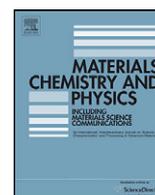




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Preparation of iron-deposited graphite surface for application as cathode material during electrochemical vat-dyeing process

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ABSTRACT

Iron-deposited graphite surfaces were prepared, characterized and employed as cathode materials for electrochemical vat-dyeing process containing very low concentration of sodium dithionite. The electrodeposition, in presence of ammonium thiocyanate and gelatin or animal glue as binding additives, were found to give finer iron deposits for improved electrochemical dyeing application. The electrodeposits were characterized using scanning electron microscopy, electron-dispersive X-ray spectroscopy and X-ray diffraction methods, before and after electrochemical dyeing process. The electrochemical activity of the iron-deposited graphite electrodes always stored in water seems to depend on the surface-bound $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox species. Vat dyes like C.I. Vat Violet 1, C.I. Vat Green 1 and C.I. Vat Blue 4 could be efficiently dyed employing these above electrode materials. The colour intensity and washing fastness of the dyed fabrics were found to be equal with conventionally dyed fabrics. The electrodes could also be reused for the dyeing process.

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1. Introduction

Eliminating or minimizing the use of sodium dithionite and other sulphur-containing compounds during the vat-dyeing process is an important challenge in environmental chemistry. Among them, chemical, electrochemical and biochemical alternative approaches are under investigation [1–5]. Direct electrochemical reduction in the vat-dyeing bath itself is of important due to its simplicity and ease of incorporation into the conventional dyeing bath. In some recent studies, Roessler et al. have reported direct electrochemical reduction of vat dye using electrodeposited Ni cathodes [6,7]. Direct reduction using other solid electrodes like Ti, Cu, Ni, and stainless steel has also been reported [8,9]. High cathode surface area could be achieved using graphite granules as well as chemically modified graphite granules as fluidized bed cathodes for vat molecule reduction [10,11]. Recently Bechtold et al. demonstrated the direct reduction of oxidised C.I. Sulphur black 1 by means of multi-stainless steel cathode electrolyser [12,13]. Cathode processes such as hydrogen evolution at iron alloys [14], reduction of organic compounds [15] and dehalogenation processes at iron metal particles [16,17] have been reported. Iron or electrodeposited iron cathode have not been employed so far as cathode material in electrochemical dyeing process.

In some recent studies ammonium thiocyanate as an additive was found to be useful in preparing fine iron deposits on silicon surfaces [18]. Electrodeposition on platinum substrate from sulphate bath has also been reported [19]. Saccharides and gelatin enhance the adhesion of iron deposits [20,21]. Based on these investigations, electrodeposition of iron on graphite substrate is reported in the present work. A useful role of ammonium thiocyanate as well as other additives in the electrodeposition process is also reported. The electrodeposited graphite was employed in the electrochemical dyeing process. The influence of electrodeposition condition on the overall efficiency of vat-dyeing process was also evaluated.

2. Experimental details

2.1. Chemicals

Technical-grade chemicals of sodium dithionite, ferrous sulphate, ammonium sulphate, sodium hydroxide, ammonium thiocyanate, animal glue and gelatin were purchased from Fischer, India. All aqueous solutions were prepared with deionised water. Vat dyes like C.I. Vat Violet 1 (Novinone Brill Violet RR), C.I. Vat Green 1 (Novinone Green FFB) and C.I. Vat Blue 4 (Novinone Blue RSN) were supplied by Novaltic, India and used as received.

2.2. Cyclic voltammetric studies

For voltammetric studies, a BAS IM6 Electrochemical Analyser (USA) was employed with a platinum foil as counter electrode and homemade $\text{Hg}/\text{HgO}/\text{OH}^-$ (1 M) as reference electrode. In a conventional three-electrode system, 3-mm diameter glassy carbon (GC) was used as the working electrode for electrodeposition studies (Section 3.1). Plane graphite and iron-deposited graphite electrode were

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employed as working electrodes for evaluation of the mechanism of electrochemical dyeing (Section 3.4). The cyclic voltammograms were recorded on Thales 3.18-USB software. Prior to the experiments, glassy carbon was polished with 4/0 emery sheets using alumina gel (0.05 μm) 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.

2.3. Metal deposition on graphite electrode

An aqueous solution of 500 mL containing 0.04 mol L^{-1} of ferrous sulphate and different concentrations of ammonium thiocyanate in 0.09 mol L^{-1} of ammonium sulphate were employed for deposition. A graphite sheet of area 27 cm^2 ($6 \text{ cm} \times 4.5 \text{ cm}$) was used as the working electrode (cathode). Ceramic porous pot filled with 20 mL of 10% sulphuric acid was used as anode compartment. Lead was used as anode. Graphite was first cleaned with nitrating mixture (1:1) and cleaned thoroughly with distilled water. The temperature of the deposition bath was maintained between 10 and 15°C and the pH around 5.5–6.5. A current of 1 A (corresponding to current density of 37 mA cm^{-2}) at a cell voltage of 6–9 V was passed for 1 h. The iron black deposit obtained on graphite plate was used for the vat dye reduction experiments. The iron-deposited graphite electrodes were always kept in water before using them in electrochemical vat-dyeing process. The iron deposition was also carried out with same procedure in the presence of the additives like animal glue and gelatin (4 mg in 500 mL).

2.4. Characterization of the metal-deposited electrode surface

Size, morphology and nature of the iron particles deposited over graphite surface was analysed using scanning electron microscopy (Hitachi-Make, S-3000H-Model, USA). EDAX analysis was also performed along with the SEM analysis to analyse the elements present in the electrode surface. Powder X-ray diffraction data sets were collected at RT on a PANalytical Expert Pro system in Bragg-Brentano geometry using $\text{Cu K}\alpha_1$ (1.540 \AA) radiation. The powder diffraction covered the $2\theta < 2\theta > 100^\circ$ range with 0.0167° steps.

2.5. Dyeing procedure

A conventional two-compartment cell (with a capacity of 200 mL each) separated with glass frit of $1.25 \mu\text{m}$ as membrane was used for the electroreduction of vat molecules under galvanostatic condition. Iron-deposited graphite surface and stainless steel were used as cathode and anode, respectively. The catholyte was 1.0 mol L^{-1} sodium hydroxide, 20 mg of vat dyes and with or without sodium dithionite and anolyte was 1.0 mol L^{-1} sodium hydroxide solution. The reduction of vat dyes was performed galvanostatically at a temperature of 60°C and current density 37 mA cm^{-2} for 3 h along with a constant agitation. The reduction process was performed under two different conditions (a) in the presence of nitrogen atmosphere and (b) in the absence of nitrogen atmosphere but with a small concentration of sodium dithionite. Sodium dithionite was used to initiate the reduction and also to stabilize the dye molecule in the reduced state.

After 3-h reduction, the bleached cotton fabric was introduced into the dye-bath and dyed for 15 min with the constant agitation by mechanical stirrer. 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 rinsed with cold water and air-dried.

2.6. Quality evaluation for the dyed fabrics

Colour depth of the dyed fabrics were characterized by colour measurement in the form of K/S value and colour coordinates $\text{CIE } L^*$, a^* and b^* with the help of the sphere spectrophotometer (SP62 X-Rite, USA) with D65 (day-light) light source, 10° viewing angle. The wavelengths used for Green FFB, Violet RR and Blue RSN are 500, 440 and 450 nm, respectively. The reflectance value measured using the above wavelength was transferred to K/S value according to the Kubelka–Munk equation. Several values were taken all over the fabric and average K/S value was presented. Dyed samples were also evaluated for washing fastness properties (Source IS 764: 1979).

3. Results and discussion

3.1. Cyclic voltammetric studies

Cyclic voltammetric experiments were carried out to study the influence of ammonium thiocyanate on electrodeposition of iron. All the cyclic voltammetric results reported here were obtained at a constant sweep rate of 40 mV s^{-1} .

Ammonium sulphate and ammonium thiocyanate alone gave a clear and a low background current on a glassy carbon elec-

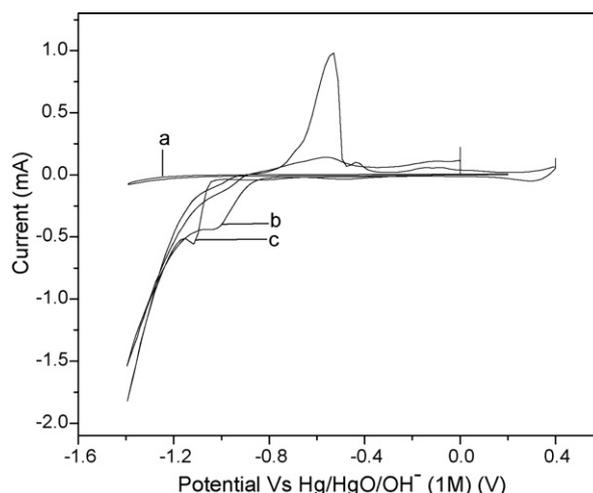


Fig. 1. Cyclic voltammograms of the solutions containing (a) 0.09 mol L^{-1} ammonium sulphate and 0.02 mol L^{-1} ammonium thiocyanate; (b) 0.09 mol L^{-1} ammonium sulphate and 0.04 mol L^{-1} ferrous sulphate and (c) 0.02 mol L^{-1} ammonium thiocyanate at scan rate 40 mV s^{-1} .

trode during cathodic cycling as shown in Fig. 1a. 0.04 mol L^{-1} ferrous sulphate in presence of ammonium sulphate gave a broad cathodic peak around -1.0 V and a small anodic dissolution peak (Fig. 1b) indicating the fairly low level of electrodeposition of iron. The charges under the cathodic and anodic peaks are 940 and $604 \mu\text{C}$, respectively. In presence of ammonium thiocyanate, however a sharp cathodic peak at -1.1 V is observed whose charge is about $1085 \mu\text{C}$. Quite significantly the anodic current peak due to dissolution of iron increases substantially as shown in Fig. 1c (i.e., charge increases from 604 to $3449 \mu\text{C}$). Thiocyanate anion adsorbed on glassy carbon surface thus shifts the deposition potential in the negative direction. However it appears that substantial iron deposition takes place in the peak potential region as well as in the more negative background reduction region leading to significantly higher overall electrodeposition.

The effect of concentration of ammonium thiocyanate in the electrolyte bath on the electrodeposition of iron was also studied. With increasing ammonium thiocyanate concentration, both cathodic and anodic current was found to increase significantly (Fig. 2). In addition to favorable adsorption of thiocyanate anion may also complex with Fe^{2+} species and facilitates the overall electrodeposition process.

Gelatin and animal glue (4 mg in 500 mL of electrolyte solution) were evaluated as potential additives for improving the adhesion of electrodeposited iron. Typical cyclic voltammograms recorded in the presence of gelatin and animal glue are shown in Fig. 3a and b, respectively. The electrodeposition of iron occurs at more negative potential of around -1.3 V in presence of these additives. The charge under the cathodic curves in the case of gelatin and animal glue are 2265 and $1934 \mu\text{C}$, respectively, indicating the increase in the quantity of iron deposit than ammonium thiocyanate alone. The anodic dissolution peak current decreases slightly in presence of these additives (compare Fig. 2a with Fig. 3).

3.2. Characterization of electrode surface

Scanning electron microscopy was used to identify the nature of electrodeposited iron under various experimental conditions. Typical SEM figure for cleaned graphite surface before electrode-

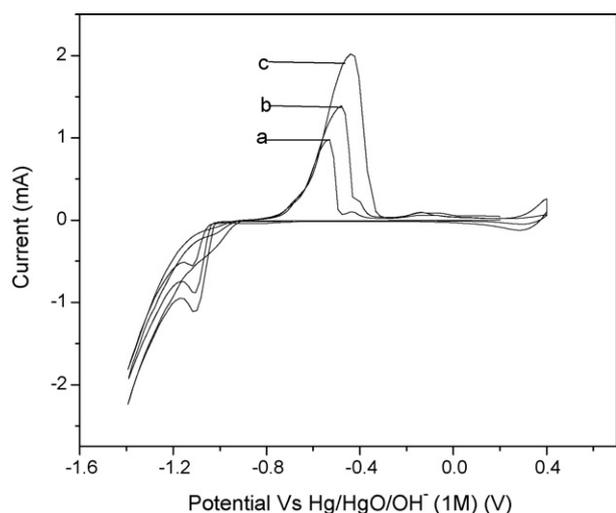


Fig. 2. Cyclic voltammograms of the solution containing 0.09 mol L^{-1} ammonium sulphate and 0.04 mol L^{-1} ferrous sulphate with different concentrations of ammonium thiocyanate: (a) 0.01 , (b) 0.02 and (c) 0.04 mol L^{-1} at scan rate 40 mV s^{-1} .

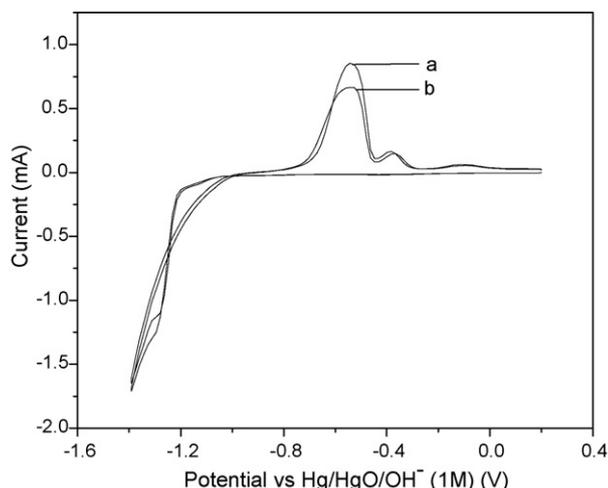


Fig. 3. Cyclic voltammograms of the solution containing 0.09 mol L^{-1} ammonium sulphate, 0.02 mol L^{-1} ammonium thiocyanate and 0.04 mol L^{-1} ferrous sulphate in presence of additives: (a) gelatin and (b) glue.

position is shown in Fig. 4A. The electrodeposited iron particles on such graphite surface (Fig. 4B) could be easily distinguished from the substrate (Fig. 4A). Addition of ammonium thiocyanate leads to even finer electrodeposited particles (less than a micron level) are shown in Fig. 4C. Iron deposits prepared in presence of animal glue were found to contain much smaller deposited particles as shown in Fig. 5A. Comparatively, the electrodeposit prepared in presence of gelatin was found to contain slightly larger iron

particles (Fig. 5B). So, it is clear that these additives were able to reduce the grain boundaries and postpone the hydrogen evolution potential.

The electrodeposited surface was also analysed by EDAX method to identify the elements present. Iron is the predominant species present in the electrodeposits prepared from ammonium sulphate (Fig. 6a) as well as the ammonium thiocyanate/ammonium sulphate (Fig. 6b) baths. In the later deposits a small peak due to sulphur is also noticed around 2.3 keV suggesting that a small quantity of adsorbed thiocyanate is incorporated into the electrodeposits [18].

Similar conclusion could also be drawn from X-ray diffraction measurements. Electrodeposited iron from ammonium sulphate solution (Fig. 7a) gave well-defined 2θ values, which match with JCPDS data file no. 897194 for iron. Electrodeposits obtained from ammonium thiocyanate/ammonium sulphate media gave additional XRD signals which may be attributed to graphite surface. The double peak observed around 2θ value of 25.9° may be due to the presence of sulphur (026) as well as carbon (002) in the electrodeposits (Fig. 7b).

3.3. Influence of electrodeposition condition on the electrochemical vat-dyeing process

The iron-deposited graphite electrodes prepared in the presence of different concentrations of ammonium thiocyanate were employed in an electrochemical vat-dyeing process using Novinone Brill Violet RR dye. Typical results obtained during the dyeing process are summarized in Table 1. For comparative evaluation electrochemical vat dyeing was attempted on a plane graphite electrode. The dye intensity obtained on a graphite electrode was indeed found to be very low (as shown in Expt. No. 1). Even in the absence of dithionite electrochemical vat dyeing could be achieved using electrodeposited iron cathode, if the entire dyeing process is carried out under nitrogen atmosphere (as shown in Expt. No. 2). Quite similar results however could be achieved in presence of a small concentration of dithionite (as shown in Expt. No. 3). The weight of dithionite used in these experiments was just 2.5% of the normally employed dithionite concentration in exhaust vat-dyeing method.

Redox potential observed during electrolysis/dyeing as function of time is presented in Fig. 8. As a result of dye reduction, redox potential in the catholyte compartment falls from $-0.640 \text{ V vs. Hg/HgO/OH}^- (1 \text{ M})$ to $-1.098 \text{ V vs. Hg/HgO/OH}^- (1 \text{ M})$, in the case of Novinone Brill Violet RR and similar behavior is observed for other dyes as well (Fig. 8). This shows that as reduction of dye proceeds, the redox potential is found to decrease indicating increase in the amount of dissolved dye. After getting the constant redox potential (after 3 h, Fig. 8) the bleached cotton fabric was introduced into the catholyte compartment. The reduction potentials of Novinone Green FFB, Blue RSN and Brill Violet RR are -0.850 , -0.880 and $-0.953 \text{ V vs. Hg/HgO/OH}^- (1 \text{ M})$, respectively [22]. The dye inten-

Table 1

Concentration effect of ammonium thiocyanate (ACT) of iron deposition from 0.09 mol L^{-1} ammonium sulphate and 0.04 mol L^{-1} ferrous sulphate

Expt. No.	C(ACT) (mol L^{-1})	No. of recycles	K/S	L^*	a^*	b^*	Washing fastness	
							Staining	Shading
1	Bare graphite	–	1.60	35.54	23.68	–21.18	3–4	4–5
2	0.18^a	–	2.50	28.54	21.12	–20.74	3–4	4–5
3	0.18	–	2.62	29.63	21.42	–20.38	3–4	4–5
4	0.01	1	3.11	23.83	20.90	–21.89	3–4	4–5
5	0.02	2	3.28	25.66	20.52	–21.43	3–4	4–5
6	0.04	2	2.68	23.50	24.51	–27.82	3–4	4–5

^a In presence of nitrogen atmosphere.

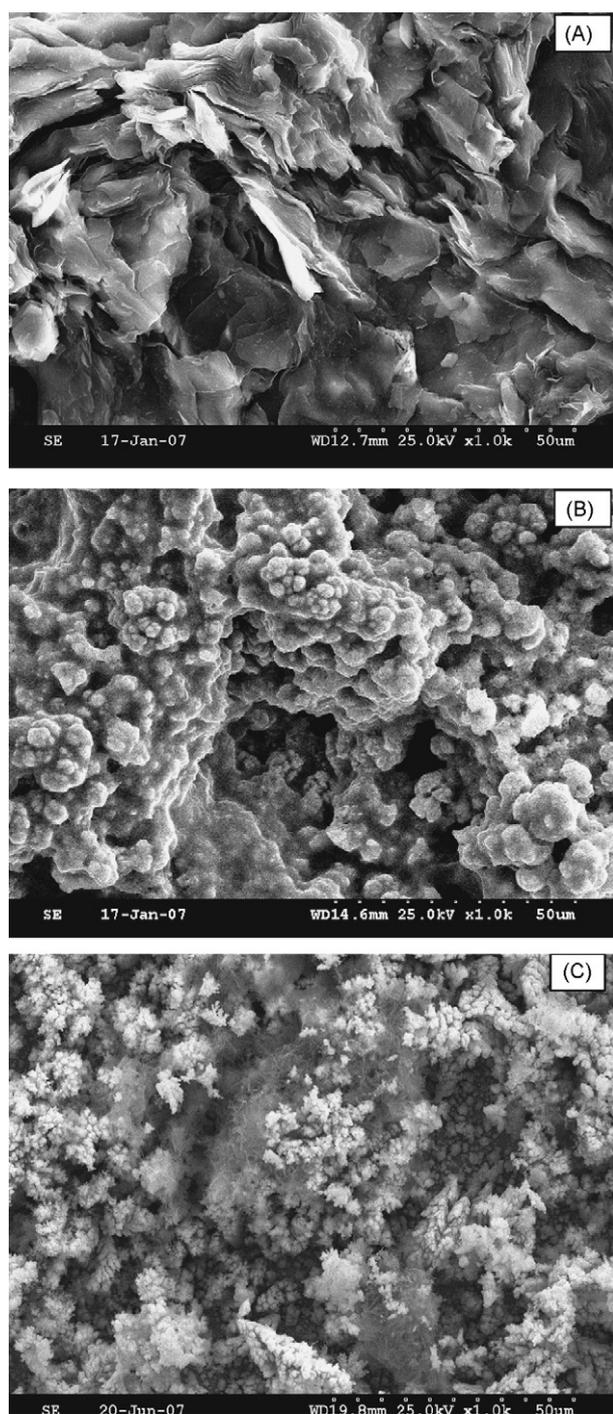


Fig. 4. SEM images of (A) graphite surface and iron electrodeposits on graphite surface obtained with (B) 0.09 mol L^{-1} ammonium sulphate and 0.04 mol L^{-1} ferrous sulphate and (C) 0.09 mol L^{-1} ammonium sulphate, 0.04 mol L^{-1} ferrous sulphate and 0.02 mol L^{-1} ammonium thiocyanate.

sity or K/S value 2.5 and above could be achieved for the dyed fabric and the CIE L^* , a^* and b^* values are presented in Table 1. However the electrodeposited cathodes prepared in presence of much lower concentrations of ammonium thiocyanate were found to be more efficient (Expt. Nos. 4–6). The electrodes also could be used at least twice. The dye intensity value up to 3.28 could be achieved. In all these cases washing fastness of the dyed cloth samples were found to be satisfied with conventionally dyed samples.

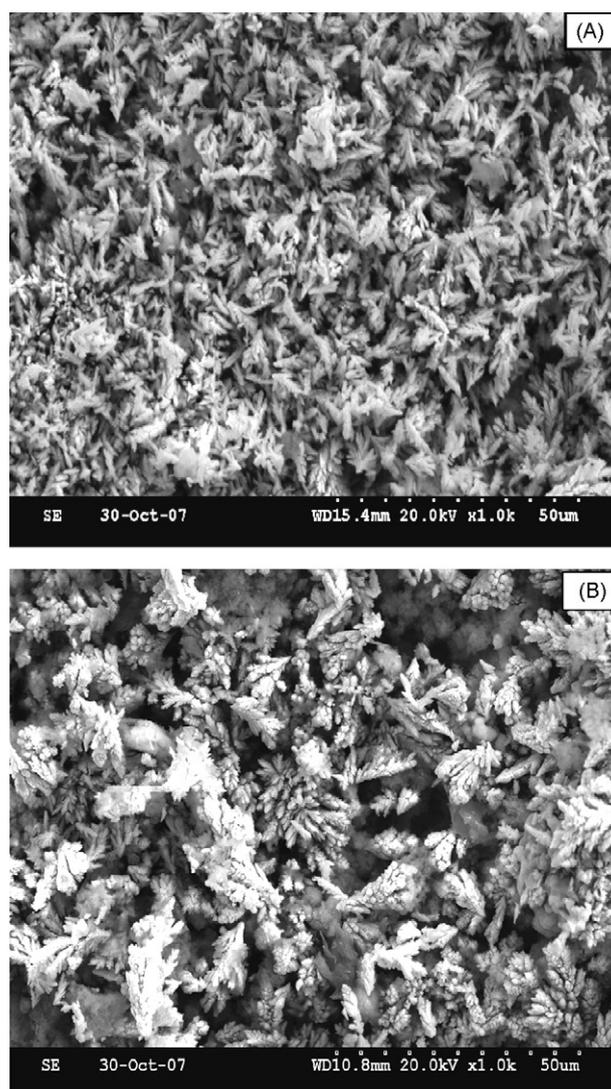


Fig. 5. SEM images of iron electrodeposits on graphite obtained with 0.09 mol L^{-1} ammonium sulphate, 0.04 mol L^{-1} ferrous sulphate and 0.02 mol L^{-1} ammonium thiocyanate in presence of additives: (A) gelatin and (B) animal glue.

The efficiency of electrodeposited iron electrodes prepared in presence of animal glue as well as gelatin is summarized in Table 2. 2.5 wt.% dithionite was employed in all these experiments. The K/S values during all the dyeing process were found to vary in the range 2.0–5.4. Electrodeposits are prepared in the presence of 0.02 mol L^{-1} ammonium thiocyanate generally found to give high K/S value above 4. A few electrodes were also successfully reused for the second batch of electroreduction and dyeing. The washing fastness both in terms of staining and shading were found to be satisfactory.

Apart from the Novinone Brill Violet RR, two other dyes mainly Novinone Blue RSN and Novinone Green FFB were also subjected to electrochemical dyeing using the same iron-deposited graphite cathodes. The dye intensity values are found to depend on the nature of dye employed (Table 3). However the dyed samples were prepared from all the three dyes show similar satisfactory washing fastness.

The SEM micrographs of iron-deposited electrode after using them in the dyeing bath twice are shown in Fig. 8. The electrodes prepared in presence of animal glue (Fig. 9A) remained relatively constant with the similar particle size (compare Figs. 5A and 9A).

Table 2
Additives' effect on iron deposition in the presence of different concentrations of ammonium thiocyanate with 0.09 mol L⁻¹ ammonium sulphate and 0.04 mol L⁻¹ ferrous sulphate

S. No.	C(ACT) (mol L ⁻¹)	Additive ^a	No. of recycles	K/S	L*	a*	b*	Washing fastness	
								Staining	Shading
1	0.18	Animal glue	1	2.62	25.96	25.50	-27.58	3-4	4-5
2	0.01	Animal glue	1	2.68	26.52	22.39	-24.46	3-4	4-5
3	0.02	Animal glue	1	5.31	18.51	16.36	-20.87	3-4	4-5
4	0.04	Animal glue	1	3.62	22.30	19.85	-23.85	3-4	4-5
5	0.01	Gelatin	2	3.12	22.15	22.66	-26.87	3-4	4-5
6	0.02	Gelatin	1	2.06	27.80	25.42	-28.34	3-4	4-5
7	0.04	Gelatin	2	2.80	24.64	21.47	-26.06	3-4	4-5

^a C(additive) is 4 mg in 500 mL.

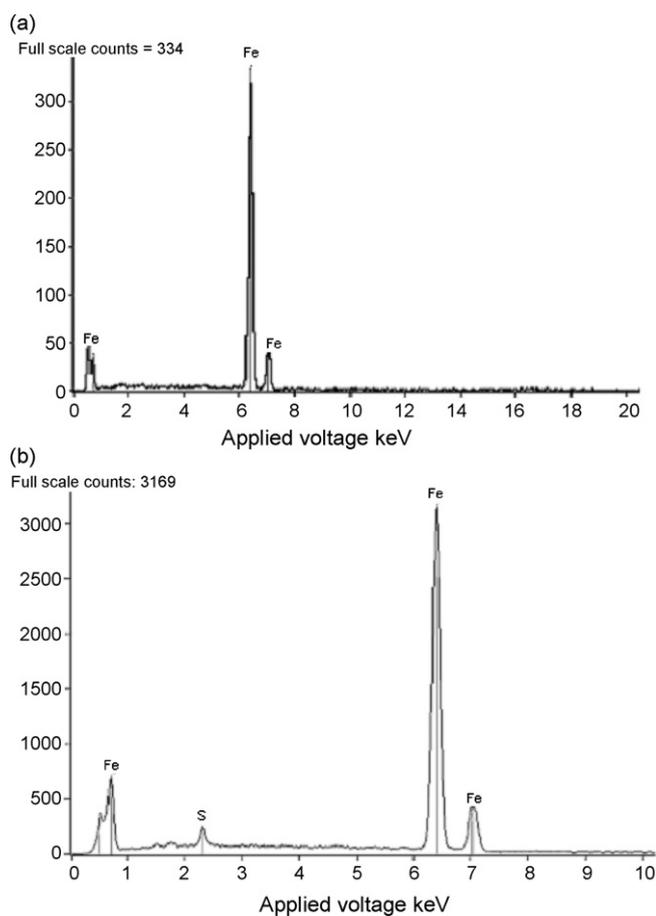


Fig. 6. EDAX patterns of iron electrodeposits obtained from ferrous sulphate with (a) ammonium sulphate alone and (b) in presence of ammonium thiocyanate.

Some agglomeration leading to larger particles was noticed for iron deposits prepared in the presence of gelatin (compare Figs. 5B and 9B). Further efforts to optimize the experimental conditions for obtaining electrode stability and consistent elec-

Table 3
Effect of different colors of vat dye in optimized iron deposition bath (0.09 mol L⁻¹ ammonium sulphate, 0.02 mol L⁻¹ ammonium thiocyanate and 0.04 mol L⁻¹ ferrous sulphate)

Dye	K/S value	L*	a*	b*	Washing fastness	
					Shading	Staining
Blue	1.69	34.85	-2.66	-25.36	3-4	4-5
Green	1.49	39.28	-34.51	0.47	4	4-5
Violet	3.12	22.15	22.66	-26.87	3-4	4-5

trochemical activity during recycling would be worthwhile. Some efforts towards achieving such goals are in progress.

3.4. Mechanism of electrochemical dyeing process on iron-deposited electrodes

The electrochemical dyeing experiments described above were carried out in presence of insoluble dye molecules. The cloths were also dyed while passing electric current the concentration of reductively solubilised dye molecule can also undergo oxidation and hence determination of the concentration could be difficult. Hence evaluation of product yield and conversion efficiency in the conventional sense is not possible. Recent literatures in this area also generally do not report electrochemical conversion efficiency [8,9,11].

However comparative cyclic voltammetric data obtained on plane graphite and iron-deposited graphite electrodes in the absence and presence of dye molecule indeed provide some insight

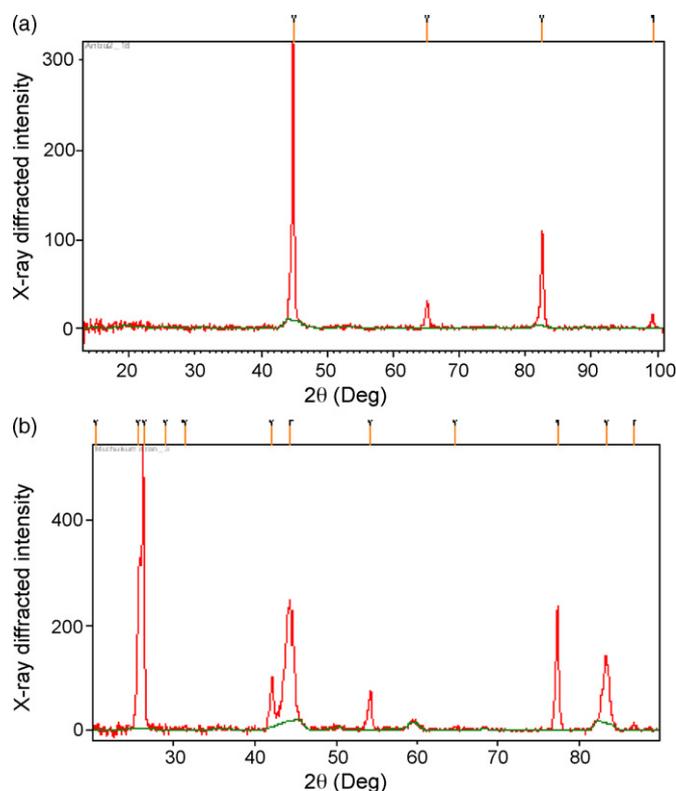


Fig. 7. X-ray diffraction patterns of iron electrodeposits obtained from ferrous sulphate with (a) ammonium sulphate alone and (b) in presence of ammonium thiocyanate.

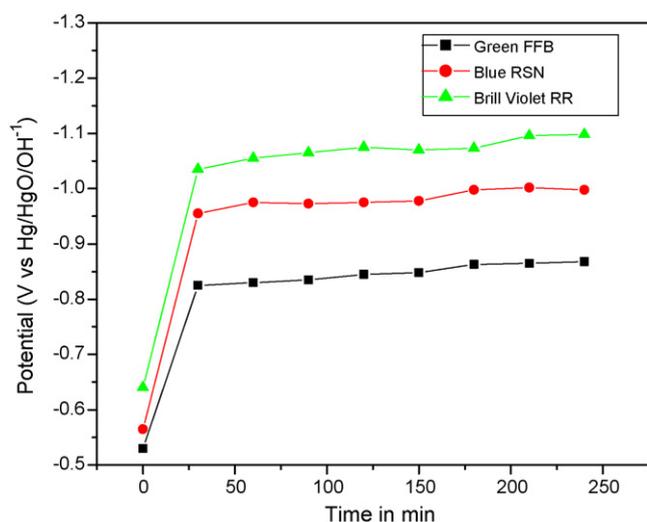


Fig. 8. Redox potential of different dyes (V vs. Hg/HgO/OH⁻ (1 M)) measured in the dyebath during dyestuff reduction as a function of electrolysis time.

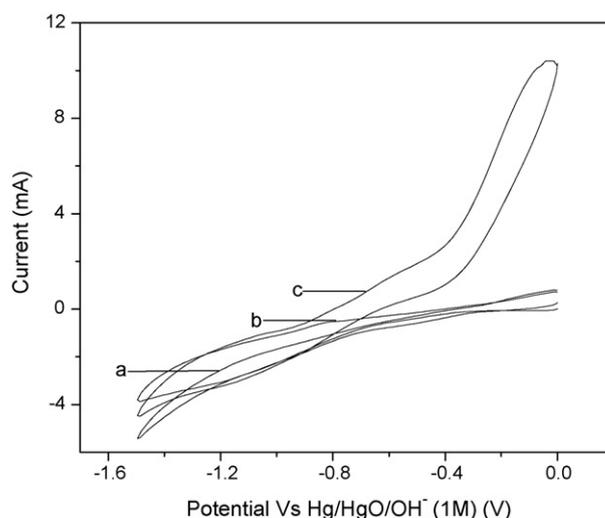


Fig. 10. Cyclic voltammograms of the graphite electrode containing in different solutions: (a) 1 mol L⁻¹ NaOH, (b) dye in 1 mol L⁻¹ NaOH and (c) dye dissolved in dithionite and 1 mol L⁻¹ NaOH at scan rate 20 mV s⁻¹.

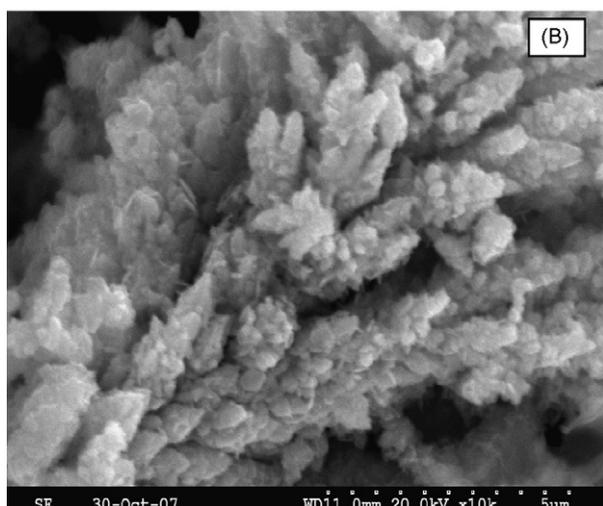
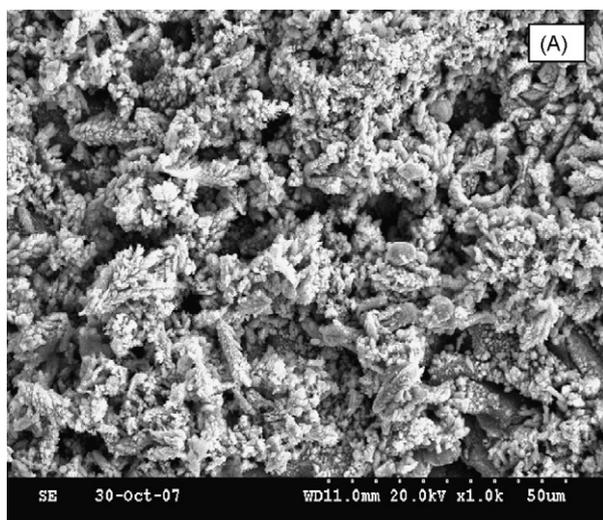


Fig. 9. SEM images of iron electrodeposits on graphite after reduction of vat dyes obtained with 0.09 mol L⁻¹ ammonium sulphate, 0.04 mol L⁻¹ ferrous sulphate and 0.02 mol L⁻¹ ammonium thiocyanate in presence of additives: (A) gelatin and (B) animal glue.

into the mechanism of electrochemical dyeing on iron-deposited electrode. Comparison of cyclic voltammograms obtained in 1 M NaOH on graphite (Fig. 10a) and iron-deposited graphite (Fig. 11a) clearly indicates substantially higher cathodic as well as anodic current on iron-deposited graphite electrodes. Distinct cathodic and anodic peaks are also observed around -1.3 and -0.55 V, respectively, these peaks typically correspond to Fe³⁺/Fe²⁺ redox couple, indicating the electroactive iron deposits prepared and stored in aqueous solutions. The iron-deposited graphite electrode contains some surface-bound Fe³⁺/Fe²⁺ redox species which catalyze the electrochemical dyeing process.

Addition of small concentration of dye molecule does not enhance the current values on a graphite electrode (Fig. 10b). However on an iron-deposited graphite electrode both cathodic and anodic peak currents increase to a noticeable extent (Fig. 11b). This suggests that surface-bound Fe²⁺ generated on iron-deposited electrodes act as a redox catalyst in reducing the vat dye molecules.

Sodium dithionite undergoes oxidation on a plane graphite electrode beyond -0.4 V (Fig. 10c). On the iron-deposited graphite electrode no distinct increase in anodic current is noticed above -0.5 V. However the cathodic and anodic peak currents due to

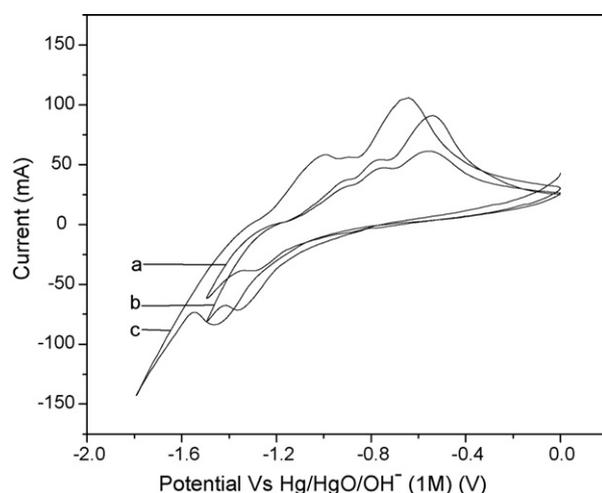


Fig. 11. Cyclic voltammograms of the Fe-deposited graphite electrode containing in different solutions: (a) 1 mol L⁻¹ NaOH, (b) dye in 1 mol L⁻¹ NaOH and (c) dye dissolved in dithionite and 1 mol L⁻¹ NaOH at scan rate 20 mV s⁻¹.

$\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple are found to increase in presence of sodium dithionite (Fig. 11c). It appears that sodium dithionite as well as electrogenerated Fe^{2+} species influence overall dye reduction process. Sodium dithionite as such is not necessary for electrochemical vat dyeing, if the electrochemical process carried out in nitrogen atmosphere (Table 1, Expt. No. 2). Hence the low concentration of sodium dithionite employed in the present work probably act as a scavenger for dissolved oxygen and prevents the reoxidation of soluble form of electrogenerated vat dyes. The catalytic role of sodium dithionite however cannot be ruled out at least initial stage of electrochemical process.

4. Conclusions

The present investigation indicates that high-surface area cathodes for electrochemical dyeing can be prepared by electrodeposition process. This appears to be a better option when compare to alternate strategy of employing multiple cathodes in the electrolyser [12,13]. The adherence and reusability of the electrodeposits may be improved significantly by employing inorganic adsorbents like thiocyanate and organic additives like gelatin and animal glue. The electrochemical activity of these electrodes depend on surface-bound $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox sites which needs to be protected by keeping them under wet conditions. The long-term stability and reuse of the same cathode material needs further investigation. However, the dye intensity as well as washing fastness of the dyed fabrics obtained in this process is found to be highly promising and satisfactory.

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