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Original Research Article

Influence of ionic strength and electrolyte type on Procion M dye fixation and surface properties of reactive-dyed cellophane

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ABSTRACT

The study explores how ionic strength and type of electrolyte affect the ability of Procion M reactive dye to fixate to the surface of reactive-dyed cellophane. In this research, cellophane was used as a model of regenerated cellulose; it was dyed in solutions containing different salts (NaCl, Na_2SO_4, KCl, and $CaCl_2$) at the same dye liquor ratio, pH, and temperature. The degree of dye exhaustion, uptake, and fixation were all determined using UV-VIS spectroscopy based on a very linear calibration curve; kinetic behavior was studied with pseudo-first order, pseudo-second order, and intraparticle diffusion models. Equilibrium dye adsorption was explained with Langmuir and Freundlich adsorption isotherm models; the extent of surface alteration was studied by means of Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements and surface metric techniques. The results show that fixation of dye increases with increasing ionic strength up to an optimal level of 0.20 M electrolyte and decreases slightly at even higher electrolyte concentrations, indicating that the positive effect of increased electrolyte concentration, in terms of improved charge screening, may be counteracted by negative effects such as dye aggregation and reduced effective diffusion. Furthermore, the results show that at constant ionic strength, the ion type has a significant effect on dyeing behavior; $CaCl_2$ exhibited the greatest fixation and the greatest equilibrium dye capacity compared to NaCl, KCl, and Na_2SO_4. Finally, the surface characterization experiments confirm that dyeing increases the roughness of the surface, reduces the contact angle, and changes the surface charge; correlation analysis also confirms that there is a strong association between the amount of dye fixed to the surface and both the surface roughness and the contact angle. Overall, the results of this study demonstrate that the type of electrolyte present during the dyeing process significantly affects the fixation of reactive dyes onto cellophane surfaces and the interfacial properties of the dyed material, and provide important insights into strategies for optimizing the efficiency of dyeing processes and the functional performance of dyed materials.

1. Introduction

The chemical conditions of the dye-bath environment play an important role in determining reactive dyeability of cellulose-based substrates (e.g., cellophane). Electrolyte additions have been shown to significantly impact the ability of the negatively charged reactive dye molecules to adsorb onto the cellophane surface by reducing electrostatic repulsion; however, their influence cannot be explained solely based on the electrolyte concentration due to factors such as the identity of the ions, the hydration behavior of the ions, the degree of ion aggregation, the effectiveness of each ion at screening the charges of the dye and substrate, and the degree of swelling that occurs as a result of the electrolyte being absorbed into the substrate. Therefore, a number of electrolytes were evaluated in order to determine the influence of monovalent vs. divalent salts, and the difference between those containing Cl^- and SO_4^{2-}. This investigation examined the influence of electrolyte type and concentration upon reactive dye fixation and surface modification of cellophane dyed with Procion M dye. The goal of this investigation was to understand the mechanisms of reactive dyeing under electrolyte assisted conditions through use of kinetic, thermodynamic, and surface analytical techniques. These included the measurement of reactive dye adsorption, kinetic and equilibrium modeling, infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements, and correlation analysis.

Carlough *et al*. [1] were among the first to focus on the diffusion of direct dyes in chitosan. Because their study focused on the diffusion coefficient, they helped demonstrate that dye uptake was based on both surface interactions and internal transport resistances in the adsorbent or film matrix. These perspectives are key in subsequent research on adsorption and membrane-based dye removal, where mass transfer limitations will usually be the primary determinant of the overall treatment rate. They also demonstrated the use of chitosan as a functional material for dye related applications, demonstrating that polymer chemistry, porosity and ionic interactions were key factors in determining how dyes move through a structural medium. Guzel *et al.* [2] built upon the previous study by creating a low-cost nanoporous carbonous adsorbent created from carob processing waste for the removal of anionic textile dye. Giannakoudakis *et al.* [3] studied the removal of reactive dyes using commercially available activated carbons under multiple parametric conditions therefore increasing the knowledge base of how multiple environmental variables functionally influence each other during adsorption. Bonic *et al.* [4] examined the use of powdered activated carbon to remove Reactive Black 5 from water-based environments. The study was specifically interested in the rate at which this occurred and the mechanisms behind the adsorption. The importance of this study lies in the fact that Reactive Black 5 is commonly used as an anionic dye in textiles, and the way it behaves during adsorption can provide insights into the treatment of other dyes present in industrial effluent. The focus on powdered activated carbon represents a particularly promising adsorbent form that has a large surface area and high uptake rates. Therefore, their analysis of the kinetics and mechanisms of the adsorption process likely determined if the process was primarily driven by external mass transfer; diffusion within the particles; or chemical reactions at the surface. This work laid a solid foundation for future studies conducted by the same research team, such as those examining the impact of concentration, pH, ionic strength and temperature on the adsorption of Reactive Black 5. Gascic *et al.* [5] expanded upon the previous works in this area through their examination of the adsorption of reactive dyes onto activated carbon and how the adsorption process is influenced by initial dye concentrations. The relevance of this study, however, is not just in terms of the influence of initial concentration on the adsorption process, but also in the fact that the initial concentration is typically the largest influencer of adsorption systems: the initial concentration influences the driving force for mass transfer, the rate of site occupation, and the apparent adsorption capacity. Husien *et al.* [6] provided a more comprehensive review of activated carbon-based adsorbents for textile dye remediation, emphasizing preparation methodologies and modeling approaches. The significance of this study, however, is not in the fact that it reviewed the results of individual experiments, but rather that it compiled existing knowledge to help provide a greater context of the research that has been completed in this area. By providing a broad overview of preparation methodologies, the authors likely demonstrated how the choice of precursor material(s), method(s) of activation and/or modification(s) to the surface influence the performance of the resulting activated carbon. The authors' attention to modeling is also beneficial as many studies of adsorption rely on isotherms, kinetic, and thermodynamic models to interpret their data and compare the relative effectiveness of the various adsorbent materials. Vojnovic *et al.* [7] demonstrated the effect of the initial pH upon adsorption of Reactive Black 5 onto powdered activated carbon, while also addressing the kinetics, mechanisms and thermodynamics of the system. This paper is very significant due to the fact that pH will significantly affect the adsorbent's surface charge as well as the ionization of reactive dyes. For an anionic dye such as Reactive Black 5, pH may control the degree of electrostatic attraction or repulsion between the dye molecules and the adsorbent surface. Additionally, this paper combines kinetic, mechanistic, and thermodynamic analyses; therefore, it provides a complete description of how solution chemistry controls adsorption performance. Finally, this study has contributed to the development of process optimization, since pH control is typically the easiest and most effective way to improve dye removal in many practical applications. Kasbaji *et al.* [8] have furthered the knowledge base of adsorption beyond traditional activated carbon systems by demonstrating the adsorption of both cationic and anionic dyes onto coffee grounds cellulose/sodium alginate double network hydrogel beads. Cetina *et al.* [9] expanded upon the previous Reactive Black 5 adsorption study by studying the effect of both ionic strength and temperature on the adsorption performance of activated carbon, focusing on kinetic, mechanism, and thermodynamic processes. This is a significant advancement as most textile wastewaters are saline and the treatment processes will vary depending on the temperature. Ionic strength can affect the solubility of the dye, reduce electrostatic interactions, and increase competition for adsorption sites whereas temperature can affect the rate of diffusion, the position of equilibrium, and the energy requirements for adsorption. By looking at all three factors, the study likely advanced toward the true nature of industrial conditions compared to many previous lab studies. Thermodynamic evaluation would assist in determining if the process is spontaneous, endothermic or exothermic and how temperature affects the feasibility of the adsorption process. Therefore, the study has a high value for converting bench-scale results to real-world wastewater treatment scenarios. Mandal *et al.* [10] returned to the theme of dye diffusion but instead examined the movement of reactive dyes through cationized cellophane films. As compared to previous diffusion studies in chitosan, this study represents a more specific and chemically modified membrane-like system. The cationization of cellophane indicates a purposeful modification of the film to improve its interaction with reactive dyes, likely through electrostatic attraction. This study is important because it illustrates that dye treatment research is not limited to adsorption onto solid matrices, but also to the transport of dyes through engineered polymer films that could be applicable to controlled separation, barrier materials, and studies of the mechanistic aspects of dye-substrate interactions. The study should provide a greater insight into the effects of the chemical modification of cellulose-based materials on the mobility and retention of dyes.

2. Materials and methods

2.1 Materials

The selection of cellophane as the model cellulose substrate was made due to the well-defined regenerated cellulose film structure and to allow for the use of reactive dyeing techniques. It would also be beneficial to describe the cellophane film in relation to the film's thickness, type of film (source/supplier) and grade (if applicable). Factors that are considered when selecting a film include swelling, diffusion and dye uptake characteristics. Typically, before dyeing the material will be thoroughly washed with DI/distilled water to eliminate surface impurities, additives or residual processing chemicals, followed by drying at ambient temperature or in a controlled oven to provide an identical initial condition. The coloring agent employed is a Procion M reactive dye. When possible it would be best to report the exact commercial name and Colour Index (C.I.) designation for the dye so that there can be accurate chemical identification and reproduction of results. Depending upon the experimental design of the comparison, selected electrolytes including NaCl, Na_2SO_4, KCl, $CaCl_2$, etc., may be used to determine the effects of salt chemistry on dyeability. As reactive dye fixation on cellulose generally occurs at alkaline pH values, suitable alkali or buffering agents, including Na_2CO_3 or NaOH, should be added to facilitate the reaction between the dye reactive groups and the hydroxyl groups of the cellophane film. Solutions should be prepared with DI/distilled water to preclude interferences from extraneous ions and thereby maintain constant ionic strength, dye solubility and fixation behavior.

Table 1: Materials and conditions used in reactive dyeing of cellophane.

Item	**Condition**
Substrate	Cellophane
Dye	Procion M reactive dye
Electrolytes	NaCl, Na_2SO_4, KCl, $CaCl_2$
Ionic strength	0.00–0.50 M
Water	DI/distilled
Alkali	Na_2CO_3 / NaOH
Liquor ratio	1:50
Temperature	298, 308, 318 K
pH	Constant
Dye concentration	Constant / variable for isotherms
Kinetic time	0–120 min
Analysis	UV–Vis, FTIR, SEM, AFM, contact angle

2.2 Experimental design

The structure of the experimental design for this study will need to be developed to provide a systematic way to examine how ionic strength, electrolyte type, and temperature affect the dyeing and fixing characteristics of Procion M dye on cellophane. The main independent variable is the ionic strength level (e.g., 0.00, 0.050, 0.100, 0.200, and 0.500 M), which could be determined by measuring the molarity of the salt(s) added to the solutions or by determining the ionic strength (I). In addition to evaluating the effect of varying ionic strengths, it would also be useful to compare various electrolytes to allow for the examination of both anion effects (for example chloride vs. sulfate) and cation valency effects (for example monovalent vs. divalent cations) using electrolytes such as NaCl, Na_2SO_4, KCl, and $CaCl_2$. If the goal of these experiments is to obtain thermodynamic data, then the experiments will need to be conducted at controlled temperatures (i.e., 298 K, 308 K, and 318 K) in order to determine if there are temperature-dependent effects and to allow for the determination of thermodynamic parameters. To ensure that any observed differences in dyeing or fixation levels are due solely to the chemical conditions of the solution, the pH or alkali concentration must remain constant throughout the experiments. Finally, the dye concentration may remain constant for kinetic and comparative fixation studies; however, it may vary across some appropriate range for the purposes of obtaining equilibrium isotherms. A matrix-based approach will provide a systematic and scientifically interpretable method to investigate the effects of solution chemistry and process conditions.

2.3 Dyeing and fixation procedure

The dye bath preparation and subsequent dyeing and fixation process needs to be carefully controlled to provide comparable results for each of the different experimental sets. Preparation of the dye bath begins by dissolving the appropriate quantity of Procion M dye into deionized or distilled water, which has been previously pre-determined as the dye bath concentration. An electrolyte of the desired ionic strength is then added to the dye bath. A pretreated cellophane sample is then placed in the dye bath at a constant liquor ratio (for example 1:50 material:liquor) for all experiments to take place under identical dyeing conditions. To evaluate the dyeing kinetic behavior, samples of the dye bath need to be removed at specific time intervals (for example 0–120 minutes or other time ranges depending on the experimental design). Samples can then be analyzed to determine the decrease in dye concentration in the dye bath as a function of time. Following the adsorption phase, an alkaline agent (such as sodium carbonate or sodium hydroxide) is added to the dye bath to begin the fixation phase of the dyeing process. The treatment is allowed to proceed for a specified period of time at a controlled temperature, whereupon covalent bonds will form between the reactive dye molecule and the available hydroxyl groups of cellophane. Upon completion of the fixation phase, the colored cellophane samples are subjected to a standard wash and soap procedure to remove unbound and hydrolyzed dye molecules from the cellophane surface, thereby providing a measure of the chemical binding of dye to the cellophane. The consistency of this dyeing/fixation procedure allows for the accurate determination of the dye exhaustion, uptake and fixation behavior under various electrolyte solutions.

2.4 Quantification (UV-Vis)

The measurement of dye exhaustion, uptake and fixation will have to be performed with the help of UV-Visible Spectrophotometry. This technique allows the measurement of the dye's residual concentration in the bath during each step of the dyeing process. First, a calibration curve needs to be drawn from the absorbance measurements of known concentrations of standard dye solutions and their respective absorbances at the dye's maximal absorption wavelength. Then the initial dye concentration (C0) and the concentration at any time t (C_t) can be measured using this calibration. With these two values the exhaustion rate can be calculated as: $\frac{C_0-C_t}{C_0} \times 100$. This value represents the fraction of dye that has been removed from the solution. The dye uptake at time t, denoted as qt, is calculated by $\frac{(C_0-C_t)V}{m} \times 100$, where V is the volume of the dye bath and mm is the weight of the cellophane sample. Thus, it describes how much dye was absorbed per unit weight of substrate. Fixation rates need to be described precisely because they are one of the most important variables when studying reactive dyeing systems; in this study, it could be expressed as follows:

$$\frac{\text{Amount of dye remaining on the cellophane after washing/soaping}}{\text{initial amount of dye absorbed before washing}} \times 100$$

This distinction allows the differentiation between truly fixed dyes and those adsorbed or loosely bound to the cellophane. As the interpretation of fixation rates depends strongly on the experimental conditions under which the retained dyes were measured, it is necessary to define this term explicitly in the paper to avoid ambiguities and ensure the reproducibility and scientific quality of the data.

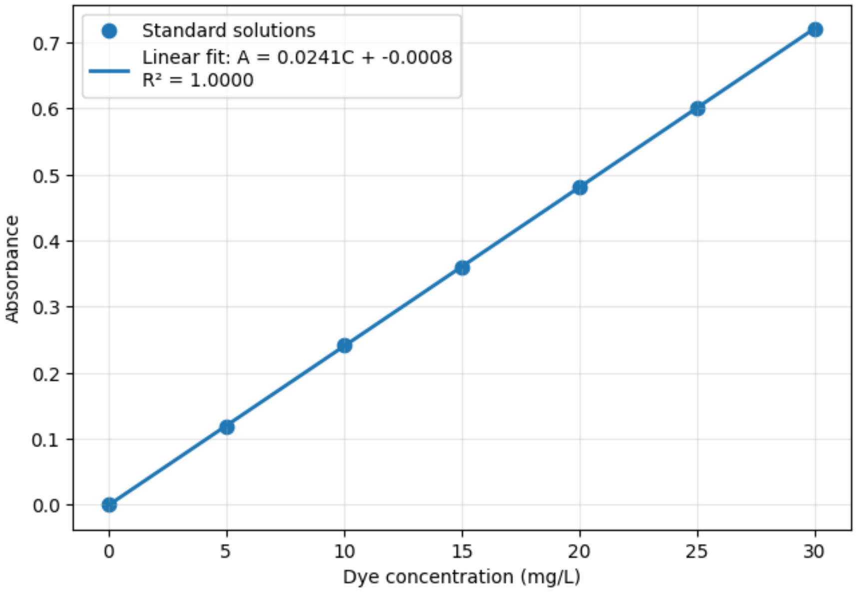

Figure 1: UV-Vis calibration curve for Procion M dye.

Figure 1 is a UV-Vis calibration curve for the Procion M dye, which as seen from the figure (the calibration curve is a straight line), absorbance directly correlates to the amount of dye being added to the solution. When using the standard solutions to create the calibration curve shown in the above graph it can be clearly demonstrated through the data collected that there is a direct linear relationship between the amount of dye being added and the absorbance measured in the UV-VIS. The relationship is defined by the equation A = 0.0241 C – 0.0008, with an R^2 value of 1.0000, therefore the calibration curve demonstrates a very high degree of linearity and a very high degree of correlation between the concentration of dye and absorbance. As such it has been demonstrated through the calibration process that Beer-Lambert Law is obeyed within the selected concentration range for the dye and therefore the calibration curve will provide a reliable basis for determining the dye exhaustion, dye uptake and dye fixation through subsequent experiments by providing a means of converting measured absorbance readings into corresponding Procion M dye concentrations.

3. Results and discussion

3.1 Effect of ionic strength on exhaustion, uptake, and fixation

The influence that ionic strength exerts on dye exhaustion, dye uptake, and dye fixation can be explained through fixing the fixation percentages in relation to the ionic strengths for all of the studied systems of electrolytes, as a plot of fixation percentage vs. ionic strength will clearly show how the environment (salt) affects the interactions between dye and substrate. Generally, as ionic strength increases, the electrostatic repulsive forces that exist between the negatively charged reactive dye molecules and the cellophane film are diminished, which results in greater proximity between the dye molecules and the substrate, thus resulting in increased dye exhaustion from the dye bath and dye uptake in the film. At most times, this improvement continues until an optimum ionic strength is reached; after which, the beneficial effects of dye fixation due to ionic strength may plateau, or even decrease. The optimum ionic strength will represent the ionic strength at which charge screening occurs and therefore maximizes dye transfer and dye fixation while minimizing adverse effects such as dye aggregation, dye mobility, and dye penetration into the cellophane matrix. Therefore, fixation does not continue to increase with increasing salt concentrations; instead, fixation typically reaches an optimal point, which varies according to the type of electrolyte used and the plotted data must be evaluated independently for each electrolyte to determine this optimum ionic strength. Plotting the curves for each of the different electrolytes is especially useful as the position and magnitude of the optimum ionic strength will depend upon the type of ions, the hydration behaviors and the valencies of the ions, thus providing insights into the mechanisms and the practical dyeing performances of the respective electrolyte-assisted reactive dye fixation systems.

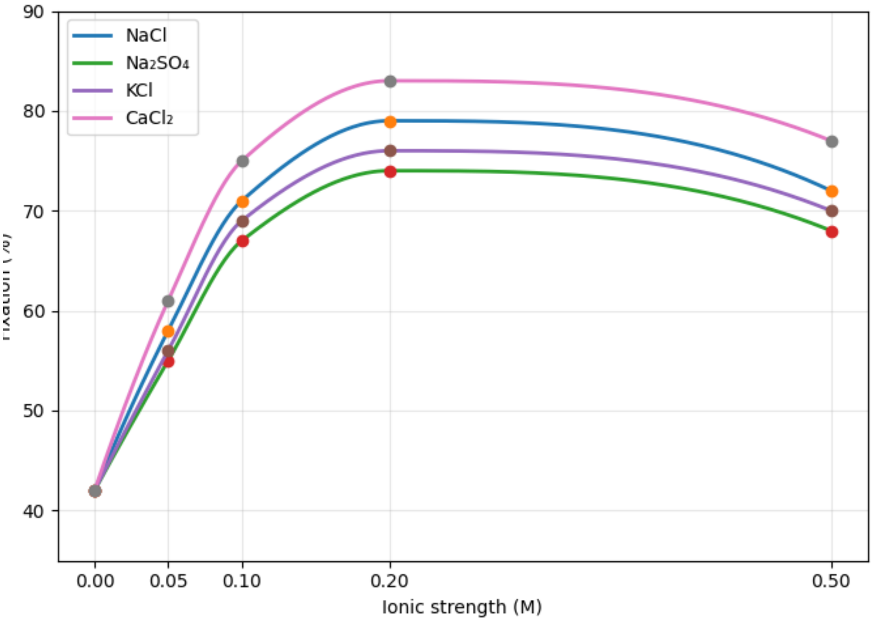

Figure 2: Fixation % vs. ionic strength for different electrolytes.

The optimum ionic strength appears to be approximately 0.20 M for all of the electrolytes since the fixation percentages reach their maximum values before they begin to drop off at an ionic strength of 0.50 M. At 0.20 M, there are some notable differences in the fixation percentages for each of the electrolytes; as shown on the plot, the highest fixation percentage is 79% for NaCl, 74% for Na_2SO_4, 76% for KCl, and 83% for $CaCl_2$. These results suggest that an ionic strength of 0.20 M provides the most favorable dyeing conditions than those provided by the other tested ionic strengths. The reason that there is an optimum ionic strength for fixing dyes onto fibers such as cellophane is that, up to a certain point, increased ionic strength will reduce the electrostatic repulsions between the negatively charged dye molecules and the positively charged fiber (cellulose). This can provide a larger amount of dye to be exhausted from the dye bath, which in turn increases the amount of dye that will be transferred to the substrate, and increases the amount of dye that will become fixed within the fiber matrix. However, if the ionic strength is too high, then the dye may form aggregates, reducing the rate of effective diffusion, and making it more difficult for the dye to penetrate into the fiber matrix. Therefore, while ionic strength has been found to be important in the fixation process, it should not be too high, otherwise the fixation will not improve, but possibly decrease slightly. As such, based upon the data presented, an ionic strength of 0.20 M appears to be the most beneficial ionic strength, since it provides the optimal balance of dye transfer and fixation.

3.2 Electrolyte-type comparison at equal ionic strength

The values shown in Figure 2 can be used to compare the salts based on their ionic strength (the same) so that we can determine whether there was an influence due to the salt or whether it was due to the ion itself. At 0.05 M, the fixation values were approximately 61% for $CaCl_2$, 58% for NaCl, 56% for KCl, and 55% for Na_2SO_4, which showed us that $CaCl_2$ had the greatest impact on dye fixation and Na_2SO_4 had the least amount of impact. At 0.10 M, the same order remained, but the fixation increased to approximately 75% for $CaCl_2$, 71% for NaCl, 69% for KCl, and 67% for Na_2SO_4. The maximum fixation for each of the salts occurred at 0.20 M. At this concentration, $CaCl_2$ produced the highest fixation, approximately 83%, followed by NaCl, approximately 79%, KCl, approximately 76%, and Na_2SO_4, approximately 74%. Although fixation decreased for each of the electrolytes at 0.50 M, the same order of fixation remained; $CaCl_2$ produced fixation of approximately 77%, NaCl produced fixation of approximately 72%, KCl produced fixation of approximately 70%, and Na2SO4 produced fixation of approximately 68%. This consistent order of fixation, $CaCl_2 > NaCl > KCl > Na_2SO_4$, shows that even when the ionic strength of the salts is the same, the salts do not act similarly. Therefore, some of the differences cannot be attributed solely to ionic strength; some are due to ion-specific influences such as stronger charge screening by divalent calcium ions, different amounts of hydration, and possibly differences in dye aggregation, and/or swelling/ accessibility of the cellophane structure. In total, Figure 2 shows that there is a measurable influence of ion identity, in addition to the general influence of ionic strength on the Procion M dye fixation.

The roles of hydration, aggregation, charge screening, and swelling are illustrated by the data provided in Figure 2. As ionic strength increases from 0 to 0.20 M, dye fixation increases for each salt, indicating that charge screening plays a significant role in increasing dye fixation. The fixation values at 0.20 M show that the cationic dyes were fixed at approximately 83% using $CaCl_2$, 79% using NaCl, 76% using KCl, and 74% using Na_2SO_4. The results indicate that all four electrolytes act to reduce electrostatic repulsions between the negatively charged Procion M dye molecules and the cellophane surface; however, they do not appear to be equally effective in reducing these repulsive forces. A possible explanation for the superior performance of $CaCl_2$ lies in its ability to provide stronger screening of charges than the monovalent cations (Na^+ and K^+) as a result of its divalent nature, thereby facilitating an increased proximity of the dye molecules to the substrate and subsequently leading to improvements in dye exhaustion, dye uptake, and dye fixation. While the previously mentioned charge-screening effect was responsible for the observed increase in fixation to 0.20 M for all salts, other factors such as hydration and aggregation effects also influenced the observed behavior of the salts. For instance, the hydration effects of the ions, as well as their interaction with water and modification of the local aqueous environment surrounding both the dye and the cellophane, can influence dye aggregation in solution. The slight decline in fixation from 83% to 77% for $CaCl_2$ and from 79% to 72% for NaCl at 0.50 M indicates that when the ionic strength becomes too high, excessive amounts of electrolyte may promote dye aggregation or limit dye mobility within the substrate, which would inhibit dye penetration. Another critical parameter that influences dye fixation is the degree of swelling of the substrate. Salt levels that are intermediate will allow for better diffusion of dye into the swollen cellophane structure, whereas excessive ionic concentrations will restrict access to internal hydroxyl groups within the substrate. Therefore, it is evident from the figure that the initial increase in fixation from 0 to 0.20 M is primarily caused by favorable charge screening and increased dye diffusion, while the subsequent decrease in fixation beyond 0.20 M is largely due to increased dye aggregation and unfavorable swelling conditions.

3.3 Kinetics results

The kinetic plots clearly demonstrate that the dyeing process occurs at a significantly greater rate due to surface reactions (adsorption) as opposed to solely due to intraparticle diffusion. The experimental qt vs. t data have a significant degree of agreement with the pseudo-first-order and pseudo-second-order models (the two models exhibit excellent fitting qualities), as opposed to the lower degree of fitting of the intraparticle diffusion model. If intraparticle diffusion were the sole controlling mechanism, then the Weber-Morris plot should be characterized by a strong linear relationship through the origin. Conversely, the lower degree of fitting along with the presence of a non-zero intercept indicates that intraparticle diffusion does contribute to the dye-uptake process, but is not the primary controlling mechanism. Thus, the dye-molecules rapidly interact with the available surface-sites on the cellophane, and the surface adsorption/reaction process dominates, whereas the diffusion process within the swollen structure of the substrate functions as a secondary process; therefore, the total fixation-behavior is primarily controlled by surface interactions and reactions, with diffusion functioning as a partial hindrance.

There is no doubt that the electrolyte affects the kinetic rate constants due to its effect on the ionic environment in which the dye molecules migrate from the solution to the cellophane surface. In general, as the concentration of electrolyte increases, the kinetic rate constants derived from the pseudo-first order and/or pseudo second order models also increase to an optimal point, indicating that the addition of salt increases the rate of dye uptake and fixation. An explanation for this phenomenon is that the added salt decreases the electrostatic repulsions between the negatively charged Procion M dye molecules and the negatively charged cellulose-based cellophane surface, thus allowing for faster and more efficient transport of dye molecules towards the substrate. Additionally, when using electrolytes that effectively screen charges (i.e., those containing divalent ions, e.g., $CaCl_2$), one would expect a higher value for the apparent rate constant as compared to monovalent salts (e.g., NaCl, KCl). Beyond the optimal ionic strength however, the kinetic rate constants may decline, since an excessive amount of salt can lead to dye molecule aggregation, reduction in dye molecule mobility, and hindered diffusion into the swollen cellophane matrix. Therefore, the observed variation in the fitted kinetic rate constants with respect to varying concentrations and types of electrolytes provides direct evidence that the kinetics of reactive dyeing are significantly affected by both ionic-strength effects and ion specific-effects.

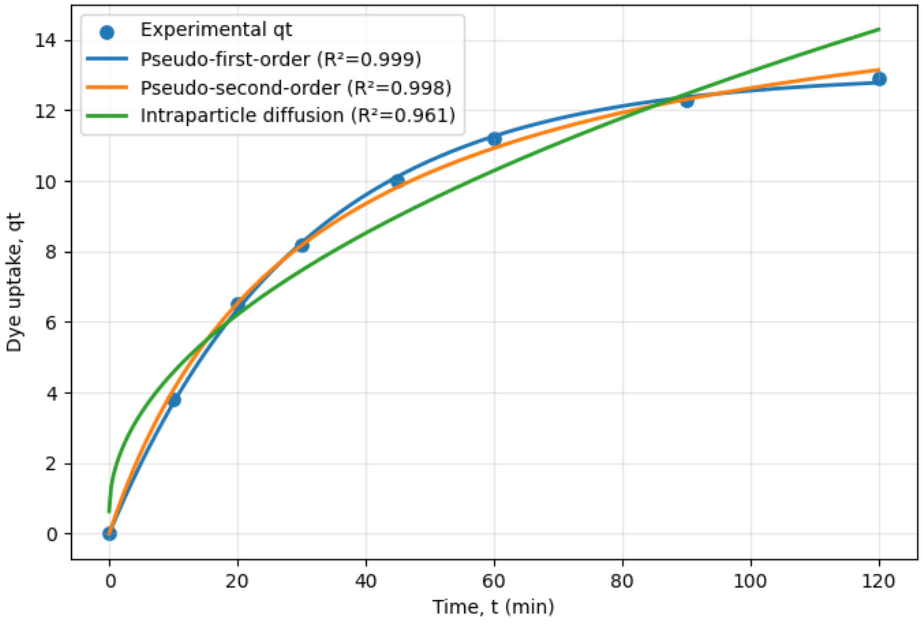

Figure 3: q_t vs. t plot with kinetic model fits.

The relationship between dye uptake (q_t) over time, along with the kinetic model curves that were best-fit to the experimental data are shown in Fig. 3. From the data presented, it appears that there was rapid dye absorption by cellophane in the beginning of the experiment and an increasingly slow approach towards equilibrium for the remaining time. There was a large amount of dye absorbed in the first 30-60 min; after this time, the amount of dye being absorbed continued to slowly increase until it approached a plateau at about 13 mg/g at 120 min. These results suggest that a large number of reactive sites on the surface of the material were quickly occupied and that the rate of dyeing decreased as the surface became saturated. Both the pseudo-first order and pseudo second order kinetic models provide a good representation of the dyeing kinetics with R^2 values of 0.999 and 0.998, respectively. However, the intraparticle diffusion model provides a less than ideal representation of the dyeing kinetics, with $R^2 = 0.961$ and with the greatest deviation from the experimental data occurring at both the beginning and end of the experiments. Thus, the results indicate that while diffusion within the particle may be contributing to the overall uptake of dye, it does not appear to be the primary controlling factor for the uptake of dye. Therefore, based upon the information provided in Fig. 3, the primary mechanisms controlling the dyeing process appear to be related to either the adsorption of dye onto the surface of the material, or to some type of reaction occurring on the surface, while the diffusion of dye into the interior of the material appears to play a secondary role.

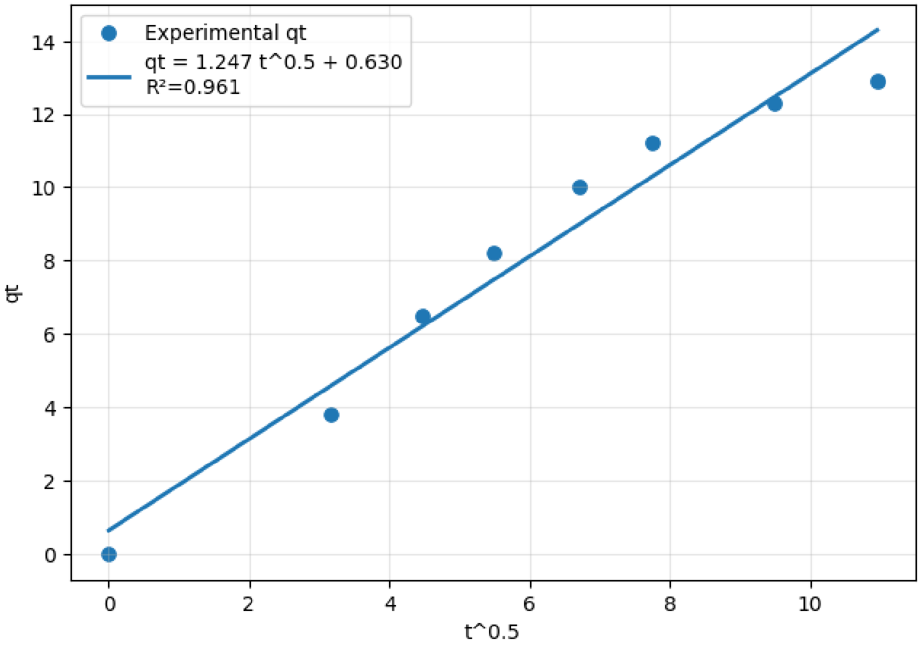

Figure 4: Intra-particle diffusion (Weber-Morris) plot.

The dye uptake on cellophane is shown in the intraparticle diffusion, or Weber–Morris, plot (Figure 4) by plotting qt versus $t^{0.5}$ to determine if internal diffusion controls the dyeing process. The fitted line in the plot $q_t = 1.247t^{0.5} + 0.630$ with an R^2 value of 0.961 represents the data reasonably well; however, it does not represent the process perfectly. A characteristic of the plot is that the fitted line does not go through the origin due to the positive intercept of 0.630, indicating that the process is influenced by more than just intraparticle diffusion and that boundary layer effects and surface adsorption are contributing factors to the overall uptake mechanism. The scatter of the experimental points about the fitted line also indicates that dyeing is influenced by more than one kinetic process. Thus, the results suggest that intraparticle diffusion is an important factor in transporting dye into the cellophane matrix; however, the dyeing behavior of the cellophane is controlled by a combination of surface interactions and internal diffusion rather than by intraparticle diffusion alone.

3.4 Equilibrium/isotherm behaviour

Table 2: Equilibrium data.

C_e (mg/L)	Control q_e (mg/g)	Na_2SO_4 q_e (mg/g)	KCl q_e (mg/g)	NaCl q_e (mg/g)	$CaCl_2$ q_e (mg/g)
5	5.71	8.46	9.54	10.95	13.18
10	7.96	11.18	12.33	13.76	16.1
15	9.14	12.51	13.65	15.04	17.48
20	9.87	13.3	14.42	15.77	18.28
30	10.78	14.24	15.31	16.6	19.2
40	11.31	14.76	15.8	17.06	19.69

Table 3: Isotherm parameter.

Electrolyte	Langmuir q_M (mg/g)	Langmuir K_L (L/mg)	Langmuir R^2	Freundlich K_F	Freundlich n	Freundlich R^2	Interpretation
NaCl	18.59	0.286	1	8.16	4.71	0.943	Moderate capacity and affinity
Na_2SO_4	16.41	0.214	1	5.89	3.83	0.95	Lower capacity/affinity
KCl	17.31	0.245	1	6.88	4.23	0.946	Intermediate behavior
$CaCl_2$	20.81	0.347	1	10.3	5.49	0.939	Highest capacity and affinity
Control (no salt)	13.22	0.151	1	3.59	3.05	0.958	Lowest uptake behavior

Isotherm parameters calculated show that electrolyte type has a strong influence on both equilibrium adsorption capacity and affinity of Procion M dye on cellophane. The Langmuir monolayer adsorption capacity (q_m) is highest for cacl2, at q_m = 20.81 mg/g and also the largest value of the affinity constant (k_1) at k_1= 0.347 l/mg indicating the most favorable conditions for dye uptake. NaCl shows relatively high adsorption capacity and affinity with q_m = 18.59 mg/g and k_1= 0.286 L/mg, followed by KCl and Na_2SO_4 while the control sample without any added salt exhibited the lowest values. Freundlich constants were in the same order as Langmuir monolayer adsorption capacity and affinity constants; K_F and n being highest for $CaCl_2$ and lowest for the control sample indicates that addition of salt improves both the amount of dye retained and the favorability of the adsorption process. Overall, the performance was as follows: $CaCl_2$ > NaCl > KCl > Na_2SO_4 > control and indicate that divalent calcium ions provide the greatest enhancement of dye–substrate interaction and sulfate provides the least amount of equilibrium uptake behavior.

Table 4: Kinetic model parameters for Procion M dye uptake on cellophane.

Model	Parameter	Value	Unit	Interpretation
Pseudo-first-order	q_e	13.016	mg/g	Calculated equilibrium dye uptake
Pseudo-first-order	k_1	0.0334	min^{-1}	First-order rate constant
Pseudo-first-order	R^2	0.9995	—	Excellent fit to experimental data
Pseudo-second-order	q_e	16.482	mg/g	Calculated equilibrium dye uptake
Pseudo-second-order	k_2	0.001989	$\text{g mg}^{-1}\ \text{min}^{-1}$	Second-order rate constant
Pseudo-second-order	R^2	0.9983	—	Very good fit to experimental data
Intraparticle diffusion	k_{id}	1.247	$\text{mg g}^{-1}\ \text{min}^{-\frac{1}{2}}$	Intraparticle diffusion rate constant
Intraparticle diffusion	C	0.63	mg/g	Boundary layer thickness/intercept
Intraparticle diffusion	R^2	0.9614	—	Lower fit; diffusion not sole controlling step

The kinetic data showed that the pseudo first order and pseudo second order models accurately described the dye uptake, with R^2 = 0.9995 for the pseudo first order model and R^2 = 0.9983 for the pseudo second order model. While the intraparticle diffusion model provided an R^2 = 0.9614, indicating some role of intraparticle diffusion in the dye uptake process, it was significantly less than those obtained for the pseudo first order and pseudo second order models. This indicated that intraparticle diffusion may be contributing to the dye uptake process but is not the primary rate controlling mechanism. The nonzero intercept C also supported this conclusion, since it suggested that there are contributions from boundary layer effects (i.e., surface interaction and external mass transport) to the total dye uptake rate. In summary, the results of the kinetic analysis suggest that dye uptake onto cellophane is primarily controlled by either surface adsorption or chemical reaction related mechanisms and that diffusion acts as a secondary mechanism.

3.6 *Surface characterization results*

Figure 5 shows the FTIR spectra of cellophane before and after reactive dyeing and indicates that the basic cellulose structure is retained after treatment, although some spectral changes occur due to dye interaction. In both spectra, the broad absorption band in the 3300–3400 cm^{-1} region corresponds to O–H stretching, while the band near 2900 cm^{-1} is assigned to C–H stretching of the cellulose backbone. After dyeing, slight differences are visible in the intensities and positions of several bands, especially around 1605, 1510, and 1224 cm^{-1}, which may be associated with dye-related functional groups or interaction between the reactive dye and the cellophane surface. The characteristic cellulose bands in the lower wavenumber region, including those assigned to C–O–C, C–O, and β-linkage vibrations, remain present in both spectra, confirming that the main polymer framework is preserved. The dashed spectrum for the dyed sample also shows somewhat stronger or shifted features compared with the untreated sample, suggesting changes in the hydrogen-bonding environment and possible surface-level dye attachment. However, these FTIR results should be interpreted cautiously, because overlap between cellulose bands and dye bands makes it difficult to confirm covalent bonding from FTIR alone. Therefore, the figure mainly provides supportive evidence of dye–substrate interaction rather than definitive proof of chemical fixation.

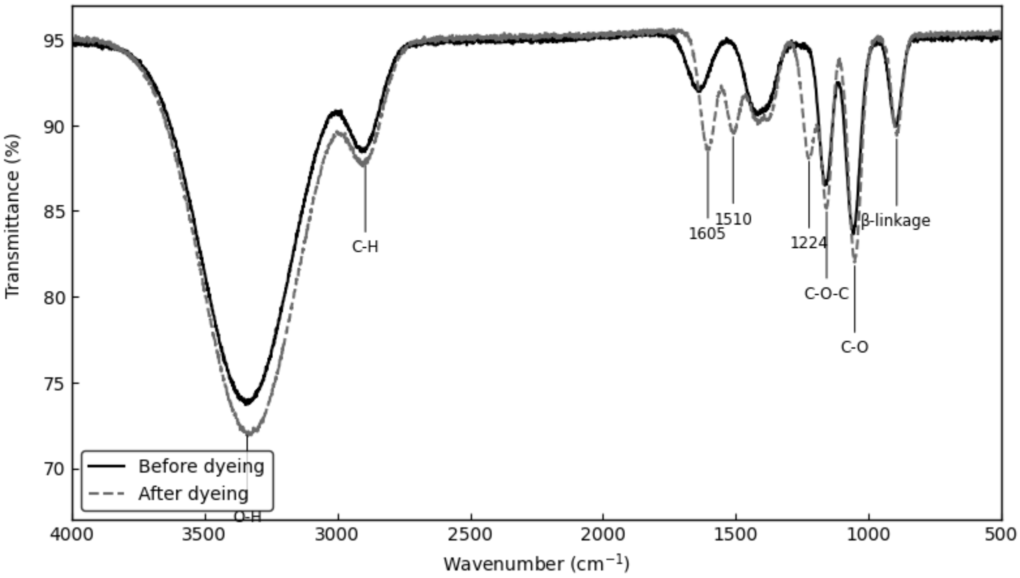

Figure 5: FTIR spectra of cellophane before and after reactive dyeing.

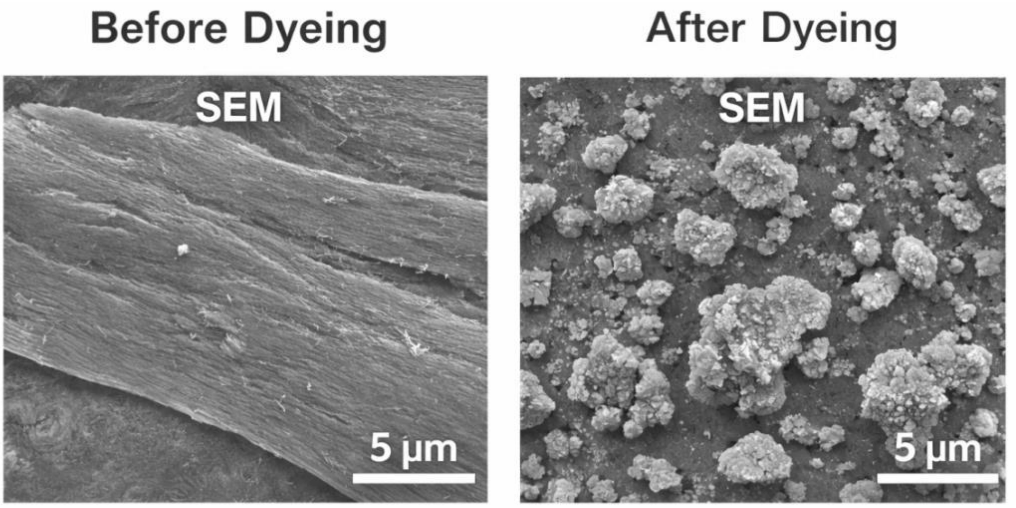

Figure 6: SEM images of cellophane before and after reactive dyeing.

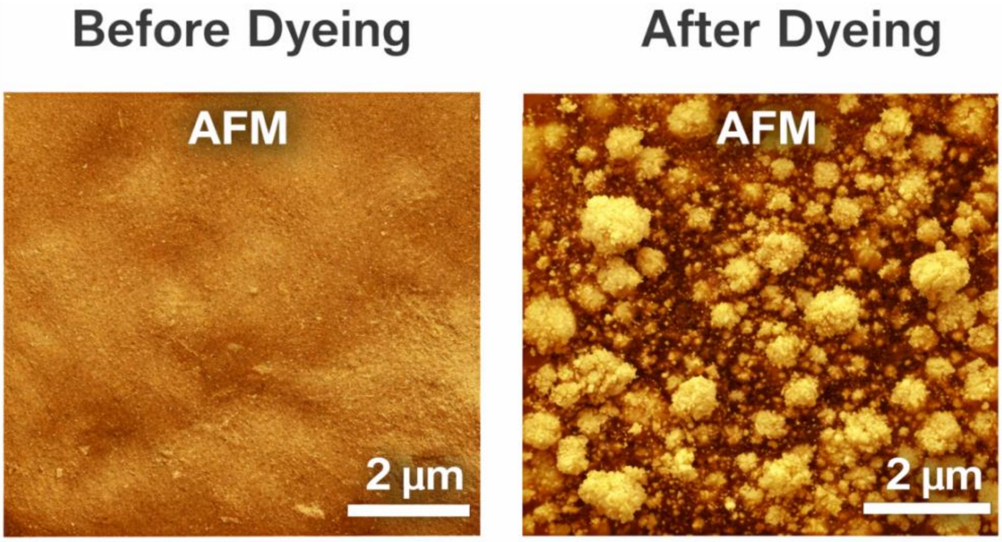

Figure 7: AFM images of cellophane before and after reactive dyeing.

Figure 6 displays SEM photographs of cellophane before and after dyeing using reactive dyes. In these photographs, there is an evident difference in the morphology of the cellophane surface as a result of dyeing. On the untreated cellophane surface, it can be seen that the surface is generally smooth and has a layered structure; however, there are some small-scale irregularities present on this surface and no evidence of particulate deposits. By contrast, the treated cellophane surface is much more uneven and is covered by many granules or clusters of particles dispersed across the surface. The particle-like structures that have been deposited onto the cellophane surface appear to indicate the presence of dye aggregates, or dye associated-surface build-up, suggesting that the dyeing process has resulted in significant alteration to the surface texture of the cellophane. The increase in surface roughness demonstrated in the SEM photograph for the dyed cellophane is consistent with the data obtained from the AFM and contact-angle experiments (as detailed above), providing strong evidence that reactive dyeing produces alterations to both the topographical structure and interfacial properties of the cellophane. Overall, the photographs in Figure 6 provide strong visual evidence that dyeing of cellophane alters its morphology and support the claim that surface modification occurs simultaneously with dye fixation.

Figure 7 shows AFM images of the cellophane samples before and after reactive dyeing to show a significant increase in the surface roughness after dyeing. In comparison to the untreated cellophane surface that has a relatively smooth aspect with mild undulations and a fairly uniform texture (i.e., relatively even topography), the surface of the treated cellophane has become substantially more uneven and dense with numerous small grainy protrusions; these suggest the presence of dye deposit(s) and/or dye associated aggregates on the surface. These morphological changes clearly demonstrate that reactive dyeing causes a considerable alteration to the nanoscale topography of the cellophane. The increased roughness of the dye treated sample are consistent with the SEM results and provide evidence for an increase in roughness parameters such as R_a and R_q. Therefore, in conjunction with the SEM findings, the AFM data shown in this figure represent strong evidence that dye fixation is associated with a major modification to the surface profile and that the dyeing process can have effects on both the coloration and the physical nature of the materials.

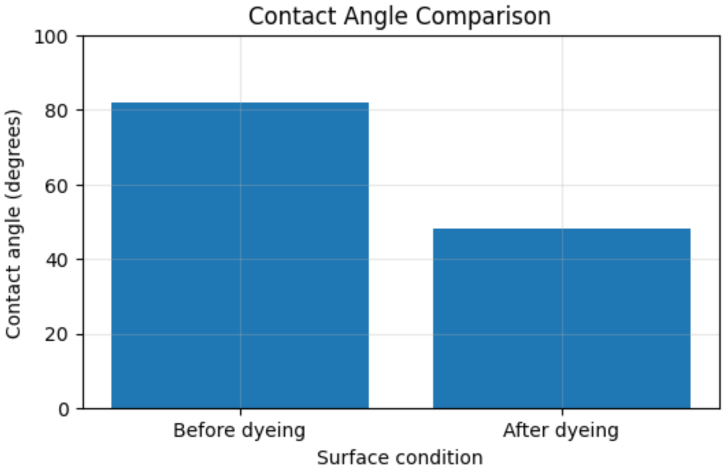

Figure 8: Contact angle bar chart.

Figure 8 clearly shows that the contact angle of cellophane decreases after reactive dyeing. This means that the cellophane surface is much more wettable than it was before dyeing. The contact angle of cellophane (about 82°) before dyeing shows a relatively low hydrophilicity and therefore low ability to support the spreading of a water droplet. However, after dyeing the contact angle drops to approximately 48°; this demonstrates that the surface of the cellophane now supports a much larger amount of water spreading and thus has much better wetting characteristics. The change in the contact angle on the cellophane surface also shows that there have been changes in both the surface chemistry and surface topography of the cellophane due to dyeing. These are likely a result of the incorporation of functional groups related to the dyes and an increase in surface roughness of the cellophane. The findings from the SEM and AFM images are consistent with these findings as they provide evidence of a much more irregular or rougher surface after dyeing. Overall, Figure 8 provides strong evidence that reactive dyeing greatly increases the hydrophilic nature of the cellophane surface.

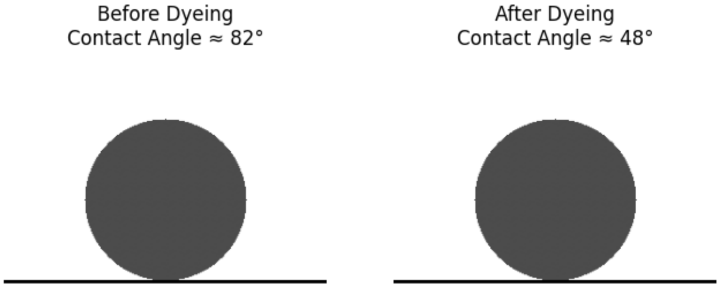

Figure 9: Representative contact angle image before and after dyeing.

Figure 9 provides some examples of the contact angles of cellophane before and after it has been treated with reactive dyes; this illustrates how the wettability of the surface changes. The contact angle of the untreated cellophane was approximately 82 degrees, illustrating that the water droplet maintains its shape (i.e., the droplet remains rounded) and does not spread much on the surface (indicating that it is not very wettable). Following dye treatment, the contact angle was decreased to about 48 degrees and illustrates that the water droplet will spread more and the surface will be more wettable. The decrease in contact angle after dye treatment illustrates an increase in surface hydrophilicity from both chemical alteration of the surface and from an increase in the roughness of the surface. As the values for the contact angles illustrate a large difference in wettability; the shapes of the droplets illustrated by the drawings are visually very similar, therefore the illustrations in the figure are to represent the differences in wettability and are meant to be illustrative, but not to depict the exact geometric differences between the two contact angles. Overall, the figure supports the idea that reactive dyeing increases the hydrophilic characteristics of the cellophane surface.

Table 5: Surface metrics of cellophane before and after reactive dyeing.

Sample	**R_a (nm)**	**R_q (nm)**	**Contact angle (°)**	**Zeta potential (mV)**	**Interpretation**
Before dyeing	32.4	40.8	82	-18.6	Smooth surface, lower wettability, moderately negative charge
After dyeing	68.7	79.5	48	-27.4	Rougher surface, higher wettability, more negative surface charge
Change	36.3	38.7	-34	-8.8	Dyeing increases roughness and hydrophilicity

Surface characteristics were modified as evidenced by the cellophane being altered through reactive dyeing. Changes in R_a and R_q indicated a significant increase in the surface roughness post-dye fixation; this can be attributed to either the adsorption or attachment of dye onto the substrate. The surface became more wettable (contact angle decreased from 82° to 48°) and therefore more hydrophilic following dyeing. Zeta potential values became significantly more negative (-18.6 mV to -27.4 mV), indicating an alteration of the charge environment at the surface resulting from dye adsorption or fixation. Therefore, these findings confirm that reactive dyeing alters the physical and interfacial properties of the cellophane film as well as its coloration.

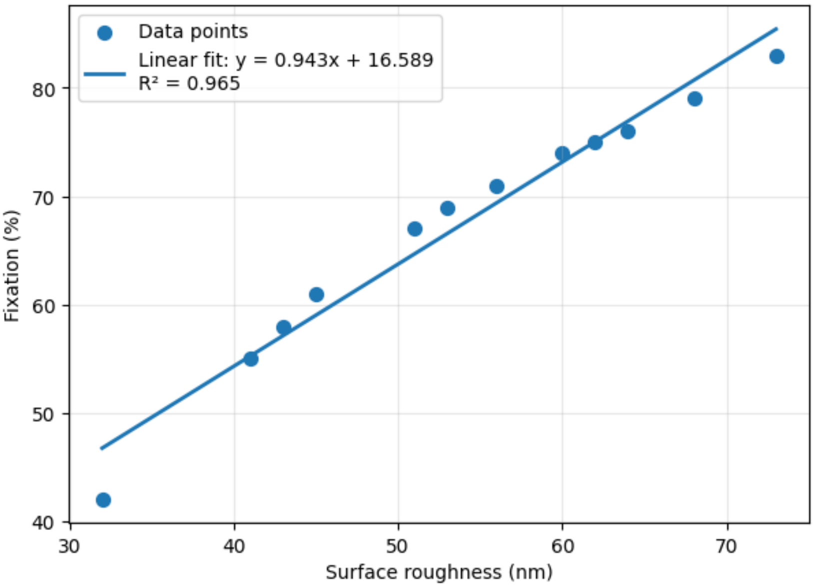

Figure 10: Correlation between fixation and surface roughness.

Figure 10 provides a clear indication of a significant positive correlation between the surface roughness of cellophane and its fixation of reactive dye (i.e., as roughness of the cellophane surface increases, so does the amount of dye retained). The linear trend of the increasing data points shown in Figure 10 indicate a strong positive linear relationship between the surface roughness and the percentage of dye fixed on the cellophane. This is further supported by the fitted equation to the data, $y = 0.943x + 16.589$, which has an R^2 value of 0.965. The significance of the positive linear relationship can be summarized as follows; as the surface roughness of the cellophane increases, so too will the fixation percentage of dye to the cellophane surface. A possible explanation for this relationship is that the cellophane surfaces with greater roughness provide more effective contact areas and/or greater accessibility of dye molecules to potential binding sites, resulting in enhanced fixation. The high R^2 value for the linear regression indicates that the surface roughness of cellophane is very strongly related to the fixation behavior exhibited in this study. Therefore, overall, it is reasonable to conclude from the data presented in Figure 10 that surface topography is a critical factor influencing the reactive dye fixation and that an increase in the degree of surface roughness enhances dye retention on cellophane.

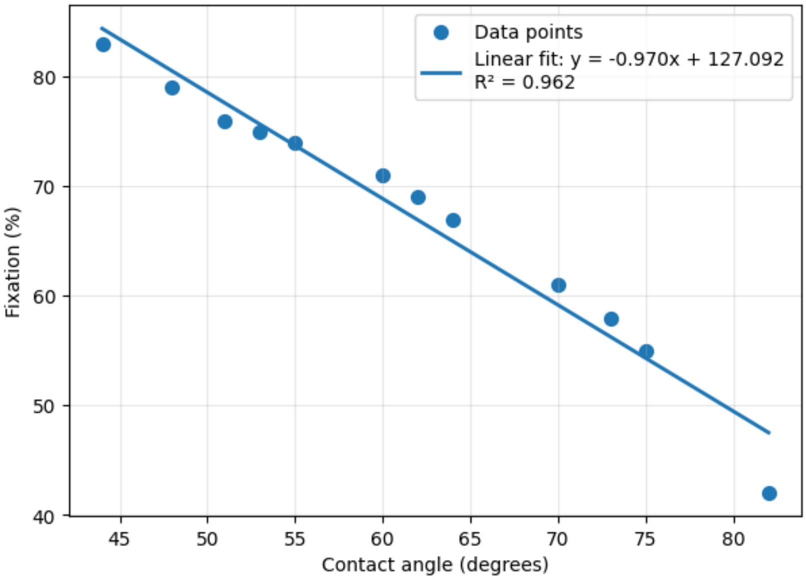

Figure 11: Correlation between fixation and contact angle.

The large negative correlation seen in Figure 11, between fixation percentage and contact angle, clearly shows that a greater amount of dye fixates onto the film when it has a smaller contact angle; that is, as contact angle decreases, fixation percentage increases. A very strong inverse linear relationship is indicated by the $R^2 = .962$ and the fitted linear equation, $y = -0.970x + 127.092$. Thus, as the contact angle decreases (i.e., as the surface becomes more wettable), the fixation percent increases. Therefore, there is evidence to suggest that a more hydrophilic surface will have better dye retention due to better dye-film surface interactions at low contact angles. The close distribution of the data about the regression line provides support for the idea that contact angle is directly responsible for fixation behavior in this case. Overall, the plot in Figure 11 indicates that the positive effect of improved wettability, leads to a larger quantity of reactive dye being fixed onto the cellophane.

4. Conclusions

In summary, the research shows that the type of electrolyte and the level of ionic strength of the dye bath have an effect on the ability of cellophane to reactively dye with Procion M dyes. The degree of fixation that occurred increased as the ionic strength increased, with the greatest amount of fixation occurring at 0.20 M ionic strength regardless of the type of electrolyte used. However, once the ionic strength exceeded this concentration, the degree of fixation decreased slightly. Therefore, it appears that there is an optimal balance of the beneficial aspects of ionic strength (charge screening) and detrimental effects (aggregation, etc.) on dyeing performance. It was also found that calcium chloride yielded the largest amounts of fixation, uptake capacity, and dye affinity compared to sodium chloride, potassium chloride, and sodium sulfate when tested at equal ionic strengths. This provides evidence that, in addition to ionic strength, there are ion specific effects that can be important in controlling the dyeing process. The results from the kinetic modeling portion of the study indicated that the rate limiting factor for the dyeing process was primarily due to either surface interactions or chemical reactions; however, intraparticle diffusion did occur and contributed to the total dye uptake. The results from the surface analysis studies provided additional evidence that reactive dyeing causes changes to the film's interfacial characteristics. These changes include an increase in roughness, decrease in contact angle, and increase in negative charge density. Overall, the results indicate that with careful control of electrolyte composition, it may be possible to enhance fixation efficiencies, modify surface properties, and gain a better understanding of how to optimize the reactive dyeing of cellulose-based films.

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Authors' contributions

The author read and approved the final manuscript.

Conflicts of interest

The author declares no conflict of interest.

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Data availability

No new data were created.

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