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ORIGINAL PAPER

Redox mediated electrochemical method for vat dyeing in ferric-oxalate-gluconate system: process optimization studies

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Abstract Preliminary efforts were made to identify alternative ligands for relatively greener and cheaper than triethanolamine (TEA), leading to a new ferric-oxalate-gluconate mixed ligand system as a potential alternative. Cyclic voltammetry was employed to study the mechanism involved. A low concentration of electrogenerated Fe^{II}-oxalate is transformed into Fe^{II}-gluconate, which is the reducing agent in the overall process. The influences of electrolyte medium, electrode material, nature of dye, dye concentration, material to liquor ratio (MLR), and other related parameters were studied to arrive at optimum experimental condition. Copper cathode and stainless steel anode were the material of choice. The optimum cathode current density was found to be 2.30 mA cm^{-2}. Under optimum condition, both cotton fabric and yarn could be efficiently dyed using this electrochemical process. The electrolyte could also be recycled. Color intensity for different dyed materials was evaluated using K/S values according to the Kubelka–Munk equation.

Keywords Indirect electrolysis · Ferric-complex · Calcium gluconate · Oxalic acid · Vat dyes · Cyclic voltammetry · Electrochemical dyeing

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1 Introduction

Among the green electrochemical and biochemical process, an alternative option being explored for vat dyeing, ferric-triethanolamine (Fe^{III}-TEA) redox complex based electrochemical route is probably the most extensively investigated process [1–3]. Bechtold and coworkers have patented this process in the early 1990s [4, 5]. The influence of Ca-gluconate additive and related improvement in the process was also patented subsequently [6–8].

Process improvements have also been reported from time to time, since 1994 [9]. Copper and stainless steel cathodes were compared to establish long-term efficiency in a divided flow cell [10]. The overall cathode surface area was improved by a flow through multi-cathode arrangement [11]. The influence of relative concentrations of ferric (Fe^{III}), ferrous (Fe^{II}), Ca-gluconate, glucose, heptagluconic acid, and calcium (Ca^{2+}) ions in the catholyte have been extensively investigated [12]. The dyeing efficiency of the overall electrochemical process was also evaluated [13]. Different membranes and separators were compared [14]. A comprehensive apparatus consisting of electrochemical reactor as well as vat dyeing units has also been described [15]. Potentiometric sensing was found to be useful in monitoring the electrogeneration of Fe^{II}-TEA complex [16]. Marken et al. have also demonstrated glucose as an environmentally benign reducing agent for indigo reduction [17].

In the present study, an attempt is being made to develop a redox system without TEA and relatively cheaper chemicals, which can give good stability in the highly alkaline condition. The basic studies on this system are reported in an earlier part of the study [18]. The mechanistic as well as optimization studies of ferrous-oxalate-gluconate system are reported here.

2 Experimental

2.1 Materials and methods

Technical grade ferric sulfate, sodium gluconate, citric acid, oxalic acid, tartaric acid, and TEA were purchased from SRL, India. Calcium gluconate, synthesized and characterized in this laboratory, was used. Estimation of ferric ion was carried out iodometrically using sodium thiosulfate, potassium iodide, and starch. Vat dyes investigated were commercial grade, purchased from M/s Atul Ltd., India. The vat dyes used are Novinone Green FFB (CI Vat Green 1), Novinone Violet RR (CI Vat Violet 1), Novinone Brown BR (CI Vat Brown 1), Novatic Yellow RT (CI Vat Yellow 2), and Novinone Olive R (CI Vat Black 27).

2.2 Cyclic voltammetry

The cyclic voltammetric experiments were performed using BAS IM6 Electrochemical Analyzer (USA) with Thales 3.18-USB software. In a conventional three electrodes system, glassy carbon (GC, 6 mm diameter) and a platinum foil were used as the working and counter electrodes, respectively. All potentials were recorded against Ag/Ag^+ quasi-reference electrode. Prior to the experiments, glassy carbon was polished with 4/0 emery sheets using alumina gel (0.05 micron) and washed with distilled water. Further, the electrode was sonicated for 5 min to remove adsorbed alumina. The test solutions were deaerated at least 30 min with N_2 before the start of the experiment to eliminate interfering oxygen. All the experiments were performed at 300 ± 2 K.

2.3 Electrochemical dyeing

2.3.1 Mediator preparation

Molar quantities of each of the constituents required for 1 L of mediator solution were individually weighed and dissolved in minimum quantity of water to obtain clear individual solution. These individual solutions were subsequently mixed together and made up to 1 L, mechanically stirred for 5 h, and finally, filtered through 1.25 μm ceramic filter to obtain clear mediator solution. A small quantity (<2% of total solid taken) of white precipitate (probably calcium oxalate) separated out, especially when calcium gluconate was used.

2.3.2 Electrochemical cell

PVC-based rectangular divided cell with 400 mL anolyte and 1,000 mL catholyte capacity was employed for galvanostatic studies. Nafion 423 membrane was used as a separator. The anode materials, made up of stainless steel plate (area 30 cm^2) or platinum (area 16 cm^2), were employed. Copper, mild steel, stainless steel plates, and copper wire (area 423 cm^2) were evaluated as cathode material. The external circulation for homogenousing the dye liquor bath was employed. A schematic illustration of the electrochemical cell is shown in Fig. 1.

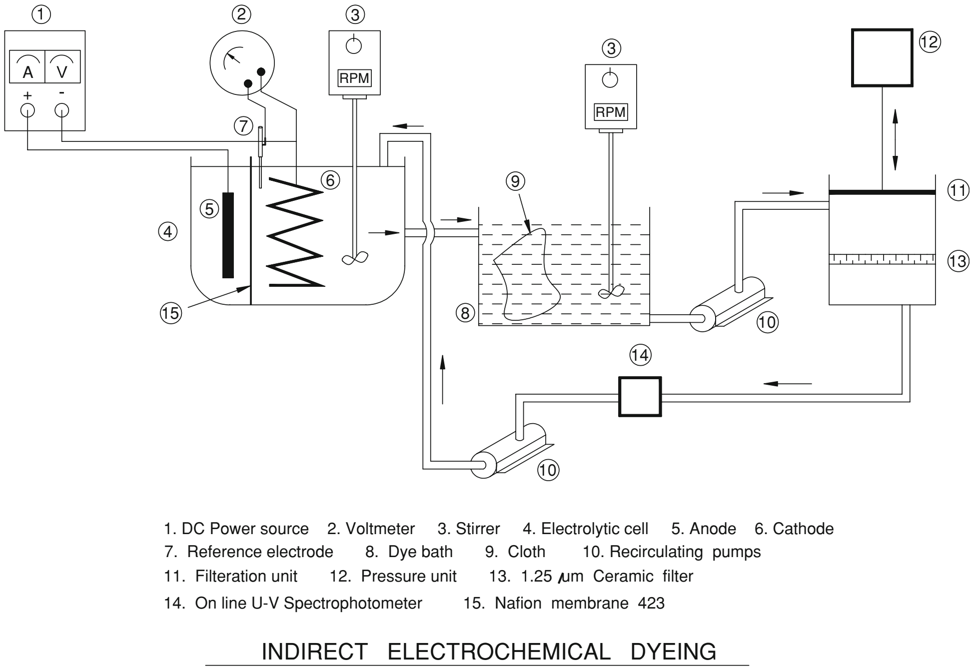

Fig. 1 Schematic illustration of the experimental set-up developed for electrochemical dyeing

2.3.3 *Dyeing procedure*

The electrolysis was carried out under galvanostatic condition by maintaining the constant current and optimizing the time required for achieving maximum current efficiency. During the electrolysis, the conversion of ferric ions was estimated by iodometric titration at different intervals of time. After achieving maximum conversion of ferric ions (no further increase in Fe^{II} concentration with time), the required quantity of selected dye was added into the catholyte. The electrolysis was continued for another 30 min for solubilization of the dye molecules. Then, the pretreated fabric sample was introduced into the dye bath. Both electrolysis and electrochemical dyeing were carried out at 300 ± 2 K. Experiments were carried out at relatively large liquor ratio value, such as 1:330, 1:80, and 1:60. In all the experiments, 0.8 wt% of the fabric on the dye was used in the dyeing recipe. The dyeing was carried out by exhaustion method for 30 min with constant stirring. After completion of dyeing, the fabric sample was washed with cold water and exposed to air, for oxidation/fixation of dye molecules. Then the fabric was soaped at boil, rinsed with cold water, and air dried.

2.3.4 *Determination of conversion efficiency and current efficiency*

Conversion efficiency was calculated using initial and final concentration of Fe^{III} ion, which is determined by iodometric titration [19].

The current efficiency (φ) was calculated using the following equation (Eq. 1):

$$\phi = \frac{ZFV_RC}{MIt} \times 100 \tag{1}$$

where Z is the number of electrons involved the reaction, F is Faraday constant (C mol^{-1}), V_R is the volume of solution (L), C is the concentration of molecule (g L^{-1}), M is molecular weight (g mol^{-1}), I is cell current (A), and t is time (s).

2.3.5 *Quality evaluation for the dyed fabrics*

Color depth of the dyed fabrics were characterized by color measurement in the form of K/S (where K denotes absorption coefficient and S corresponds to Scattering coefficient) value and color coordinates CIE L*, a*, and b*. (Color-opponent space with dimension L* for lightness and a* and b* for the color-opponent dimensions, based on nonlinearly compressed CIE XYZ color space coordinates.) Sphere spectrophotometer (SP b2 X-Rite, USA) was used along with D65 (day-light) light source, 10° viewing angle. The wavelengths used for Green FFB, Violet RR, Brown BR, Yellow RT, and Olive R were 500, 440, 540, 420, and 580 nm, respectively. The reflectance value measured using the above wavelength was transferred to K/S value according to the Kubelka–Munk equation. Dyed samples were also evaluated for washing fastness properties (Source IS 764: 1979).

3 Results and discussion

3.1 Cyclic voltammetric studies

As reported by Bechtold et al., it is very difficult to reduce Fe^{III}-gluconate system electrochemically [20]. Typical cyclic voltammogram obtained for Fe^{III} in the presence of calcium-gluconate system is shown in Fig. 2a. No distinct cathodic reduction peak was observed in the system.

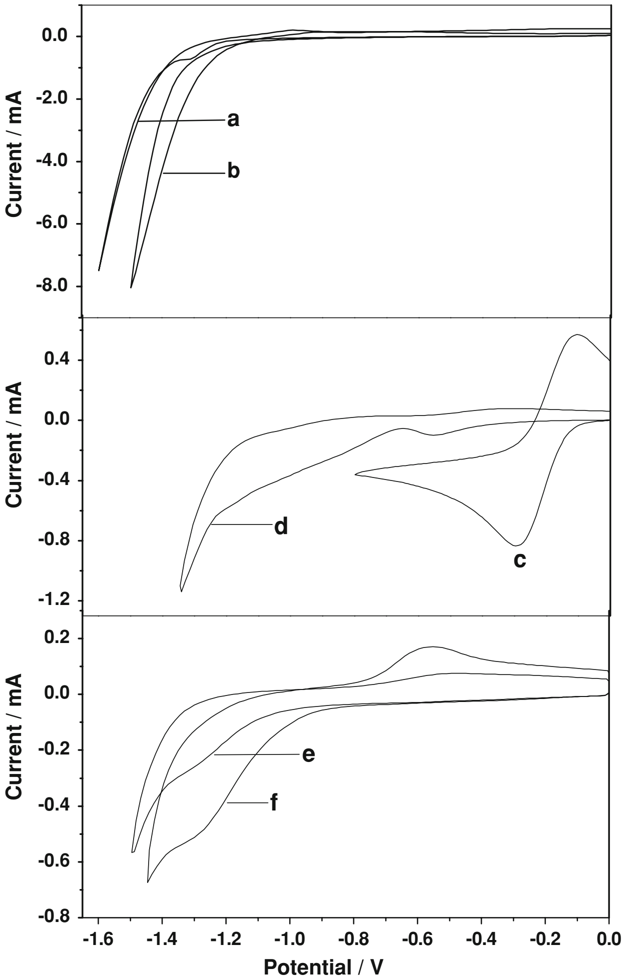

Fig. 2 Cyclic voltammograms of (a) ferric–calcium gluconate at pH 13, (b) ferric–sodium gluconate at pH 13, (c) ferric oxalate at pH 8, (d) ferric oxalate gluconate at pH 8, (**e**) ferric oxalate gluconate at pH 13, and (f) ferric oxalate gluconate at pH 13 in presence of vat dye at a scan rate of 40 mV s^{-1}

However, a small concentration of Fe^{III}-gluconate probably gets reduced along with hydrogen evolution reaction as evidenced by the appearance of a small and broad anodic peak during the reverse sweep (around -1 V). Similar voltammetric responses were obtained for calcium gluconate and sodium gluconate (compare Fig. 2a, b) except the shift of the background current toward more negative region by about 100 mV.

Conventionally, industrial vat dyeing is preferably carried out above pH 12 and very few Fe^{III} complexes are stable in such alkaline conditions. Many well-known complexes like Fe^{III}-oxalate precipitate out in such alkaline medium [21]. During the preliminary experiments, when the ferric sulfate was added to 1 mol L^{-1} NaOH and 0.1 mol L^{-1} oxalic acid, a brown precipitate was obtained. The Fe^{III}-oxalate complex was found to be stable at pH values of less than or equal to 8. Typical cyclic voltammograms of Fe^{III}-oxalate at pH 8 is shown in Fig. 2c. This redox system also gives rise to a well-defined quasi-reversible voltammograms. However, for vat dyeing purpose, the redox potential as well as the pH value is too low to be of any use.

Quite interestingly, in presence of excess gluconate, the Fe^{III}-oxalate complex did not lead to any hydrolysis or precipitation. The pH of ferric-oxalate-gluconate system could be raised beyond 13. As shown in Fig. 2d, the reduction peak below 0.5 V was found to decrease in presence of gluconate. Another broad peak was observed at more negative potential. Typical cyclic voltammograms of ferric-oxalate-gluconate system recorded with two different pH values of 8 and 13 are shown in Fig. 2d and e, respectively. All these observations suggest that Fe^{III} is quite stable in such a medium containing oxalate and gluconate ligands.

In the preparative scale experiments, copper was found to be quite efficient cathode material in this medium. Hence, a few cyclic voltammetric experiments were also carried out using copper working electrode. The obtained current potential for copper in this alkaline medium was found to be around -0.7 V. Cyclic voltammogram obtained on glassy carbon and copper electrodes from their corresponding rest potentials voltammograms under identical experiment conditions are shown in Fig. 3a and b, respectively. The small cathodic reduction peak around -1.15 V and the small anodic peak around -0.9 V were observed on copper electrode as well. The following dynamic equilibrium probably explains the above observation (Eq. 2).

$$\text{Fe(III)-Gluconate} + \text{Oxalate} \rightleftarrows \text{Fe(III)-Oxalate} + \text{Gluonate} \tag{2}$$

Fe^{III}-gluconate is probably more stable. However, a small concentration of Fe^{III}-oxalate would still be available for electrochemical reduction (Eq. 3).

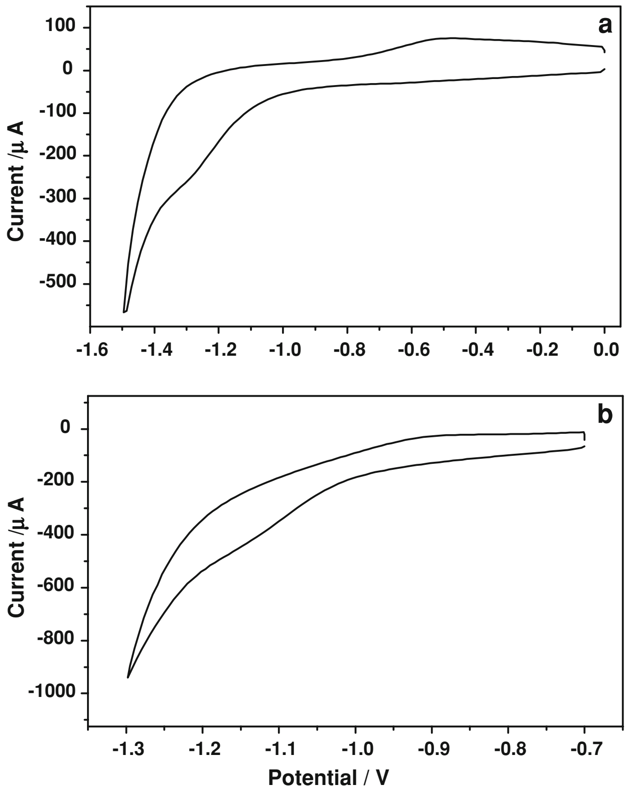

Fig. 3 Cyclic voltammograms of ferric-oxalate-gluconate mediator under optimized experimental conditions at pH 13 on **a** glassy carbon and **b** copper electrodes at a scan rate of 40 mV s^{-1}

$$\text{Fe(III)-Oxalate} + 1\text{e}^{-} \rightleftarrows \text{Fe(II)-Oxalate} \tag{3}$$

A decrease in the concentration of Fe^{III}-oxalate due to electro-reduction at the interface will shift equilibrium (Eq. 2) toward the right direction to ensure continuous availability of former species at the electrode surface. The redox peaks due to ferric-oxalate-gluconate complex was found to increase in presence of insoluble dye molecule (compare Fig. 2e, f in the absence and presence of dye molecule, respectively). The cathodic peak current was found to increase with increasing concentration of the dye molecules. This is probably due to the catalytic influence by the mediator.

$$\begin{aligned}&\text{Fe(II)-Oxalate} + \text{Fe(III)-Gluconate} \rightleftarrows\\ &\qquad \text{Fe(III)-Oxalate} + \text{Fe(II)-Gluconate}\end{aligned} \tag{4}$$

$$\begin{aligned}&\text{Fe(II)-Gluconate} + \text{Insoluble dye} \rightleftarrows\\ &\qquad \text{Fe(III)-Gluconate} + \text{Soluble dye}\end{aligned} \tag{5}$$

Hence in this media, the ultimate reducing agent for the dye molecule is Fe^{II}-gluconate (Eqs. 4 and 5). It is interesting to note that similar catalytic influence of Fe^{II}-gluconate operates in the presence of Fe^{II}-TEA complex as well [22].

3.2 Effect of complexing agents

Preliminary experiments indicated that gluconate as a common ligand could stabilize many other mixed ligand complexes of Fe^{III} in an alkaline solution. Typical experimental results obtained during the electrochemical dyeing in 1.0 mol L^{-1} NaOH solution containing gluconate with different additional ligands are summarized in Table 1. Citric acid, tartaric acid, and acetic acid also gave reasonable electrochemical conversion. The dye intensity, as measured by K/S values, was also found to be below 2.3. The dye intensity was also not uniform throughout the cotton surface. In the presence of acetic acid, coagulation was observed either during or after electrolysis. Therefore, these three complexing agents are not suitable for the preparation of mediator system (Experiment Nos. 1–3 in Table 1). Quite interestingly, oxalic acid–gluconate mixture ligand system exhibited good conversion efficiency and satisfactory current efficiency. The electrochemical dyeing efficiencies were similar in the presence of Ca-gluconate (Experiment No. 4 in Table 1) as well as sodium gluconate (Experiment No. 5 in Table 1). This suggests that the ligands play a major role when compared to Ca^{2+} or Na^{+} cations in the overall process. Performance of ferric-oxalate-gluconate system (Experiment No. 4 in Table 1) is quite similar to ferric-TEA-gluconate system (Experiment No. 6 in Table 1) under otherwise identical conditions. Quite similar results were also obtained for the more commonly studied ferric-TEA system in the absence of calcium gluconate (Experiment No. 7 in Table 1).

3.3 Effect of electrolyte composition

Further optimization studies were carried out to determine the optimum concentration of ferric sulfate, oxalic acid, and Ca-gluconate and the results are summarized in Table 2. The conversion efficiency increases when the ligand concentrations are significantly higher than the Fe^{III} concentrations (Experiment No. 1 and 2 in Table 2). When the ferric sulfate concentration increased beyond 25 mM

Table 1 Effect of Complexing agent in mixed salt system (mediator composition: 0.02 mol L^{-1} $Fe_2(SO_4)_3$, 0.05 mol L^{-1} complexing agent 1 and 0.1 mol L^{-1} complexing agent 2 in 1.0 mol L^{-1} NaOH)

Exp. No.	Complexing agent 1	Complexing agent 2	Conversion efficiency (%)	Current efficiency (%)	K/S value	Recycle
1	Calcium gluconate	Citric acid	25.92	35.46	1.87	Not possible
2	Calcium gluconate	Tartaric acid	30.91	43.07	1.99	Not possible
3	Calcium gluconate	Acetic acid	34.50	30.37	2.26	Not possible
4	Calcium gluconate	Oxalic acid	73.23	56.23	2.27	Possible
5	Sodium gluconate	Oxalic acid	66.66	50.91	2.22	Possible
6	Calcium gluconate	TEA	58.06	47.01	2.31	Possible
7	–	TEA	68.12	52.48	2.11	Possible

0.8 wt% shade of Novinone Green FFB dye was produced on the pretreated fabric

Table 2 Effect of chemical composition of ferric-oxalate-gluconate system in 1.0 mol L^{-1} NaOH

Exp. No.	Concentration of mediator composition			Conversion efficiency (%)	Current efficiency (%)	K/S value
	$Fe_2(SO_4)_3$ (mol L^{-1})	Oxalic acid (mol L^{-1})	Ca-gluconate (mol L^{-1})			
1	0.015	0.100	0.050	61.05	35.46	2.08
2	0.020	0.100	0.050	73.23	56.23	2.27
3	0.025	0.100	0.050	58.07	46.22	1.35
4	0.075	0.100	0.050	55.50	30.66	1.13
5	0.020	0	0.050	30.54	26.74	1.52
6	0.020	0.025	0.050	47.31	29.06	1.57
7	0.020	0.050	0.050	50.25	37.66	2.05
8	0.020	0.075	0.050	54.70	34.38	2.02
9	0.020	0.150	0.050	38.10	13.71	1.37
10	0.020	0.100	0.005	46.66	24.55	1.49
11	0.020	0.100	0.025	58.55	37.99	1.47
12	0.020	0.100	0.075	37.93	18.85	1.45

0.8 wt% shade of Novinone Green FFB dye was produced on the pretreated fabric by retaining the oxalic acid concentration at 100 mM and calcium gluconate concentration at 50 mM, the conversion efficiency decreases probably due to the insufficiency of ligands for complete complex formation (Experiment No. 3 and 4 in Table 2).

When the oxalic acid concentration was increased from 25 mM to 100 mM (Experiment No. 6–8 and 2 in Table 2) both conversion efficiency and current efficiency were found to increase with increasing oxalic acid concentration. When the oxalic acid concentration rose beyond 100 mM (Experiment No. 9 in Table 2) the conversion efficiency was found to decrease sharply. Hence, 100 mM oxalic acid concentration for 20 mM ferric sulfate (ligand to mole ratio was 5:1) was selected as the optimum condition.

At constant Fe^{III} (0.02 M) and oxalic acid (0.1 M) concentrations conversion efficiency increased with calcium gluconate concentration up to 0.05 M calcium gluconate (Experiment Nos. 10, 11 and 2 in Table 2). Still higher calcium gluconate concentrations also lead to lower conversion efficiency (Experiment No. 12 in Table 2).

3.4 Effect of electrode material

Both the conversion efficiency and the current efficiency values obtained for the electro-generation of Fe^{II}-oxalate-gluconate system employing different cathode and anode materials are summarized in Table 3. Both platinum and stainless steel may be employed as anode material (Experiment Nos. 1 and 2 in Table 3). In fact, the conversion as well as current efficiency values were found to be slightly lower (around 5%) for platinum anode when compared to stainless steel. Since oxygen evolution appears to be the predominant anodic reaction, both anodes could be employed. Stainless steel is the material of choice as anode due to cost consideration. Copper plate as well as wounded copper coil could be employed as the cathode material with reasonable efficiency (Experiment Nos. 2 and 3 in Table 3). Conversion efficiency was found to be slightly low for both stainless steel and mild steel cathodes. The mild steel corrodes at a fast rate in the catholyte employed. Electrolysis in a single compartment cell without membrane also gave very poor results indicating that membrane is always necessary for efficient electrochemical dyeing. In the absence of ion-exchange membrane, the ferrous generated at the cathode can be reoxidized at the anode surface without reducing the dye molecule leading to poor efficiency.

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad (6)$$

As shown in Fig. 4, both conversion and current efficiencies were found to depend significantly on the cathodic current density. An optimum current density of 2.30 mA cm^{-2} is obtained for copper plate.

3.5 Effect of dye concentration and material to liquor ratio

In all the previous experiments, Novinone Green FFB dye (100 mg) was employed for optimizing the electrolyte composition, pH, and electrode material. The effect of

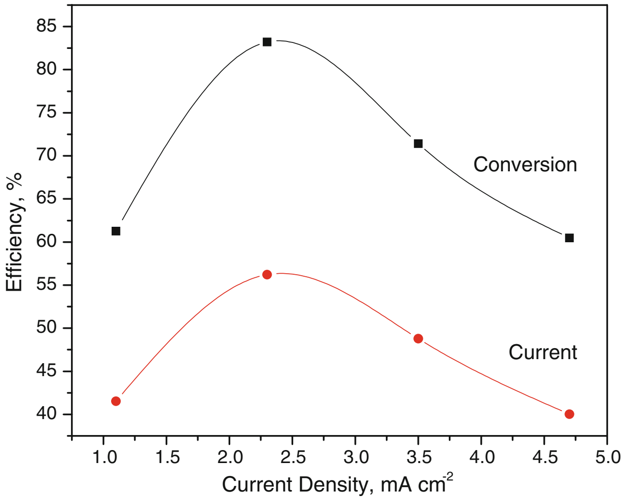

Fig. 4 Current and conversion efficiency against current density for the optimized concentration of ferric-oxalate-gluconate mediator system

Table 3 Effect of electrode materials with the Ferric-oxalate-gluconate system (mediator composition: 0.02 mol L^{-1} $Fe_2(SO_4)_3$, 0.05 mol L^{-1} Ca-gluconate and 0.1 mol L^{-1} oxalic acid in 1.0 mol L^{-1} NaOH)

Exp. No.	Anode material	Cathode material	Conversion efficiency (%)	Current efficiency (%)
1	Platinum	Cu-plate	67.74	47.15
2	Stainless steel	Cu-plate	73.23	56.23
3	Stainless steel	Cu-wounded	68.75	56.27
4	Stainless steel	Stainless steel	46.66	34.41
5	Stainless steel	Mild steel	20.00	20.69
6[a]	Stainless steel	Cu-plate	33.33	25.85

[a] Without membrane (single compartment) cell system

Table 4 Effect of dye concentrations (Novinone Green FFB) and MLR with the ferric-oxalate-gluconate system (mediator composition: 0.02 mol L^{-1} $Fe_2(SO_4)_3$, 0.05 mol L^{-1} Ca-gluconate and 0.1 mol L^{-1} oxalic acid in 1.0 mol L^{-1} NaOH)

Exp. No.	Concentration of dye (mg)	Percent shade (%)	MLR	K/S value	L*	a*	b*
1	100	0.8	1:330	2.27	34.19	−43.10	1.29
2	100	0.8	1:80	2.42	32.24	−41.21	1.10
3	100	0.8	1:60	2.65	30.15	−40.26	1.15
4	200	1.6	1:330	3.80	23.72	−28.26	0.67
5	300	2.5	1:330	6.39	19.52	−16.34	−0.77
6	400	3.3	1:330	6.91	18.70	−16.26	−0.61
7	500	4.2	1:330	6.42	19.14	−17.60	0.62

Table 5 Effect of different colors of vat dyes with the ferric-oxalate-gluconate system (mediator composition: 0.02 mol L^{-1} $Fe_2(SO_4)_3$, 0.05 mol L^{-1} Ca-gluconate and 0.1 mol L^{-1} oxalic acid in 1.0 mol L^{-1} NaOH)

Exp. No.	Color of dye	Percent shade (%)	K/S Value	L*	a*	b*	Washing fastness	
							Staining	Shading
1	Green FFB	0.8	2.27	34.19	−43.10	1.29	4–5	4
2	Violet RR	0.8	2.05	29.70	28.19	−30.86	4–5	3–4
3	Brown BR	0.8	3.00	45.14	9.02	3.85	4–5	3–4
4	Yellow RT	0.8	1.24	75.89	9.04	33.88	4–5	4
5	Olive R	0.8	1.65	53.41	−2.43	6.52	4–5	4

0.8 wt% shade of Novinone Green FFB dye was produced on the pretreated fabric

initial concentration of this material on the dye intensity values and CIE Lab color coordinates (L*, a*, and b*) values are summarized in Table 4. The dye intensity values increased with initial amount of the dye molecule. However, beyond 400 mg of initial dye concentration, dye intensity decreased slightly.

The material to liquor ratio (MLR) indicates how much liquor is to be taken for dyeing at a given weight of material. Total volume of the solution is calculated according to the weight of the fabric and MLR.

Dyeing of fabric in ferric-oxalate-gluconate system was carried out with different MLR values viz., 1:330, 1:80, and 1:60. Even dyeing was noticed for all MLR values, but depth of the dyeing varied with increasing MLR. When compared the better shade was obtained with MLR value of 1:60. Thus, the liquor amount can be reduced from 240 to 60 in the case of Fe^{III}-TEA system [16] by employing the present mediator system. The low MLR value saves the consumption of chemicals, water, and cost of the dyeing process.

Fig. 5 Photograph of dyed samples **a** fabric and **b** yarn with different vat dyes 1. Green FFB, 2. Violet RR, 3. Brown BR, 4. Yellow RT, and 5. Olive R under optimized experimental conditions

Table 6 Recycling of the Ferric-oxalate-gluconate system (mediator composition: 0.02 mol L^{-1} $Fe_2(SO_4)_3$, 0.05 mol L^{-1} Ca-gluconate and 0.1 mol L^{-1} oxalic acid in 1.0 mol L^{-1} NaOH)

No. of recycles	Conversion efficiency (%)	Current efficiency (%)	K/S value	Washing fastness	
				Staining	Shading
0	73.23	56.23	2.27	4–5	4
1	67.00	47.10	2.09	4–5	4
2	69.21	50.20	1.82	4–5	4
3	72.77	49.90	1.86	4–5	4
4	68.30	45.06	1.97	4–5	4
5	70.05	54.37	1.81	4–5	4
6	71.43	55.60	1.83	4–5	4
7	68.75	55.89	2.02	4–5	4
8	66.96	46.52	1.87	4–5	4
9	71.42	49.05	1.77	4–5	4
10	65.57	48.60	1.73	4–5	4

0.8 wt% shade of Novinone Green FFB dye was produced on the pretreated fabric

3.6 Efficiency of the mediator system for different vat dyes

Apart from Novinone Green FFB dye, four other dyestuffs were also evaluated for over all dyeing efficiency. In Table 5, K/S values and CIE Lab coordinates for all of these dyes are shown. In general, a variety of vat dyes could be effectively dyed using the same ferric-oxalate-gluconate mediator system. Yarns could also be dyed under similar conditions with different vat dyes. The colored fabrics as well as yarn samples were electrochemically dyed under optimum experimental conditions and are shown in Fig. 5.

3.7 Effect of recycling of electrolyte dye bath

The same catholyte solution after dyeing was air oxidized and filtered to remove the insoluble dye molecule. This electrolyte, after addition of 10–15% fresh electrolyte, could be recycled at least 10 times as shown in Table 6 using Novinone Green FFB dye (0.8 wt%) during each recycles. The conversion as well as current efficiencies remain reasonably same during each of this recycling experiment. The dye intensity measured as K/S values were also found to be reasonably stable in all the 10 dyeing recycles.

In all experiments discussed, so far, the electrochemical reduction was allowed to continue during the dyeing experiment. The dyeing process as well as recycling experiments was also carried out to study the dyeing efficiency without applying any electric current. Such a procedure is, indeed, necessary for continuous process development, where the dyeing unit should be separated from electrolyzer unit.

4 Conclusions

Ferric-oxalate-gluconate system thus appears to be a suitable candidate for further optimization and scale-up operation. This greener mediator system can be electrogenerated with good conversion efficiency. The current efficiency values are comparable to the TEA-based system reported in the literature. The MLR value is found to be good for the new mediator system. Removal of excess dye from the baths and reuse of the electrolyte are also possible. Both fabric and yarn could be efficiently dyed using the same mediator system.

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