BIOFLOCCULANT PRODUCTION FROM EXCESS-ACTIVATED SLUDGE AND ITS APPLICATION IN TEXTILE WASTEWATERS

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ABSTRACT

Azo dye-containing wastewaters are considered a liability due to the environmental problem it may cause when improperly discharged. This work focuses on the production of a novel bioflocculant from excess-activated sludge from the textile industry and its application in the flocculation of commercial azo dyes. The resultant flocculant agent presented fractions of 27% proteins, 12% carbohydrates, and 12% lipids. pH and zeta potential were taken into consideration during flocculation assays to elucidate the driving flocculation mechanisms. Color removal outcomes attained 91 and 100% for reactive and dispersive dyes, respectively, at pH 5. This study presents the feasibility of the eco-friendly bioflocculant as well as its potential for precipitating textile dyes.

Keywords: Waste valorization. Flocculant agent. Azo dyes. Reactive red 194. Disperse red 343.

1 INTRODUCTION

The presence of dyes and chemicals used in dyeing and washing processes within the textile industry heightens concerns regarding textile wastewater. Azo dyes, identified by their characteristic structure (-N=N-) that contributes to their chemical stability, deserve special attention due to their resistance to photolysis and microbial degradation[1]. These conditions limit the efficiency of conventional biological wastewater treatment and require prior management strategies to mitigate environmental impact and harmful consequences for human well-being[2]. Flocculation is a well-known approach to reduce the presence of contaminants in industrial wastewater. However, some inorganic and synthetic flocculating agents have been associated with diseases[3]. In this scenario, bioflocculants emerge as a sustainable alternative for wastewater treatment, offering an eco-friendly solution. These compounds primarily consist of proteins and polysaccharides derived from microorganisms and they exhibit the capability to aggregate and precipitate both dissolved and suspended substances in water[4].

On the other hand, conventional wastewater treatment results in the formation of huge amounts of excess-activated sludge, which constitutes a residue considered an environmental liability that demands appropriate disposal. In the textile industry, it is estimated that a treatment plant produces 25 m^3 of activated sludge per million tons of textile wastewater[5]. In this sense, the present study aims at developing a novel bioflocculant using the excess-activated sludge from a textile wastewater treatment plant and verifying its ability to precipitate commercial azo dyes employed in textile dyeing.

2 MATERIAL & METHODS

The activated sludge, obtained from a local textile industry, was dried and milled before experiments. The extraction of the bioflocculant was performed by an alkaline-thermal hydrolysis[6]. The reaction medium consisted of activated sludge and 50 mL of NaOH solution (0.5 M) and was kept in a heating thermal mantle at boiling point. Firstly, the sludge mass was varied between 0.5 to 4.0g and, subsequently, a kinetic study was conducted with the optimized conditions. Two synthetic dyes were employed on the flocculation tests, the Disperse Red 343 ($OD_{584\ nm}$, CAS: 99031–78-6) and the Reactive Red 194 ($OD_{539\ nm}$, CAS: 23354–52-1), both at a concentration of 150 mg/L. The flocculating activity was determined by mixing 200 µL of the hydrolyzed supernatant and 20 mL of reactive dye solution, then, the pH was reduced to 3. After 30 min at repose, the solution was centrifuged and followed to color removal quantification by spectrophotometry. The effect of pH on the flocculation system and zeta potential was considered in the range between 3 and 8 for both dyes using the methodology described. Additionally, the sludge and bioflocculant were characterized by centesimal analysis. The influence of bioflocculant dosage in the presence and absence of a naphthalene-based dispersant (0.5 and 1.0 g/L for reactive and disperse dyes, respectively) was also accessed and further compared to the commercial flocculant PAC efficacy. The bioflocculant and PAC dosage varied between 137.75 and 688.75 mg/L (50 to 250 µL of crude bioflocculant) and 30 to 300 mg/L, respectively, in 20 mL of the dye solution.

3 RESULTS & DISCUSSION

Figure 1A presents the outcomes from bioflocculant extraction. It is possible to infer that the maximum concentration of flocculant agents in the supernatant fraction is attained with 3 g of dried activated sludge in 50 mL of NaOH solution (0.5 M) at 100°C. The subsequent kinetic test showed the best time at the predefined conditions. The effectiveness of the bioflocculant in precipitating the dye started at 38% when the solution initiated boiling, it reached its maximum in between 10-15 min and after decreased due to excess exposure to high temperatures. So, optimized conditions were set at 100°C for 10 min. The centesimal analysis of the activated sludge presented 11.68% of moisture and volatile. Considering only a solid fraction of components, carbohydrates, protein, and lipids correspond to 8.6, 35 and 15%, respectively. For supernatant used as bioflocculant, the moisture and volatile content correspond to 94.49 % of the bioflocculant total mass, and carbohydrates, protein, and lipids represent 12, 27, and 12% of the solid fraction, respectively.

The pH of the medium interferes drastically with the floc formation by dissociating the functional groups on active sites of flocculant agents. In this sense, color removal variation is depicted in Figure 2B, where high flocculation rates for both dyes in the study are achieved as the pH becomes acidic. It presents the effect of pH in color removal and zeta potential of reactive (black) and disperse (red) dyes flocculating systems, along with the zeta potential of bioflocculant solely in distilled water (blue). At pH 5 the color removal was 91% and 100% for reactive and disperse dye, respectively. At pH 7 and 8, the color removal is below zero due to the turbidity of the medium promoted by the addition of crude bioflocculant, where no apparent flocculant activity under these conditions.

It is well-known that high pH induces negative properties for the biomolecules, which suffer deprotonation, promote repulsion among molecules, hinder the formation of the bioflocculant-dye complex, and low color removal. The zeta potential for the blank sample presented a net electrical charge near zero from pH 3 to 6.4, decreasing rapidly to −19 mV above pH 6.9. These results correlate directly to the color removal, when zeta potential tends to zero molecules lose stability and flocculation is attained. Considering the solubility of the reactive dye molecule, it is possible to infer that its charge neutralization is not the driving force that promotes settling but the charge neutralization of bioflocculant molecules, which surfers modification due to pH reduction and precipitates in the medium. During precipitation, the bridging effect starts flocs formation, so both charging neutralization and the bridging effect play a significant role in the process.

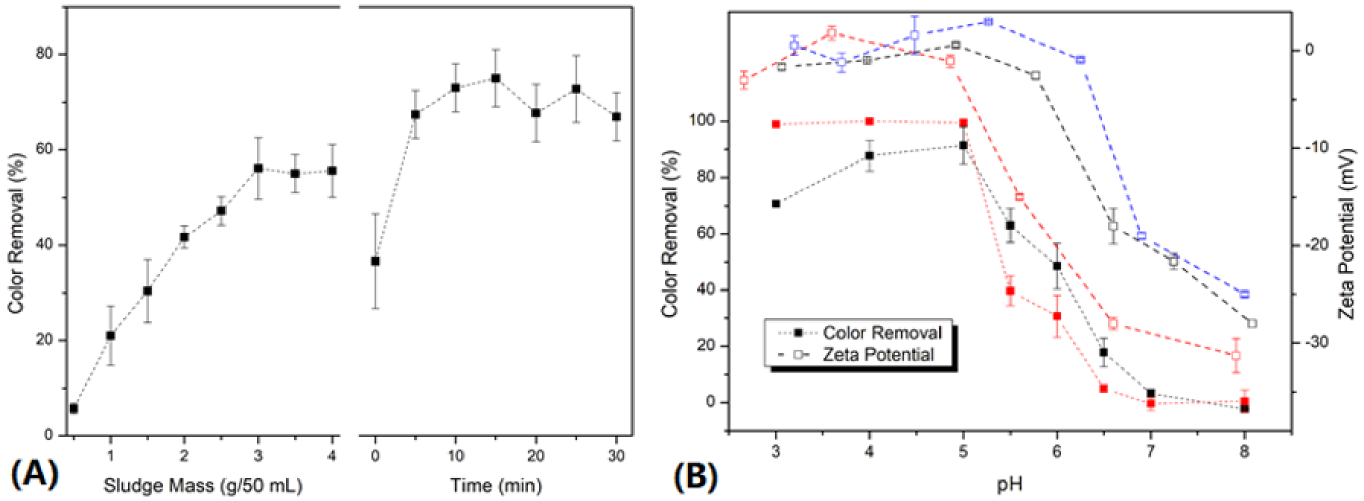

Figure 1: (A) Flocculating activity for extraction optimization: sludge load variation and hydrolysis kinetic. **(B)** Effect of pH in color removal and zeta potential of reactive (black) and disperse (red) dyes flocculating systems. Zeta potential of bioflocculant solely in distilled water (blue). Adapted from Artifon *et al.* (2023)[7].

Figure 2 presents an efficiency comparison of color removal between PAC and the bioflocculant and their ability to overcome the presence of the dispersant in the concentration of 0.5 g/L for reactive dye solution and 1.0 g/L for disperse dye solution. The color removal results from bioflocculant for reactive dye started at 30% at the initial dosage and increased to 84% with 551 mg/L (200 µL). When the dispersant was added to the medium the bioflocculant effect was delayed, starting at 413 mg/L (150 µL) with a final color removal of 76%. For the disperse dye a color removal above 80% was attained with 275 mg/L (100 µL) of bioflocculant addition and, when in the presence of dispersant, a comparable color removal result was achieved at 620 mg/L (225 µL).

Similar results showing the inhibitory effect of dispersant in the medium were obtained with PAC. The color removal for the reactive dye system was 11% at the starting point and increased accordingly with PAC addition to 97% at 210 mg/L. The delay in color removal with dispersant in the medium is visible and only surpassed at 240 mg/L of PAC dosage. For disperse dye, a PAC concentration of 30 mg/L presented 45% of dye precipitation, increasing abruptly to 96% at 60 mg/L, and decreasing continuously as the PAC content augmented. In this case, the presence of dispersant showed slight variation in color removal outcomes.

From the outcomes of both flocculant agents, it is possible to infer that the bioflocculant is comparable to PAC. For the reactive dye system, a color removal near 70% is achieved at 120 mg/L of PAC or 345 mg/L of bioflocculant, and for disperse dye medium 90% of the dye precipitates in the presence of 60 mg/L of PAC or 275 mg/L of bioflocculant. These results feature the excess-activated sludge as a source of potential flocculant agents for dye-containing wastewater.

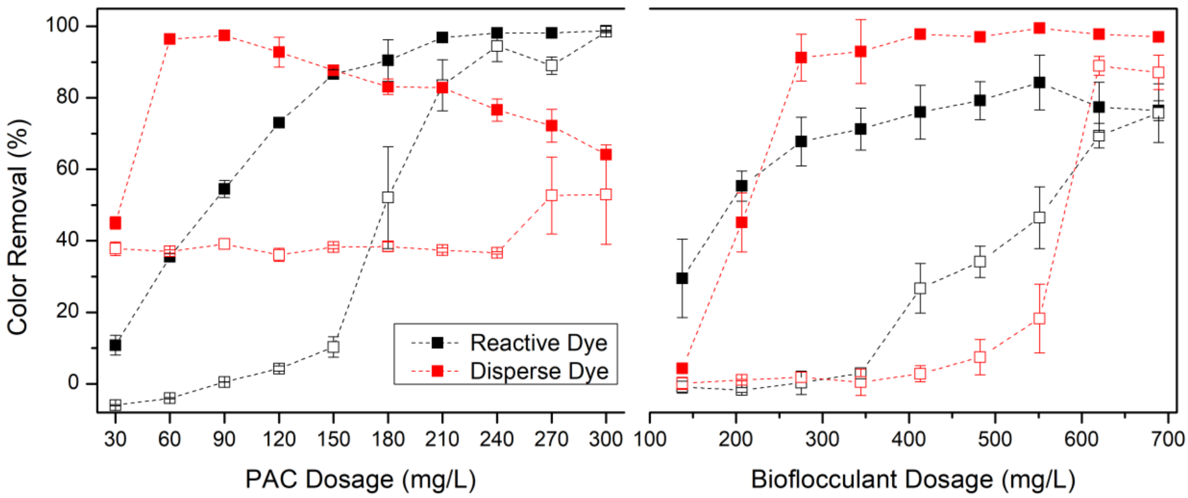

Figure 2: Color removal outcomes considering PAC and bioflocculant (dry mass) variation for reactive and disperse dyes. Tests in the absence (■) and presence (□) of dispersant. Adapted from Artifon *et al.* (2023)[7].

4 CONCLUSION

This work proposes utilizing excess-activated sludge from wastewater treatment plants as a valuable component in the textile industry for wastewater treatment, aiming at minimizing the need for commercial flocculants. The bioflocculant featured in this study demonstrates efficiency in precipitating recalcitrant azo dyes under slightly acidic conditions and shows potential for treating various contaminants, including metals, petrochemicals, and algae harvesting. Additionally, it can overcome the dispersant effect and is comparable to the precipitation efficacy of PAC in dye-containing wastewater systems. Although higher dosages of bioflocculants are required compared to PAC for achieving similar color removals, the advantages of circular economy and chemical reduction make bioflocculants a feasible eco-friendly option. Future studies focusing on industrial residues and low-cost biomass could lead to the development of new sources of desirable chemical compounds, which, after addressing limitations such as counter-effect treatment and extraction step optimization, could yield novel bioflocculants.

REFERENCES

[1] K. HENDAOUI, F. AYARI, I. BEN RAYANA, R. BEN AMAR, F. DARRAGI, M. TRABELSI-AYADI, Real indigo dyeing effluent decontamination using continuous electrocoagulation cell: study and optimization using response surface methodology, **Process Saf. Environ. Prot.** 116 (2018) 578–589.
[2] K. SARAYU, S. SANDHYA, Current technologies for biological treatment of textile wastewater–a review, **Appl. Biochem. Biotechnol**. 167 (2012) 645–661.
[3] C. RUD´EN, Acrylamide and cancer risk—expert risk assessments and the public debate, **Food Chem. Toxicol**. 42 (2004) 335–349.
[4] K. NOUHA, R.S. KUMAR, S. BALASUBRAMANIAN, R.D. TYAGI, Critical review of EPS production, synthesis and composition for sludge flocculation, **J. Environ. Sci.** (China) 66 (2018) 225–245.
[5] X. WANG, C. LI, Z. LI, G. YU, Y. WANG, Effect of pyrolysis temperature on characteristics, chemical speciation and risk evaluation of heavy metals in biochar derived from textile dyeing sludge, **Ecotoxicol. Environ. Saf.** 168 (2019) 45–52.
[6] W. ARTIFON, L. P. MAZUR, A. A. U. DE SOUZA, D. DE OLIVEIRA, Production of bioflocculants from spent brewer's yeast and its application in the treatment of effluents with textile dyes, **J. Water Process Eng.** 49 (2022).
[7] W. ARTIFON, A. P. S. IMMICH, A. SILVA, A. A. U. DE SOUZA, D. DE OLIVEIRA, A novel bioflocculant extracted from excess-activated sludge for dye-containing wastewater treatment, **J. Water Process Eng.** 56 (2023).

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