur (Davis 2010): (i) compression of electrical double layer, (ii) adsorption and charge neutralization, (iii) adsorption and interparticle bridging, and (iv) enmeshment in a precipitate. The destabilized particles are then induced to form larger agglomerates through slow agitation (flocculation), facilitating subsequent removal by sedimentation, filtration, or flotation (Teh et al. 2016).

Typically, chemical coagulants based on iron or aluminum salts or synthetic organic polymers are used. However, these coagulants are non-biodegradable; their use promotes secondary pollution and produces toxic sludge whose treatment is expensive and complex (Omar, Zin, and Salleh 2018). Natural-derived coagulants have emerged as alternatives considering their expected greener production and usage (Ang and Mohammad 2020). These coagulants, biodegradable and non-toxic, may be easily produced from abundant raw materials and have demonstrated a high removal efficiency for different pollutants (Ang and Mohammad 2020; Al-Gheethi et al. 2020).

Natural-derived coagulants can be of animal, microbial or vegetal origin. Of the vegetable-derived coagulants, there has been a growing interest in applying tannin-based coagulants since tannins extraction is simple and does not require a purification step. Their chemical modification is a well-established process (Ibrahim, Yaser, and Lamaming 2021). Tannins are polyphenolic compounds, one of the largest classes of secondary plant metabolites (Lima and Abreu 2018). The presence of phenolic groups is responsible for an anionic nature, observed in almost pH conditions, due to their ease deprotonation to form phenoxide, which is stabilized by resonance. Zero points of charge, or isoelectric points, of tannin materials have been observed at pH values around 2 (Bacelo et al. 2022; Sun, Zhang, and You 2021), indicating that cationic properties are only observed at strong acidic conditions.

High levels of tannins can be found in *Schinopsis balansae* wood (Sánchez-Martín, González-Velasco, and Beltrán-Heredia 2010) or in *Acacia mearnsii* (Grenda et al. 2018), but they can also be obtained from unconventional materials, such as the bark of trees and biomass from industrial and forest residues. Tannins can be extracted by different techniques. Various organic solvents, such as methanol, ethanol, and acetone, have been used over the years, but special attention has been recently paid to replacing these solvents with water and ionic liquids (ILs) (Tomasi et al. 2022) and exploring greener extraction techniques involving supercritical fluid extraction, ultrasound-assisted extraction, microwave-assisted extraction, pressurized liquid extraction, and pressurized hot water extraction. As recently reviewed by Tomasi et al. (2022), water and ILs may lead to similar or even superior performance in tannins extraction, depending on the tannin source, extraction method and conditions, and extract purposes. For instance, some ILs extracted proanthocyanins from grape skins more effectively than with methanol (Ćurko et al. 2017). Bacelo et al. (2022) compared extraction yields and total extracted phenols obtained from pine bark using alkaline aqueous solutions and ethanol and, in various conditions, better values were found in the aqueous extraction. After the extraction process, tannins are usually subjected to a cationization process, in which a quaternary nitrogen is introduced into the polyphenolic structure through a reaction with an amine and an aldehyde (Ibrahim, Yaser, and Lamaming 2021). This reaction is known as the Mannich reaction and significantly influences the tannins' coagulation efficiency. Polymerized tannin products usually present insignificant emissions of formaldehyde. Even though, free-aldehyde reactions have been investigated for the tannin coagulant/flocculant synthesis (Machado et al. 2020).

Tannin-based coagulants have been evaluated in the treatment of surface and synthetic waters, mainly for turbidity removal (Arismendi et al. 2018; Barrado-Moreno, Beltrán-Heredia, and Martín-Gallardo 2016; Heiderscheidt, Leiviskä, and Kløve 2016; Kukić et al. 2015), domestic and municipal wastewaters (Hameed et al. 2016; Fabres et al. 2017; Grehs et al. 2019), and industrial effluents, such as textile effluents (Costa et al. 2018; Grenda et al. 2020; Grenda et al. 2018; Lopes et al. 2019), agricultural effluents (Dela Justina et al. 2018; Turunen, Karppinen, and Ihme 2019), and landfill leachate (Banch et al. 2019; Ibrahim and Yaser 2019). Within industrial effluents, special attention has been given to textile and dyeing effluents. The textile industry is one of the largest water consumers and producers of effluents, contributing to water pollution worldwide due to the release of effluents containing dyes into waterways, which threatens the quality and aesthetics of water resources (Ibrahim, Yaser, and Lamaming 2021). Reactive dyeing and rinsing operations, commonly used in cellulose fibers, produce colored effluents containing a complex mixture of unfixed dyes, salts, acids, bases, and industrial additives. Color removal by conventional methods is usually challenging, particularly for reactive dyes, which present fixation degrees onto the fibers of 50-90 % (Islam et al. 2019).

In this work, *Tanfloc SG* was evaluated on the decolorization of a simulated dyehouse effluent containing a reactive dye (Reactive Blue 19, RB 19), salts (NaCl, NaOH, and Na_2CO_3), and industrial additives (lubricant and wetting agents), usually used in cotton dyeing baths. According to the authors' knowledge, studies regarding the decolorization of reactive dyeing effluents using coagulants derived from natural materials are rather uncommon in literature, and are limited to the use of chitosan, gelatin, and cellulose derivative flocculants (El-Gaayda et al. 2021). In this work, *Tanfloc SG*, a tannin-derived coagulant produced from *A. mearnsii* and one of the few natural coagulants already on the market (*TANAC*, Brazil) was employed. Coagulation experiments were performed in batch mode (Jar test). For comparison, similar assays were conducted for two conventional coagulants: the metallic salt aluminum sulfate and *Rifloc 6548*, a synthetic organic polymer widely used in industry to treat this type of effluents.

2. Materials and Methods

2.1. Coagulants

The tannin-based coagulant *Tanfloc SG* (designated by T) was supplied by *TANAC*, Brazil. A 20 g/L solution was prepared from its powder form by dissolving the required amount in distilled water. For comparison, two chemical coagulants were used. A solution of aluminum sulfate (designated as S), $Al_2(SO_4)_3.14H_2O$, was prepared at 50 g/L. A 10 times diluted solution of *Rifloc 6548* (designated as R) was also prepared. This coagulant was used in diluted form to facilitate its measurement, as it is a viscous yellow liquid.

2.2. Effluent preparation

A cotton dyeing effluent was simulated with the reactive dye *Remazol BrBlue R spec* (Reactive Blue 19), supplied by *DyStar*. Figure 1 shows Reactive Blue 19 dye chemical structure. The effluent preparation consisted of heating, under stirring, of 1.0 L of tap water, with the addition of 50 g of sodium chloride, 1 g of each auxiliary dyeing product (wetting and lubricant agents), and 0.64 g of dried dye.

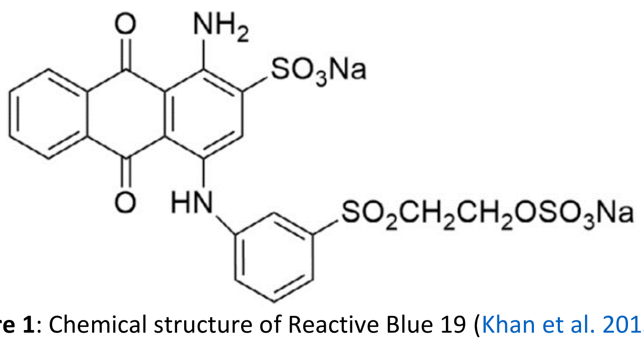

Figure 1: Chemical structure of Reactive Blue 19 (Khan et al. 2015)

The wetting agent is a colorless liquid, with anionic behavior in aqueous solution, whereas the lubricant is a non-ionic viscous yellow liquid (Santos 2009). A temperature of 55-60°C was kept for 10 minutes for complete dissolution. Then 2.0 g of sodium hydroxide and 10 g of sodium carbonate were added, and the solution remained at 55-60°C for an hour. This procedure simulated the composition of a typical dyeing bath of cellulosic fibers using reactive dyes

(Santos 2009). After cooling, the colored solution was diluted to 8.0 L to simulate the subsequent rinsing, soaping, and softening operations, which conduct to a simulated effluent obtained from the dyeing bath after a dilution factor of 8 (Santos 2009). Finally, the pH was adjusted with sulfuric acid solutions to obtain effluent at pH 7 and pH 9. The final effluent was then composed of a dye concentration of 80 mg/L and 0.125 g/L of each one of the two auxiliary dyeing chemicals. Since dyeing effluents are normally alkaline, the pH 9 simulated a situation in which coagulation/flocculation is employed with no previous pH correction on the generated effluent. The pH 7 was representative of a condition in which the effluent to be treated go on (or exit) a biological treatment and then required a previous pH neutralization.

2.3. Coagulation/Flocculation assays

Coagulation/Flocculation assays were conducted in batch mode using a Jar test equipment (*ISCO*) with six stirrers and a fluorescent lamp to observe floc formation. In all assays, 800 mL beakers containing 500 mL of effluent at pH 7 or 9 were used.

2.3.1.Preliminary assays

Preliminary assays were conducted to determine the minimum dosages of coagulants T, S, and R that generate primary flocs. Increments of coagulants were successively added to the 500 mL effluent. After each addition, the solutions went through a rapid mixing stage (150 rpm) for 1 min, followed by a slow mixing stage (20 rpm) for 3 min (enough to check for floc formation). Floc formation was then evaluated by visual observation, and the final pH was measured.

2.3.2.Optimization assays

Additional studies were performed for *Tanfloc SG* to optimize the decolorization process at pH 9 and pH 7 in terms of coagulant dosages. These assays were also conducted for *Rifloc* at pH 9, using the minimum coagulant dosage. Increasing amounts of coagulants were added, starting from the minimum dosage. Experiments included a rapid mixing stage of 3 min (150 rpm) and a slow mixing stage of 15 min (20 rpm), followed by 15 min of sedimentation. These experimental conditions were selected based on previous studies (Lopes et al. 2019). Floc size and settling velocity were observed visually. Turbidity and color removal were assessed by samples taken from the supernatant, approximately 2 cm below the surface. The final pH was measured.

2.4. Analytical methods

Color removal was evaluated by absorbance measurement at 590 nm (maximum absorption wavelength for a Reactive Blue 19 dye solution) in a UV-vis spectrophotometer (*UV-6300PC double beam, VWR*). Samples were previously filtered on fiberglass membranes. The first 5 mL of filtered samples were discarded to eliminate the interference of possible retention of the dye on the filter. Turbidity was measured by the nephelometric method using a turbidimeter (*HANNA Instruments*, HI 88703). pH was analyzed by a portable meter (*HANNA Instruments*, HI 88733).

3. Results and Discussion

3.1. Preliminary assays

The minimum coagulant dosage required to start the formation of primary flocs was determined for each effluent pH and coagulant. The results are presented in Table 1. Coagulant dosages are expressed in mL/L (volume of the prepared coagulant solution per liter of effluent) and mg/L (milligram of coagulant, in its original powder or undiluted form, per liter of effluent).

Coagulant	Initial pH	Minimum dosage (mL/L)	Minimum dosage (mg/L)	Final pH
T	7.19	6.0	120	7.50
	9.04	1.2	24	8.96
S	7.19	10.0	500	6.46
	9.04	> 12.0	> 600	6.70
R	7.19	0.8	96	7.24
	9.04	0.8	96	8.87

Table 1: Minimum dosages for coagulation obtained for *Tanfloc SG* (T), Aluminum sulfate (S) and *Rifloc 6548* (R), at pH 7 and pH 9

Preliminary assays allowed to determine the minimum *Tanfloc SG* dosage that generates primary flocs: 6.0 and 1.2 mL/L (corresponding to 120 and 24 mg *Tanfloc SG* powder per L of effluent), respectively for pH 7 and pH 9. Lopes et al. (2019) determined minimum *Tanfloc SG* dosages required to start the formation of primary flocs in an effluent containing a direct dye (80 mg/L), salts (e.g., sodium chloride at 2.5 g/L), wetting, lubricant, and sequestering agents, each one in a concentration of 0.25 g/L. Although the dye used (Direct Blue 85; azo dye) is different from the one here used (Reactive Blue 19; anthraquinone dye), both are anionic and have sulfonic acid groups. At pH 7, the authors reported a minimum T dosage of 140 mg/L, which is close to the value here obtained (120 mg/L). However, at pH 9, the value here found (24 mg/L) is much lower than the 120 mg/L reported by them. This may suggest that the reactive dye, which has a smaller molecular structure than the direct dye, undergoes more easily in interparticle bridging and enmeshment with the tannin-based coagulant.

At pH 7, minimum dosages of 10 mL/L (500 mg/L) and 0.8 mL/L (96 mg/L) were respectively obtained for aluminum and *Rifloc* coagulants. At pH 9, Al coagulant dosages up to 12 mL/L (600 mg/L) did not cause flocs formation, whereas 96 mg/L of *Rifloc* were enough for coagulation.

Although direct comparisons of dosages of different coagulants should be taken with care, these results suggest a higher performance of the organic coagulants (T and R) over the metal salt coagulant. Indeed, considering the anionic nature of the dye and the charge of the expected Al complexes formed in different pH conditions (Figure 2), at pH 7 and pH 9, coagulation by charge neutralisation is not possible. The dye retention in the $Al(OH)_3$ precipitate should be the prevailing coagulation mechanism. This also explains the poor coagulation ability of S at initial pH 9, where the precipitate $Al(OH)_3$ is expected to be almost absent, according to Al hydrolysis speciation diagram. With organic polymers, hydrogen bonding and a coagulation mechanism based on interparticle bridging should prevail and justify the flocs formation observed.

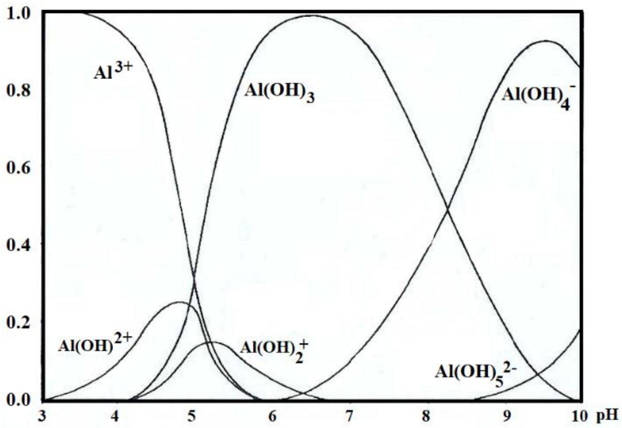

Figure 2: Distribution of Aluminum hydrolysis as a function of pH

The addition of coagulants usually causes changes in the final pH, and this is a common cause of efficiency inconsistencies. However, as can be seen (Table 1), pH variations were not very significant when organic coagulants were used. The maximum variation recorded was 0.3 pH-units for *Tanfloc* and 0.2 pH-units for *Rifloc*. On the other hand, aluminum sulfate caused significant changes in the final pH value, as the result of sulphuric acid generation in the chemical reaction (Equation (1)) between the coagulant and the effluent, and insufficient alkalinity to sustain pH. The low pH variation is an advantage of organic coagulants since it is no longer necessary to add large amounts of base or acid to correct the effluent pH and alkalinity, enabling a more consistent process performance and decreasing operating costs (Lopes et al. 2019).

$$Al_2(SO_4)_3.14H_2O \rightarrow 2Al(OH)_3.3H_2O + 3H_2SO_4 + 8H_2O \quad (1)$$

3.2. Optimization assays

Optimization assays were conducted to determine the optimal dosage of *Tanfloc SG*. The results obtained for settling velocity, floc size, turbidity, and colour removal, for each pH condition, are presented in Table 2. The settling velocity and floc size were visually evaluated and given a qualitative classification (+ - Very small, ++ - Small, +++ - Medium). Once again the coagulant dosages are expressed in mL/L (volume of the prepared coagulant solution per liter of effluent) and in mg/L (milligram of coagulant in its original, undiluted form per liter of effluent). The visual results obtained after the 15-minute rest of the solutions are shown in Figure 3.

Initial pH	Dosage (mL/L)	Dosage (mg/L)	Settling velocity	Floc size	Turbidity (NTU)	Color removal (%)	Final pH
7.08	6.0	120	++	+	17.00	38.2	7.44
	8.0	160	++	+	13.00	67.1	7.46
	10.0	200	+++	+++	9.30	79.7	7.51
	12.0	240	++	++	20.00	86.4	7.54
9.00	1.2	24	+	+	5.25	10.5	8.96
	2.4	48	+	++	10.00	17.0	8.98
	3.6	72	+	++	6.95	29.7	8.91
	7.2	144	+	++	20.00	42.4	8.72

+ - Very small; ++ - Small; +++ - Medium

Table 2: Settling velocity, floc's size, turbidity and color removal obtained in coagulation assays using different dosages of *Tanfloc SG*, at pH 7 (initial pH 7.08) and pH 9 (initial pH 9.00)

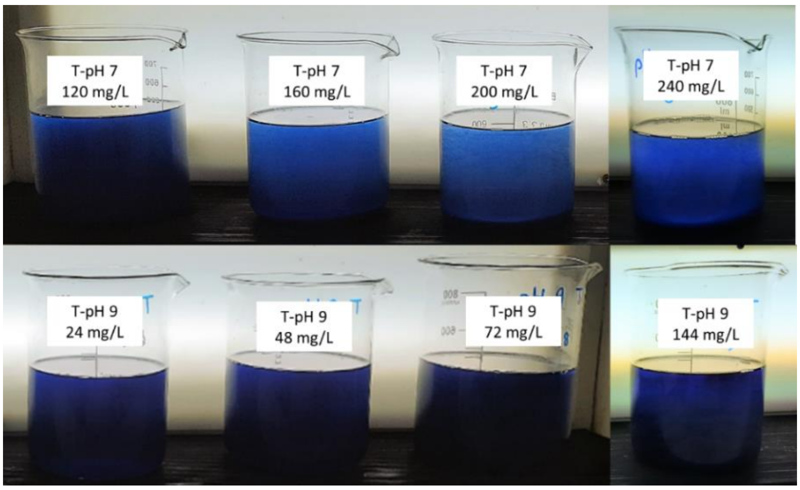

Figure 3: Appearance of the effluents treated with different dosages of *Tanfloc SG* at the end of the sedimentation process

The settling properties of the sludge are also a critical factor in evaluating the performance of a coagulant. In general, the settling velocity of the sludge generated within the conditions studied is quite slow, especially in the effluent treated at pH 9, resulting in a dark blue "apparent color". The highest settling velocity was verified at pH 7 for the dosage of 200 mg/L. Although flocs formation was observed in all cases, they were mostly of small dimensions. Again, for a dosage of 200 mg/L at pH 7, the flocs formed had larger dimensions, which may explain the higher settling velocity observed. These results, which were corroborated by the photos in Figure 3, suggest that a solid/liquid separation by sedimentation is not feasible. The use of a flocculant should then be evaluated in future studies. Even though it is interesting to see that final turbidity values are quite acceptable. As the textile wastewater to be treated did not contain suspended matter, turbidity was measured in this work only as an additional index of the settling properties of the flocs, *i.e.,* of the residual particles that remain suspended after rest. As it can be seen (Table 2), low turbidity values, equal to or below 20 NTU, were always obtained. Visually it was hard to determine and distinguish the settling rate and the size of the flocs. However, it is known that the highest settling velocity would be observed for the largest flocs size.

At pH 7 and pH 9, the increase in the *Tanfloc SG* dosages (120-240 and 24-144 mg/L, respectively) led to an increase in the decolorization efficiency, although not always to a better settling of the sludge. Within the conditions studied, maximum color removals of 86.4 % and 42.4 % were found at pH 7 (T dosage: 240 mg/L) and pH 9 (T dosage: 144 mg/L), respectively. Therefore, these dosages were selected as the optimal ones for the decolorization of the effluent. However, considering the consistent increasing trend of the color removal with coagulant dosage, there is room to test still higher coagulant dosages. At pH 7, a quite similar efficiency (91 %) was reported by Grenda et al. (2020) on the decolorization of a cosmetic colored effluent using 200 mg/L of a tannin-based coagulant (also derived from *A. mearnsii*), combined with 5 mg/L of cationic polyacrylamide (PAM). Lopes et al. (2019) achieved total decolorization (100 %) at pH 7 using T dosages of only 150 mg/L, which shows the more challenging treatment of the reactive dyeing effluent. In contrast, at pH 9, the decolorization efficiencies achieved in the present work are higher than the values recorded by Lopes et al. (2019) for similar T dosages. For instance, using 120 mg/L of *Tanfloc SG*, a color removal of 25 % was measured by Lopes et al. (2019), whereas the efficiency expected by with the present results is between 29.7 and 42.7 %. It is worth noting that optimum coagulation efficiency using tannin-based coagulants for textile effluents has been reported at optimized acid (Grenda et al. 2018; Lopes et al. 2019) or circum-neutral pH (Costa et al. 2018). However, it is important to conduct studies at alkaline pH, as this condition is representative of most dyehouse and mixed textile effluents, and pH adjustment for the huge volumes of effluents generated is expensive. These results of Table 2 confirmed that *Tanfloc SG* causes marginal pH variations (< 0.3 pH-units), even when used at significantly higher dosages than the minimum ones (Table 1). This happens because organic coagulants do not consume alkalinity, and it is an operational advantage over metal coagulants (Yin 2010).

3.3. Comparison with Rifloc 6548

For comparison with the tannin coagulant (144 mg/L), *Rifloc 6548* was tested at pH 9 and 96 mg/L (minimum dosage for coagulation). Table 3 shows the performance indicators and the cost associated with the use of each coagulant. The synthetic organic polymer, *Rifloc 6548*, even under a lower dosage than *Tanfloc SG*, achieved a superior performance (81.2 % of color removal compared to 42.4 %). Based on these results, a comparison of T and R coagulants at the same dosages was not judged as necessary. Considering these coagulant dosages, the treatment costs of this effluent using *Tanfloc SG* and *Rifloc* were estimated based only on the coagulant addition. The estimated cost of *Tanfloc SG* use was calculated as 0,21 EUR/m^3 (corresponding to a dosage of 144 mg/L, which provides 42% color removal). This value is around twice the *Rifloc* when used at 96 mg/L, generating 81% treatment efficiency. In addition to the superior performance, *Rifloc* seems more economical than *Tanfloc SG* at pH 9. However, *Tanfloc* still showed promising results and presented a better performance than *Rifloc* in sedimentation velocity and floc size. Furthermore, the tannin coagulant is a natural-derived coagulant, which may have fewer negative impacts on the environment than *Rifloc*.

Coagulant	pH	Dosage (mg/L)	Settling velocity	Floc's size	Turbidity (NTU)	Color removal (%)	Final pH	Cost (EUR/m^3)
T	9	144	+	++	20.00	42.4	8.72	0.21
R	9	96	+	+	23.00	81.2	8.84	0.12

+ - Very small; ++ - Small.

Table 3: Comparison between the utilization of *Tanfloc SG* and *Rifloc 6548* at pH 9

3.4. Comparison with other methods for Reactive Blue 19 removal

Removal of reactive dyes from aqueous solution can also be accomplished by other methods. Although many of these are destructive methods, contrary to coagulation/flocculation or adsorption, in which the pollutant is transferred between phases, a comparison was made regarding the efficiency of the different treatments.

Various treatment processes (sonolysis, photolysis, catalysis, sonocatalysis, photocatalysis, and sonophotocatalysis) were investigated in the degradation of RB 19 (Khan et al. 2015). The sonophotocatalytic degradation process was successfully carried out using sulfur-doped TiO_2 nanoparticles, being the most efficient method. The RB 19 solution (20 mg/L) was degraded to 90 % within 120 min. However, with increasing dye concentration, the dye degradation rate decreased while keeping the catalyst amount constant. This process is not fully accepted due to the costs associated with UV light and the catalyst, especially when applied to higher dye concentrations (Siddique, Farooq, and Shaheen 2011).

Electrochemical degradation was studied for RB 19 removal in chloride medium to treat textile dyeing wastewater (Rajkumar, Song, and Kim 2007). For different concentrations of RB 19 (50 – 400 mg/L), complete color removal was achieved in a short period of electrolysis. However, for 400 mg/L of dye concentration, the removal of chemical oxygen demand and total organic carbon was limited to 55.8 and 15.6 %. Although there is no consumption of chemical products and accumulation of sludge, there is additional production of hazardous materials (Katheresan, Kansedo, and Lau 2018). Electrochemical degradation is considered an expensive method.

Khrueakham et al. (2021) compared the decolorization efficiency of RB 19 (75 mg/L) wastewater by ozonation membrane contactor and Fenton oxidation. For the Fenton reaction, optimum conditions were identified at pH 3, achieving a decolorization efficiency of 91.2 %. Despite the high efficiency achieved, the Fenton process generates high iron sludge and only works at low pH (Katheresan, Kansedo, and Lau 2018), which for cotton dyeing wastewater will require a tremendous consumption for acidification. In the ozonation membrane contactor process, 98.6 % decolorization was achieved with a 40 mg/L ozone concentration at pH 3. The ozonation process was more efficient than the Fenton oxidations, removing nearly all RB 19. Nevertheless, it is pretty expensive, produces toxic by-products, and is an unstable method with operational problems (Katheresan, Kansedo, and Lau 2018).

Bacillus megaterium was found effective on RB 19 biodegradation (Erdem et al. 2019). Glucose (20 g/L) was the most suitable carbon source, and a decolorization efficiency of 92 % was reached at neutral pH conditions. Compared to other chemical and physical processes, biodegradation of dyes is one of the most cost-effective solutions. However, since the effluent is highly variable in terms of chemical and physical characteristics, the biological processes are not very flexible (Katheresan, Kansedo, and Lau 2018).

Dehvari et al. (2016) studied the removal of RB 19 (100 mg/L) from synthetic textile wastewater by adsorption with pomegranate seed power. At pH 3 and 60 min equilibrium time, a biosorbent dosage of 5 g/L achieved a removal efficiency of 88 %. Adsorption is an effective method for treating textile effluents, mainly due to the simplicity of design and easy operation. The regeneration of the adsorbent is usually considered a critical point (Katheresan, Kansedo, and Lau 2018; Siddique, Farooq, and Shaheen 2011), but when low-cost and biodegradable materials are used as adsorbents, their lifetime or desorption requirements may not be economically attractive.

As it can be seen, there are several efficient methods for Reactive Blue 19 removal, with removal efficiencies close and slightly surpassing the highest decolorization value (86.4 %) achieved in this work for coagulation/flocculation using *Tanfloc SG*. The results obtained here are still in an exploratory stage, and further studies are necessary to improve this removal efficiency and enhance the settling properties of the generated sludge. There are also additional issues on the use of tannin-derived coagulants to be investigated, namely, residual coagulant concentrations, as there are some works reporting significant values when high coagulant dosages are applied (Lopes et al. 2019). Although the use of natural coagulants, in comparison to other methods, is more widely accepted because of its high biodegradability, low cost, simple operation and design, flexibility, and no hazardous residual material production in the treated effluent (Katheresan, Kansedo, and Lau 2018; Siddique, Farooq, and Shaheen 2011). Potential adverse effects of residual concentrations related to polyphenols toxicity should be investigated as there is vast and conflicting literature on the overall effects of tannins on human health (Chung et al. 1998).

4. Conclusions

The decolorization of a simulated dyehouse effluent containing a reactive dye (Reactive Blue 19), salts, and industrial additives were studied by coagulation-flocculation-sedimentation in batch mode, using the tannin-based coagulant *Tanfloc SG*.

Preliminary assays allowed to determine the minimum *Tanfloc SG* dosages that generate primary flocs. At pH 7, 6.0 mL/L (corresponding to 120 mg of coagulant per L) was determined, whereas at pH 9, 1.2 mL/L (24 mg/L) was obtained. For comparison, similar assays were conducted for two conventional coagulants, aluminum sulfate and *Rifloc 6548*. At pH 7, minimum dosages of 500 mg/L (10 mL/L) and 96 mg/L (0.8 mL/L) were obtained for aluminium and *Rifloc* coagulants. At pH 9, Al coagulant dosages up to 600 mg/L (12 mL/L) did not cause flocs formation, whereas 96 mg/L of *Rifloc* were enough for coagulation. These results suggested the higher performance of the organic coagulants over the metal salt.

Additional studies were performed for *Tanfloc SG* to optimize the decolorization process in terms of coagulant dosages. At pH 7 and 9, the increase in the *Tanfloc SG* dosages (120-240 and 24-144 mg/L, respectively) led to an increase in the decolorization efficiency, although not always to a better settling of the sludge. Maximum color removals of 86 % and 42 % were found at pH 7 (240 mg/L) and pH 9 (144 mg/L), respectively. *Tanfloc SG* has caused minimum pH variations, an operational advantage over metal coagulants. For comparison, *Rifloc 6548* was tested at pH 9 and 96 mg/L (minimum dosage for coagulation), and 81% of color removal was achieved, indicating a superior performance compared to *Tanfloc SG*. Considering the coagulants' costs and applied dosages, *Rifloc* seemed more economical than *Tanfloc SG* at pH 9. However, *Tanfloc* still showed good results and presented a better performance than *Rifloc* in sedimentation velocity and floc size. The tannin coagulant is a natural-derived material, biodegradable and non-toxic, unlike *Rifloc*, which may have negative impacts on the environment. This work is a preliminary assessment, and additional studies should be done in the future to explore better coagulants comparison, process optimization, and combination between coagulants and flocculants.

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Acknowledgments

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC). S. Santos acknowledges postdoctoral scholarship (SFRH/BPD/117387/2016), awarded by FCT.