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Optimization of dye transfer inhibition properties of polyvinyl pyrolidine for reactive dye on cotton fabric

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This study focuses on the optimization of the amount of dye transfer inhibition (DTI) agent in the in-wash liquor using response surface methodology. Polyvinyl pyrrolidone, one of the DTI polymers, has been used to analyse its dye transfer inhibition properties on reactive dyed cotton fabric against the commercial detergent. The Box and Benkhen experimental design has been adapted to study the optimum concentration of DTI and washing condition for the better dye transfer inhibition. The CIELAB color difference (ΔE) and color strength (*K/S*) values are studied for the cotton fabric used in the in-wash liquor. The result shows that the higher the DTI polymer concentration the better is the dye transfer inhibition property. The performance of the DTI agent is majorly influenced by the surfactant present in the detergent powder due to its ionic nature. The influence of washing *p*H on the efficacy of the DTI is observed as minimal. The developed model shows higher values of R^2 for the selected parameters, around 0.82 for color difference and 0.91 for color strength. The optimum values of process parameters for the improved performance of DTI polymer with minimum quantity are found to be DTI polymer concentration 0.24 g/L, detergent concentration 2.9 g/L, alkaline *p*H level in one liter of water, and 3% (owm) of reactive dye. The washing efficiency analysis shows that the stain removal percentage of detergent remains the same in presence of DTI polymer. The water hardness property has a major influence on the DTI performance. The environmental impact of the DTI polymer is found negligible, except the chemical oxygen demand.

Keywords: Color difference, Cotton fabric, Dye transfer inhibitor, In-wash dye transfer, Polyvinyl pyrrolidone, Reactive dye, Washing efficiency

1 Introduction

Fading of dyes is more prevalent from new, unlaundered or infrequently washed goods. The clothing with considerable fastness to washing still may continue to bleed small amount of dye or colorant in to the wash bath based on washing conditions[1]. When fabrics of different shades and wash fastness properties are laundered together, there exists persistent problem of dye release into the laundering solution by colored fabric, which may get transferred onto other fabrics. This is called as dye carry-over phenomenon or commonly referred to as 'dye transfer'[2]. This causes the dyed article to change color, and the other articles in the washing bath may be stained due to the transfer (or migration) of dyes to the other articles during the process[3,4]. Dye transfer during the wash cycle is caused by the higher water temperature, longer cycle time and much higher surfactant concentration in the wash cycle as compared to the less stringent conditions of the rinse cycle[5].

Some of the textile dyes are readily transferred from the aqueous solution onto the fibre surface by absorption on the internal structure of the fibre. Absorption is a reversible process. The dye can therefore return to the aqueous medium from the dyed material during washing, a process called desorption[6]. The improperly applied dyes may also release into the wash solution. Cotton fabrics have a strong propensity to pick up solubilized or suspended dyes from solution. To avoid this kind of re-deposition of dye particle in the laundry operation, the dye transfer inhibitors (DTI) are used in washing. It is believed that the DTI polymer may act to inhibit the deposition of dye by several different mechanism[7].

The DTI may be water-soluble polymers containing nitrogen and oxygen atoms with molecular weight from about 1000 to 30000. These polymers have an amphiphilic character with polar groups conferring hydrophilic properties and apolar groups conferring hydrophobic properties. Polyvinylpyrrolidone is one of the most commonly known polymer for dye transfer inhibition[8]. The previous studies mentioned the use of

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polyvinylpyrrolidone as DTI along with the detergents component[9]. Other polymers like polyamine N-oxide[10], poly(4-vinylpyridine-n-oxide) (PVPNO)[11-14], vinyl pyridine copolymers[15], poly vinyl alcohol(PVA)[16], polyvinyl imidazole (PVI)[17], cationic starches[18], and a few minerals like magnesium aluminate and hydrotalcite[19] along with the cationic surfactants[20] are also used as DTI. In this study, the effects of laundering variables like washing detergent concentration, and wash liquor *p*H on the performance of PVP are evaluated. It is also important that, too much of dye transfer inhibitor present in the wash liquor can significantly negate benefits derived from the laundry brighteners. In the extreme, there is also evidence to suggest that the use of excess dye transfer inhibitor in the wash liquor can actually cause a reaction with non-extraneous dyes on the items being laundered, results in fading or non-uniform appearance of the laundered items[7,21]. Hence, this study aims at determining the minimum required amount of DTI polymer per liter of wash liquor along with detergent concentration.

2 Materials and Methods

2.1 Materials

The DTI polymer, polyvinylpyrrolidone (PVP), was procured from Sigma Aldrich, USA (molecular weight 3,60,000; 99.999% purity). Reactive Red 198A (C27H18ClN7Na4O15S5; Molecular weight–968.21), was procured from Mahalakshmi Chemicals, Coimbatore. The commercial detergents/ soap powders used were obtained from retail outlets in Coimbatore and used as such. 100% cotton single jersey knitted fabric with 54 CPI and 40 WPI was used after chemical bleaching for this study.

2.2 Methods

2.2.1 Washing Method to Evaluate Dye Re-deposition

For the evaluation of dye re-deposition from wash liquor, the wash bath with excess dyes was simulated using hydrolysed reactive dye. About 0.03 g (owm) of dye (3% dye conc.) was added to one liter of tap water and the solution was stirred well to ensure the dye particles dissolve homogeneously in the water. After hydrolysis, the commercial washing powder/detergent powder of 5 g (one scoop) was added into the solution. The solution was again stirred well for dissolution of the detergent particles. Along with detergent, the DTI polymer was also added in the solution and allowed to dissolve. After this process, 4 pieces of white cotton fabrics (10cm^2) were immersed into the solution. The wash liquor bath was allowed to agitate as like a domestic washing machine for 30 min. The samples were removed from the wash liquor, and washed under running water and then left to air dry. The dried samples were used for color strength (*K*/*S*) and color difference (ΔE) value analysis.

2.2.2 Color Strength and Color Difference Evaluation

The CIELAB color values (L*, a*, b* and ΔE) of the dyed fabric was determined by measuring their surface reflectance using a computer-aided Spectra Scan 5100 A spectrophotometer (Premier colorscan India Pvt Ltd) followed by calculating the *K/S* values using Kubelka Munk[22] equation with the help of relevant software. The measurement range was 360 - 750 nm at an interval of 10 nm as per AATCC – test method – 153 – 1985.

2.2.3 Numerical Optimisation Process

Basically, this optimization process involves three major steps, namely (i) performing the statistically designed experiments, (ii) estimating the coefficients in a mathematical model, and (iii) predicting the response and checking the adequacy of the model[23]. Central composite[24], Box-Behnken and Doehlert designs[25] were used in experimental design. It has been applied for optimization of several chemical and physical processes[26,27]. This design is generally used for fitting the second order polynomial model as shown below:

$$q = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i \right) 2 + \left(\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \right)$$

where q is the predicted response; b_0, the constant coefficients; b_i, the slope or linear coefficients of the input factor x_i; b_{ii}, the linear by linear interaction coefficients or quadratic coefficients between the input factor *xi* and x_j and b_{ij}, the interaction coefficients of input factor x_i[28].

2.2.4 Performance Evaluation

Performance evaluation was done in terms of water quality impact, commercial detergent and environmental impact assessment. For assessment in terms of water quality and their impact on PVP performance, the average amount of calcium carbonate (g/L) in each hardness range was chosen and then added to the test wash liquor. The samples were tested under spectrophotometer and the ΔE values plotted.

For the performance against commercial detergents, three handmade stains (coffee, tea and juice) were applied on the fabric swatches[29], as per the "International Association for Soaps, Detergents" specified test procedures. The influence of DTI on washing performance and stain removing ability was analysed. To test this particular performance, optimised values of PVP, detergent and *p*H were used. The stain swatches were immersed in the wash bath and after 30 min, they were washed thoroughly under running water as per ASTM D 2960-05[30]. The spectrophotometric values of the swatch with no PVP in the bath were compared against the other swatches.

For environmental impact assessment, pollution level of wastewater was assessed in terms of biological oxygen demand, chemical oxygen demand, total suspended solids, total dissolved solids, odour, turbidity and temperature of the discharging effluent after the addition of DTI in washing[31].

3 Results and Discussion

The initial trial was conducted to analyse the influence of process parameters, such as DTI polymer concentration, washing detergent powder concentration and washing *p*H on the dye transfer inhibition properties of DTI polymer.

3.1 Effect of PVP on Dye Transfer Inhibition

Figure 1 shows that the addition of PVP concentration from 0.3 g/L to 0.35 g/L uniformly reduces the dye uptake in the fabric. After 0.35 g/L, further increment in its concentration has no effect on the dye trasfer inhibition property of the material. This may be because of the saturation levels of the PVP in the washing solution. The lowest color difference is noted for the of 0.35g/L concentration of DTI.

3.2 Effect of Detergent on Dye Transfer Inhibition

In one liter of water, along with 3% dye (owm), PVP concentration of 0.35g and detergent quantity from 0.5 - 5 g/L was added separately along with pre-washed white samples. The performance of DTI was analysed using color difference values.

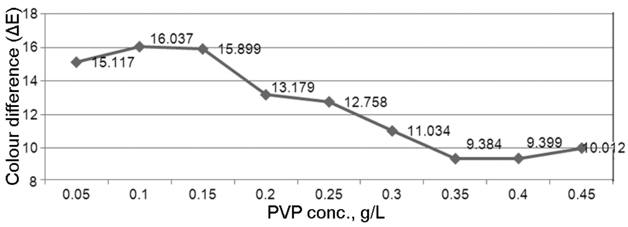

Fig. 1—ΔE values at different concentrations of PVP

The color difference analysis testing of the fabric swatches shows that the addition of detergent in the wash bath has strong influence on the dye inhibiting property. Up to 3.5g of detergent, the PVP functions properly and the color deposition on white fabric is restricted. After the addition of 4g of detergent, there is a drastic increase in color absorption of the fabric, even in the presence of PVP in the wash bath. From Fig. 2 it is clear that at 4g detergent the color change is maximum to 24.618. Hence, the detergent range from 3g to 3.5g has been selected as the maximum allowed quantity of the detergent per litter. However, here the composition and the active material of the commercial powder/detergent, and the proportion of anionic and non-ionic surfactants are not considered in order to simulate the commercial and practical application.

3.3 Effect of *p*H on Dye Transfer Inhibition

The influence of *p*H value on the dye transfer inhibition properties was analysed by keeping the other parameters as constant. At different *p*H level the samples were immersed in the wash bath with dye along with the detergent and DTI polymer. The evaluated color absorption (36.944) on the white fabric at 5 *p*H is found higher than that at an alkaline *p*H of 9 (12.81). The Δ E value is noted around 13.787 at *p*H 7. Hence, the alkaline *p*H is taken generally better for the optimum performance of PVP.

In general, from the above study it can be noted that maximum PVP concentration 0.35 g/L; maximum amount of detergent 3-3.5 g/L; and *p*H 9 (alkaline) are suitable for the optimization process. The dyes used in this experiment are representative of free dye molecules which are releasing from poorly bonded dyed textile material (hydrolysed reactive dyes). The influence of *p*H change on the further hydrolysis effect for reactive dye has not been considered in this study.

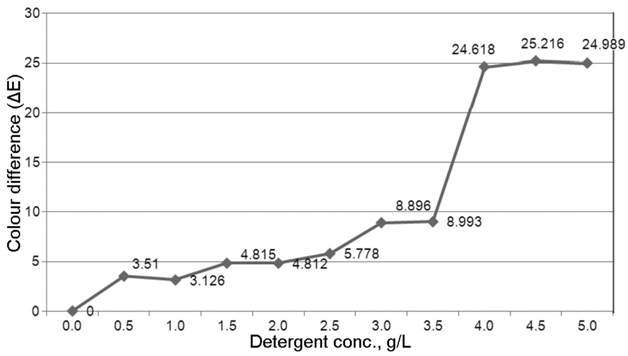

Fig. 2—ΔE values at various concentrations of detergent along with 0.35g/L PVP

3.4 Process Optimisation using Design of Experiments

A multiple regression analysis is done to obtain the coefficients, and the equation can be used to predict the response. The design is preferred because relatively few experimental combinations of the variables are adequate to estimate potentially complex response functions. A total of 15 experiments is necessary to estimate 10 coefficients of the model using multiple linear regression analysis. In this study, the variables like polymer (PVP) concentration (0.25, 0.3 and 0.35g/L), detergent concentration (2.5, 3 and 3.5g/L) and washing bath *p*H (5,7 and 9) were found to be the significant variables, designated as X_1, X_2 and X_3 respectively. The low, middle and high levels of the variables are designated as -1, 0 and +1 respectively. The calculation was carried out using multiple regression analysis and the least square method.

3.4.1 Experimental Design

In the present investigation the factors influencing the dye transfer inhibition properties of DTI polymer are optimized by Box-Behnken method. The influence of three factors, such as DTI concentration, detergent concentration and washing bath *p*H for three levels is investigated. The regression equation obtained after analysis of variance gives the level of dye transfer inhibition ability of DTI polymer as a function of different DTI polymer concentration, detergent powder concentration and washing *p*H. The process variables, color difference value (ΔE) and color strength value (*K*/*S*) of fabric at 560 nm for each experiment point are summarized in Table 1.

Table 1—Responses on Box and Behnken design experiments

Soap	PVP	*p*H	ΔE	*K*/*S* at 560 nm
-1	-1	0	5.627	0.123
+1	-1	0	13.790	0.228
-1	+1	0	10.857	0.163
+1	+1	0	11.033	0.173
-1	0	-1	11.245	0.149
+1	0	-1	9.349	0.155
-1	0	+1	12.596	0.165
+1	0	+1	4.818	0.097
0	-1	-1	11.223	0.177
0	+1	-1	14.503	0.214
0	-1	+1	9.316	0.125
0	+1	+1	5.157	0.097
0	0	0	9.283	0.155
0	0	0	8.540	0.138
0	0	0	8.549	0.138

3.4.2 Development of Empirical Models

Table 2 shows the empirical relationships between the main process parameters, namely PVP polymer concentration X_1, detergent concentration X_2, and washing bath *p*H X_3. The regression equation obtained after analysis of variance gives the level of color strength and color difference at each experiment point as a function of X_1, X_2 and X_3.

Here Y_1 and Y_2 are the predicted response, namely color difference (ΔE) and color strength value (*K*/*S*) at 560 nm. For all the responses, the significant level of quadratic regression equation, square regression are given in Table 2 with the F ratio and P -values. The smaller the P value the bigger is the significance of the corresponding process parameter[32]. It can be interpreted by the fact that in model Y_1, the model F-value of 1.155 implies that the model is significant.

The fitness and adequacy of the model was judged by the coefficient of determination (R^2)[33]. Models with R^2 value of ≥0.6 (60%) can be considered as a valid model[34]. The closer the R^2 value to 1, the better the empirical model fits the actual data[35]. R^2 value for the responses of regression models are 0.82 (Y_1) and 0.91 (Y_2) close to unity. This suggested that, for both the responses, the predicted second order polynomial models define well the real behavior of the system. In addition, the values of adjusted R^2 (0.67 (Y_1) and 0.84 (Y_2) are also found very high to advocate for a high significance of the model. The adjusted R^2 is a corrected value for R^2 after the elimination of the

Table 2—Empirical model developed for the process parameter

Response	Equation	R^2	Adj R^2	F-Ratio	P -value
ΔE (C.D)	$Y_1=51.672-8.103X_1+34.202X_2-11.245X_3-79.870X_1X_2+4.034X_1X_3-9.689X_2X_3+0.002X_1^2+615.469X_2^2+0.154X_3^2$	82	67	1.155	0.461
K/*S* at 560nm	$Y_2= -0.874+0.836X_1-4.531X_2+0.110X_3-0.950X_1X_2-0.009X_1X_3-0.275X_2X_3-0.105X_1^2+21.762X_2^2-0.003X_3^2$	91	84	2.961	0.122

unnecessary model terms. If there are many non-significant terms included in the model, the adjusted R^2 would be remarkably smaller[36] than the R^2. In this study, the adjusted R^2 is found to be very close to the R^2 value in the case of Y_2. The response Y_1 is slightly deviated from the R^2.

3.4.3 Effect of PVP Concentration and Detergent Quantity along with pH

Effect on ΔE Value

The effect of process parameter on the ΔE values has been plotted in the contour graphs. The result shows that the increase in the detergent quantity has the direct influence on the ΔE value. It represents that the addition of detergent into the wash liquor reduces the effectiveness of the dye transfer inhibition properties of the polymer PVP. This may be because of the use of (anionic or nonionic) surfactant in the detergent. These results are in line with the findings of Carrion *et al*[37]. They have mentioned that the addition of anionic surfactant improves the staining of fabric over the DTI polymers inhibition property. The basic mechanism was explained by Imai *et al*[38]. The use of an anionic surfactant causes a problem in wash liquor; the vinyl lactam polymer (DTI) and the surfactant interact with each other to aggregate and thereby the functions as the dye transfer inhibitor are deteriorated[39]. There are two accepted mechanisms of polymer-surfactant complex formation[40], one involves association of the surfactant to the polymer as unimers; and the other involves micellization of the surfactant on or in the vicinity of the polymer chain. In this case, PVP is a hydrophilic polymer and hence the reaction of this polymer with the detergent surfactant is micelle formation. The surfactant micelles may also cross-link the polymer molecules and results in gel-like structure. Thus, it reduces the active nature of the PVP and hence, the inhibition properties of the DTI is reduced[41].

From Fig. 3, it can be noticed that the increase in PVP concentration has reduced the dye absorption on the material up to a value of 0.3 g/L. After that, the addition of PVP in the wash bath has very less influence. The performance of PVP is because of the interaction between the dipolar momentum of the polymeric subunits and the polar dye groups[42]. However, the quantity of the PVP is restricted to the minimum based on their adverse effect and also because of cost factor.

The effect of *p*H on the effectiveness of the dye transfer inhibition is also analysed. From the statistical analysis, it can be noted that the *p*H variation has very less influence on the dye transfer inhibition properties. The ΔE values show very minimum amount of variation with the changes in *p*H. However, it is noted that the acidic *p*H causes the high ΔE value than the alkaline *p*H. This may be attributed to the ineffectiveness of PVP in the acidic *p*H.

Effect on K/S Value at 560 nm

The effect of process parameters like PVP concentration, detergent concentration and *p*H on the color strength values are plotted as contour plots at 560 nm. The addition of detergent up to 3 g/L to the wash bath initially reduces the dye absorption of the immersed fabric. But after 3 g/L, the further addition of detergent increases the color strength value gradually. In the other case, increment in PVP concentration reduces the color strength value drastically (Fig.4). However, the effect of PVP is influenced by the quantity of detergent in the wash bath as aforementioned. The change in *p*H from the acidic medium to alkaline has very less effect. But in the case of acidic *p*H, the color strength value appears

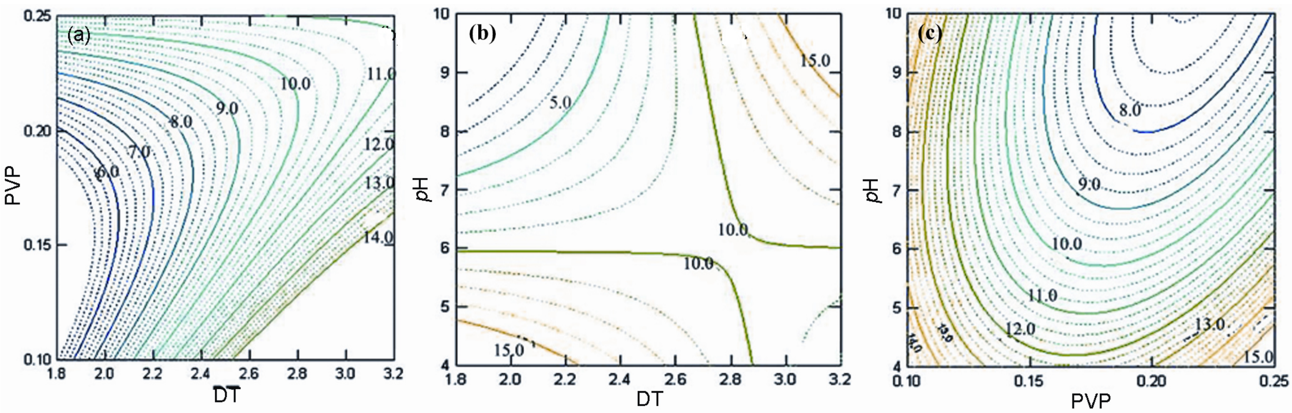

Fig. 3—Effect of PVP concentration and detergent quantity along with *p*H on ΔE value

to be high thanin alkaline region. However, the addition of detergent in the wash liquor causes increase in *p*H of the solution to above[9].

3.5 Numerical Optimisation

The optimization of process parameters against the responses is performed by numerical optimization method, with the help of design expert software. In this study, achieving the lowest color re-deposition on the textile fabric is the major objective. Hence, the added emphasis and higher importance are given for the color differences and color strength values. Based on the above-stated condition the numerical optimization analysis provides a set of top 14 combinations of the process parameters which give lower color strength and color difference. From the results, it is noted that the detergent concentration of 2.98 g/L, PVP quantity of 0.24 g/L and the *p*H value of 8.97 will give higher dye transfer inhibition ability of the textile material.

3.6 Evaluation of Optimised Conditions

To evaluate the performance of the optimized process parameters, the detergent concentration of 2.9 g/L, PVP concentration of 0.24 g/L and alkaline *p*H level was maintained in wash liquor. For one liter of water 3% of reactive dye (owm) was used for the analysis. The cotton fabric sample of 10 cm^2 (4 numbers) were immersed in the wash bath and allowed to agitate for 30 min. Then the fabric samples were rinsed in the running water and the color value and color difference were evaluated by keeping the normal bleached white sample as a standard. The results are given in Table 3.

The results show that the optimized DTI polymer concentration with detergent and alkaline *p*H gives better performance on the fabric than all other combination. Table 3 shows the ΔE values and *K*/*S* values of the standard and optimized samples. From the results, it can be noticed that the color strength values of the optimized sample is very close to the standard sample. The ΔE value is found to be 7.454 for optimized sample. The experiment was designed to measure the minimum quantity requirement of DTI for a liter of wash liquor. Hence, this finding suggests the minimum level of DTI polymer content in wash bath to obtain the best possible dye transfer inhibition against reactive dyes.

3.7 Performance Evaluation

3.7.1 Influence of Water Hardness

With increasing water hardness, the performance of PVP has been evaluated with its optimized quantity (0.24g/L). The result indicates that the increase in water hardness decreases the performance of DTI (higher ΔE value) as shown in Fig.5. These findings are in line with the findings of Carrion[37]. He evaluated the performance of vinyl pyridine and nitrogen oxide (PVNO) and PVP (K30) at the different water harness and observed the decreased performance in both the cases.

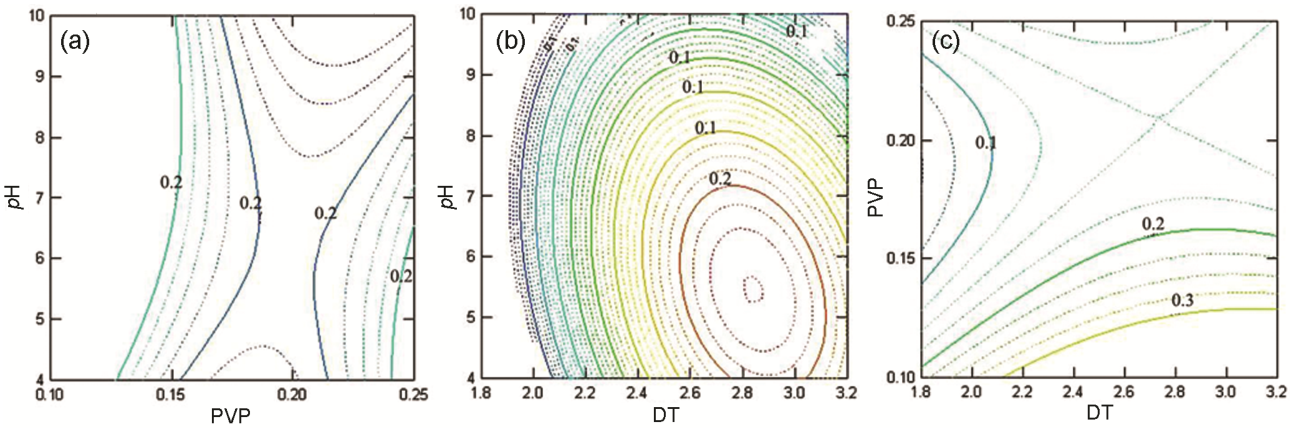

Fig. 4—Effect of PVP concentration and detergent quantity along with *p*H on *K*/*S* value at 560 nm

Table 3—ΔE and *K*/*S* values of standard white fabric and optimized sample

Sample	*K*/*S* at 410 nm	L*	a*	b*	C	H	ΔE
Standard white sample	0.304	96.283	1.475	-10.725	10.826	277.864	-
Optimised sample	0.231	91.140	5.575	-14.229	13.282	291.423	7.454

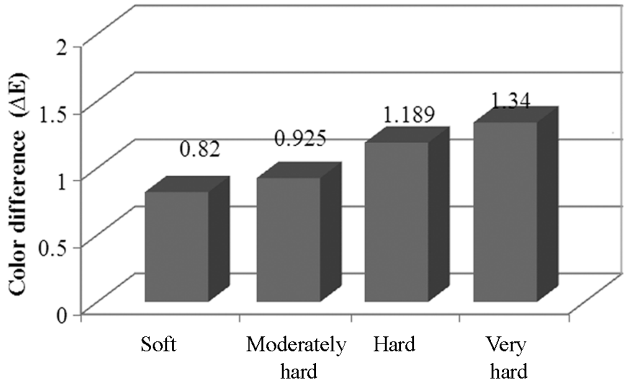

Fig. 5—DTI performance with different hardness of water

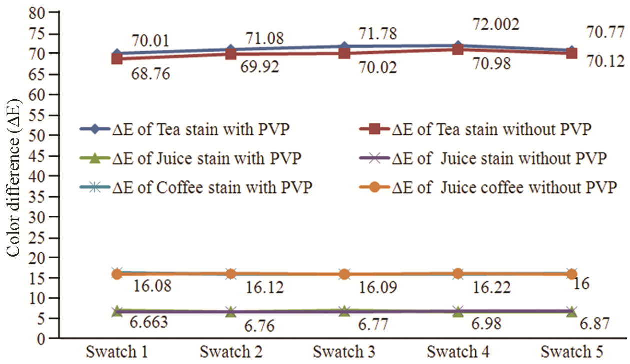

Fig. 6—Effect of PVP in wash liquor on washing efficiency

3.7.2 Influence of DTI on Washing Efficiency

The optimized amount of PVP has been used with detergent against different stains. Figure 6 shows that the detergent efficiency is unaffected by the concentration of PVP. Infact in all three stains, the stain removal efficiency remains unaltered. Even though there is a difference in the ΔE value between the fabrics washed with and without PVP, the differences between the values are very low and negligible. Only in the case of tea stain the less performance is noted (higher ΔE value) in both the cases. This may be due to the effectiveness of the stain. This result confirms that the presence of PVP (0.24 g/L) in the wash liquor does not affect the soil removal property of the detergent.

3.7.3 Eco-toxicological Studies

In order to evaluate the eco toxicology parameters, one litre of waste water from the above mentioned experiment (after washing with PVP) was analysed for their eco toxicology. The results are presented in Table 4 along with other major wastewater effluent parameters such as *p*H, temperature, turbidity, color and odour. The analysis reveals that all the parameters are within limits of the Indian standards (as per the notification of Ministry of Science, Technology and Environment. www.cpcb.nic.in)[43], except for COD value. Also, we compared the ratio of BOD/ COD with the standard. The value is found 0.07, indicating that it is beyond the range of untreated waste water.

Table 4—Comparison of washing outlet wastewater properties with ecotoxicological standard

Effluent parameter	Standard value for public sewage	Waste water with PVP
*p*H	5.5 - 9.0	8
Color	Colorless	Colorless
Temperature	No value specified	NA
Odour	Acceptable level	Within acceptable limits only
Chemical oxygen demand	Max 250 mg/L	614 mg/L
Biological oxygen demand	Max 350 mg/L	43 mg/L
Total suspended solids	Max 600 mg/L	14 mg/L
Total dissolved solids	600 mg/L	346 mg/L

4 Conclusion

In this research, the extraneous free dye molecule deposition on fabric from in-wash liquor is measured. The results show that the addition of DTI polymer (PVP) increases the dye transfer inhibition from the wash liquor to fabric. The addition of detergent on the wash liquor has the negative impact on the process. Higher the detergent concentration the lowers is the DTI polymer performance. This phenomenon is explained by polymer and surfactant interaction mechanism. The *p*H of the wash liquor also has the considerable impact on the color deposition on the fabric in the wash.

The developed model to analyse and optimize the process parameter shows the higher values of R^2 for the selected parameters. The best process parameters for the improved performance of DTI polymer are DTI polymer concentration 0.24 g/L, detergent Concentration 2.9 g/L, alkaline *p*H level in one liter of water, and 3% (owm) of reactive dye. The performance evaluation analysis reveals that the addition of PVP in commercial washing has no influence on the washing efficiency. However, the effect of water hardness has a major influence on the performance of the PVP in wash liquor. The pollution assessment study reveals that the wastewater with PVP possesses a high amount of COD value than the standard.

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