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Effective separation of organic dyes using ionic liquids as green mobile phase and polyaniline-modified silica gel nanocomposite-based thin-layer chromatography

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Abstract

Background: Organic dyes are used for a wide variety of purposes including their applications in textiles, foods, printing cosmetics and pharmaceuticals. Thus, these are industrially very important and their analysis is always required before putting to particular use.

Methods: To develop the extremely efficient thin layer chromatographic system for the resolution of co-existing dyes, the silica gel was modified with the conducting polymer polyaniline. Silica gel and polyaniline modified silica gel were used as stationary phase while the different formulations based on aqueous solutions of ionic liquids such as 1-methyl-imidazolium chloride, 1,2,3-trimethylimidazolium methyl sulphate and 1-ethyl 3-methyl-imidazolium tetrafluoroborate were used as mobile phase to study the migration behaviour of organic dyes.

Results: Comparatively better separation efficiency was observed in case of polyaniline modified silica gel with respect to unmodified silica gel. Densitographic presentation of separation of organic dyes achieved using polyaniline modified silica gel (Pani@SG-ES) was also presented. The thin layer chromatographic system comprising of polyaniline modified silica gel (Pani@SG-ES) as stationary phase and 2% aqueous 1- methyl-imidazolium chloride as green mobile phase was observed to be most efficient towards separation of several three-component mixtures of organic dyes. The effect of presence of impurities on the efficiency of separation was examined and the detection limits of the dyes were also calculated. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM with EDX) and transmission electron micrograph (TEM) studies were undertaken to characterize silica gel and polyaniline modified silica.

Conclusions: A new thin layer chromatographic system consisting of polyaniline modified silica gel (S2) as stationary phase with 2 % aqueous (1-methylimidazolium chloride) as eco-friendly mobile phase is most favourable for the identification and separation of three-component mixtures of organic dyes.

Keywords: Thin-layer chromatography, Polyaniline-modified silica gel nanocomposites, Efficient separation of organic dyes, Ionic liquids

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Background

A wide variety of colours and shades imparts beauty to our planet, and everyone is attracted towards anything that is colourful and beautiful, but natural dyes are highly unstable and undergo degradation during the industrial processing. The counterparts of natural pigments are the synthetic dyes that are coloured aromatic compounds having strong affinity to the substrates on which they are applied. Although the dyes are used for a wide variety of purposes, their application such as in textiles, foods and printing is industrially very important (Alves et al. 2008; Amini et al. 2011; Charumathi and Das 2012). Food dyes are the most controversial but essential group of food additives as they are unavoidable colourants of foods, cosmetics and drugs for aesthetic reasons (Piccin et al. 2009; Wrolstad and Culver 2012). The tinge of colour of a product psychologically improves its attractiveness, freshness and taste.

Thin-layer chromatography (TLC) is one of the most efficient and versatile separation methods for many classes of chemical compounds. It has advantages over the other chromatographic techniques such as low cost of instrumentation, the ability of making simultaneous separations and shorter time required in analysis. All these make TLC a convenient choice for a variety of chemical procedures including monitoring the progress of a reaction, analysing a compound or mixture of compounds, determining optimal chromatographic conditions for the separation of components in a mixture and identifying the components in a mixture (Oka et al. 1994; Hoodless et al. 1971). TLC has also been established as an essential educational tool for the teaching of chromatographic principles in organic chemistry laboratories worldwide (Clark 2007; Atayan et al. 2003).

It is a simply known fact that the double-distilled water (DDW) has occupied the top position in the list of green solvents due to its non-toxicity, amazing solubilising properties, ease of availability and low thermal conductivity (Mohammad and Mobin, 2015a, 2015b). On the other hand, certain ionic liquids have attracted a lot of attention of researchers working in the areas of organic synthesis (Friedmann et al. 2016), chromatography (Tabar Heydar et al. 2013; Wang et al. 2014; Yoshinaga et al. 2014; Yoshinaga et al. 2014; Yoshinaga et al. 2014), biotechnology and environmental engineering (Jones et al. 2002) mainly due to their unique combination of physicochemical properties such as very low volatility, non-flammability, high thermal and chemical stability and a large range of temperatures of their liquid state (Seddon 2003; Gutowski et al. 2003). The ionic liquids have also become greatly useful in spectroscopy and electrochemistry (López-Lorente et al. 2013; Lee et al. 2014; Sun et al. 2012; Ejigu et al. 2011).

The coupling of favourable properties of polyaniline (Pani) such as good environmental stability, high electrical conductivity, electrochromism, reversible transformation

of various oxidation states, and catalytic, antistatic and anticorrosion activity with the favourable properties of silica gel such as good heat resistance, high strength and hardness will be expected to produce a new and novel stationary phase of improved structural and chromatographic characteristics (Ge and Wallace 1991). The Pani@SG-S₂ enhances the selectivity and chemical stability of the stationary phase (Siddiq et al. 2014) while the ionic liquids as green mobile phase have been used due to their versatility and environmental friendliness. In TLC, the ionic liquids have been found useful as mobile phase for the separation of peptides and in the determination of naphazoline nitrate in nasal drops (Marszall et al. 2013).

In the present study, the polyaniline-modified silica gel nanocomposite (Pani@SG-S₂) has been prepared by in situ polymerisation of aniline to be used as stationary phase with several aqueous ionic liquid mobile phases for thin-layer chromatographic analysis of six dyes, viz. alizarin red S, xlenol orange, bromo-cresol purple, brilliant blue, tartrazine and carmoisine. Chromatographic parameters have been calculated for ternary separations of dyes on Pani@SG-S₂ stationary phase in the presence of 2% aqueous 1-methyl-imidazolium chloride as mobile phase. The use of green mobile phase as well as polyaniline-modified silica gel nanocomposite as stationary phase is a novel approach to develop an environmental-friendly TLC method. Thus, prepared Pani@SG-S₂ stationary phase has also been characterised by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM with energy-dispersive X-ray (EDX)) and transmission electron micrograph (TEM).

Methods

Apparatus

Glass plates 20 × 3.5 cm were coated with silica gel and polyaniline-modified silica gel using a TLC applicator (Toshniwal, India). The micropipette (Triplette, Germany) was used for spotting of analytes and 24 × 6 cm glass jars were used to perform TLC.

Experimental temperature

All the experiments were performed at 25 ± 2 °C.

Chemicals and instrumentation

Silica gel (Fisher Scientific, India); methanol, ethanol, propanol-1, potassium persulphate, copper sulphate, zinc sulphate, manganese sulphate and nickel nitrate (HCl); sodium salts of bromide, chloride, carbonate, acetate and nitrate (Central Drug House; CDH, India); 1-methyl-imidazolium chloride, 1,2,3-trimethylimidazolium methyl sulphate and 1-ethyl 3-methyl-imidazolium tetrafluoroborate (Sigma-Aldrich) and aniline (E-Merck India Ltd.) were used as received. Brilliant blue, tartrazine and

carmoisine (Roha Dyechem. Pvt. Ltd., Mumbai, India) as well as alizarin red S, xylenol orange and bromo-cresol purple (CDH India) were used. All chemicals were of analytical reagent (AR) grade. The water used in these experiments was double distilled.

The Fourier transform infrared (FTIR) spectra were recorded using the Perkin-Elmer 1725 spectrometer operating in the 400–4000-cm⁻¹ range. X-ray diffraction (XRD) data were recorded by using the Bruker D8 diffractometer with Cu K α radiation at 1.540 in the range of 5° ≤ 2θ ≤ 70° at 40 kV. The morphology of stationary phase was observed by a JSM-6510LV system with a JEOL scanning electron microscope (SEM) with EDX. Transmission electron micrograph (TEM) was done with the help of JEM 2100, JEOL instrument to study the morphology and the particle size.

Test solutions

Solutions 5% (w/v) of dyes were prepared in double-distilled water (DDW).

Stationary phase

The following were used as stationary phase:

S₁=SG, S₂=Pani@SG(ES), S₃=Pani@SG(EB₁) and S₄=Pani@SG(EB₂).

Mobile phase

The mobile phases used are listed in Table 1.

Composition of Roscillin^R syrup and Ambrodil^S syrup

The Roscillin^R syrup from Ranbaxy Laboratories Ltd. (Bhatoli Kalan, Himachal Pradesh, India) and Ambrodil^S syrup from AISTO Pharmaceutical Pvt. Ltd. (Raisen, Madhya Pradesh, India) were studied to identify tartrazine and brilliant-blue food dyes, respectively. The pharmaceutical formulation of Roscillin^R contains ampicilline IP (ampicilline trihydrate equivalent to anhydrous ampicilline, 125 mg), paracetamol IP 125 mg and colouring agent tartrazine. The pharmaceutical formulation of Ambrodil^S contains ambroxol hydrochloride IP 15 mg, salbutamol sulphate IP 1 mg, flavoured syrup base and colourant brilliant blue FCF.

Preparation of polyaniline-modified silica gel nanocomposite

Pani@SG nanocomposites were prepared by simple in situ oxidative polymerisation of aniline using potassium

persulfate as an oxidising agent in the presence of different amounts of silica gel (SG). Aniline (1.02 g) was dissolved in 200 mL of 1 M aqueous solution of HCl. Different amounts (30 and 60 g) of silica gel were added in an aniline solution. Later, potassium persulphate (5 g), dissolved in 1 M HCl (500 mL), was added dropwise in the aniline solution for the polymerisation. The reaction mixture was put under continuous stirring for 22 h. The resultant mixture containing emeraldine salt turned slowly into greenish black slurry which was filtered, washed thoroughly with DDW and undoped with 500 mL of 1 M ammonia solution for making Pani@SG (EB). The resultant product was washed with DDW and methanol to remove the impurities until filtrate became neutral and colourless. The prepared nanocomposites were dried at 70–80 °C for 12 h in an air oven, converted into fine powders and were stored in a desiccator for further investigations of Pani@SG(EB₂) (Table 2).

Characterisation

FTIR spectroscopic studies

The FTIR spectra of silica gel (SG) and Pani@SG(ES) nanocomposite are shown in Fig. 1. The main characteristic peaks of silica gel in spectrum are broad absorption band around 3435 cm⁻¹ corresponding to Si–OH stretching vibrations; the peaks at about 2857 and 2926 cm⁻¹ are due to symmetric and asymmetric –CH stretchings, respectively (Behera et al. 2006). 1633 cm⁻¹ is for the Si–OH bending mode of vibration; the strong absorption band at 1098 cm⁻¹ is due to the asymmetric stretching vibration of Si–O–Si bond because of the formation of SiO₂ network; the absorption peak at 800 cm⁻¹ represents Si–O–Si bending vibrations, and the band around 469 cm⁻¹ is due to the deformation vibration of Si–O–Si (Musicic et al. 2011; Kamitsos et al. 1993; Wood and Rabinovich 1989). In the case of Pani@SG(ES) nanocomposite, apart from the peaks of SG, the characteristic peak of 3440 cm⁻¹ due to the free (non-hydrogen bonded) N–H stretching vibration is present, confirming the presence of Pani in Pani@SG(ES) (Ansari and Mohammad 2012; Ansari et al. 2013). The FTIR spectrum of Pani@SG(ES) nanocomposite is almost similar to that of silica gel. However, the absorption of stretching vibration of alkyl groups becomes weak in IR spectra of Pani@SG. The stretching vibration of the alkyl group in the IR spectrum of pure silica gel seems to be due to the presence of traces of the alkyl group as a

Table 1 The composition details of mobile phases

Code	Composition of mobile phase
M ₁ -M ₅	10, 5, 2, 1 and 0.1% (w/v) aqueous 1-methyl-imidazolium chloride respectively
M ₆ -M ₁₀	10, 5, 2, 1 and 0.1% (w/v) aqueous 1,2,3-trimethylimidazolium-methyl sulphate, respectively
M ₁₁ -M ₁₅	10, 5, 2, 1 and 0.1% (w/v) aqueous 1-ethyl 3-methyl-imidazolium tetrafluoroborate, respectively

Table 2 Preparation details of Pani@SG nanocomposite-based stationary phases

Stationary phase	Code	Weight of aniline (g)	Weight of K ₂ S ₂ O ₈ (g)	Weight of silica gel (SG) (g)
Pure SG	S ₁	–	–	–
Pani@SG(ES)	S ₂	1.02	5.0	30.0
Pani@SG(EB ₁)	S ₃	1.02	5.0	30.0
Pani@SG(EB ₂)	S ₄	1.02	5.0	60.0

result of incomplete hydrolysis of tetraethylorthosilicate which is suppressed by the incorporation of polyaniline in silica gel (Sharma et al. 2015; Kausar and Siddiq 2015).

XRD studies

The XRD patterns (Fig. 2) show a broad peak at 2θ (21.98°) corresponding to the amorphous nature of silica with low intensity centred at an angle of around 2θ = 22.5 (Thuadaj and Nuntiya 2008) in the case of silica gel. However, Pani exhibits the characteristic peak around 2θ = 23 (Huang et al. 2008). The XRD pattern of Pani@SG(ES) nanocomposite is similar to that of silica gel.

SEM studies

The shape and surface morphologies of silica gel and Pani@SG(ES) nanoparticles have been demonstrated in Fig. 3a–d at two different magnifications. SEM images of silica nanoparticles shown in Fig. 3a, b are indicative of irregular, porous and spherical shape with relatively smooth surface. In Fig. 3c, d, Pani@SG(ES) nanoparticles show rougher surface probably due to the polymerisation of aniline on the surface of silica gel. The porosity of the surface of nanoparticles may increase due to presence of polyaniline (Goren et al. 2000; Guo et al. 2013).

However, both the micrographs are relatively similar and silica gel nanoparticles are mechanically very strong and not very distinct in nanocomposite.

EDX analysis

To identify the presence of different elements in the nanocomposites, EDX technique was used, and the representative EDX image of Pani@SG(ES) nanoparticles (Fig. 4) shows the presence of C, O, N and Si elements in nanoparticles.

TEM studies

Silica gel and Pani@SG (ES) nanocomposite were characterised to identify shape and size of their particles by TEM. Most of the silica gel particles are ellipsoidal with particle size ranging between 12 and 26 nm as evident from Fig. 5a. However, some irregular particles are also visible which finds support from the work of Wu et al. 2012. In the case of Pani@SG (ES) nanocomposite, it appears that the Pani undergoes polymerisation on the surface of silica gel leading to the formation of interconnected tubular nanostructures containing silica gel in the core (Fig. 5b). However, the SG surfaces became rough indicating the formation of Pani onto the SG surface with the size range of 21–35 nm. Thus, the material particles are in the nano range where Pani is tightly

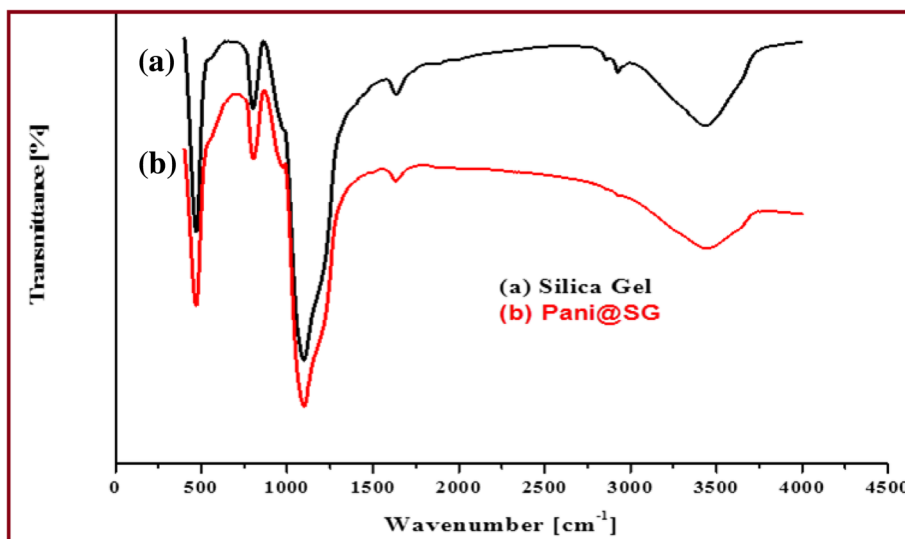


Fig. 1 FTIR spectra of (a) silica gel (S₁) and (b) Pani@SG (ES)-S₂ nanocomposites

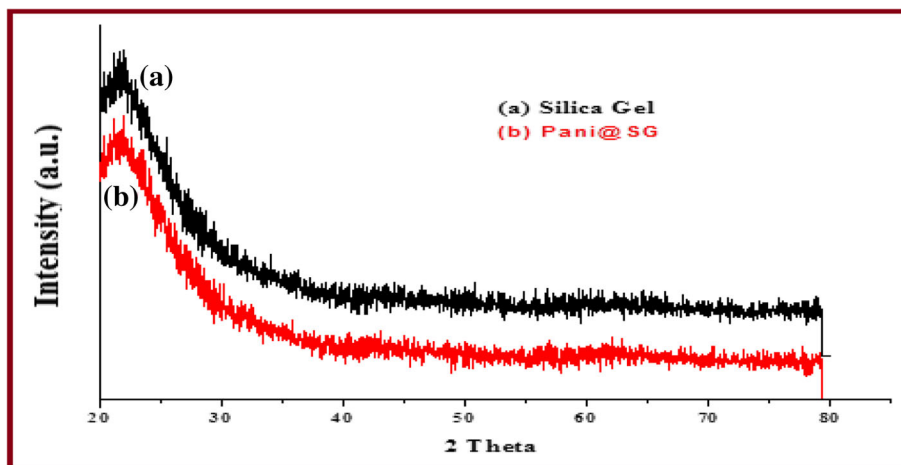


Fig. 2 XRD spectra of (a) silica gel (S_1) and (b) Pani@SG (ES)- S_2 nanocomposites

bound to SiO_2 facilitating its use in electronic and separation techniques (Chen et al. 2012).

Thin-layer chromatography

The preparation of TLC plates and chromatographic procedure were followed as reported earlier (Mohammad and Mobin, 2015a, 2015b). Aliquots (0.1 μ L) of

dyes were spotted on prepared TLC plates with stationary phases S_1 , S_2 , S_3 and S_4 . The plates were developed using different mobile phases M_1 – M_{15} . After development, spots were visualised and the R_F values were calculated for individual dyes. For mutual separations of dyes, equal volumes (1 mL each) of dyes viz. tartrazine (TZ), carmoisine (CS), brilliant blue (BB), alizarin red S

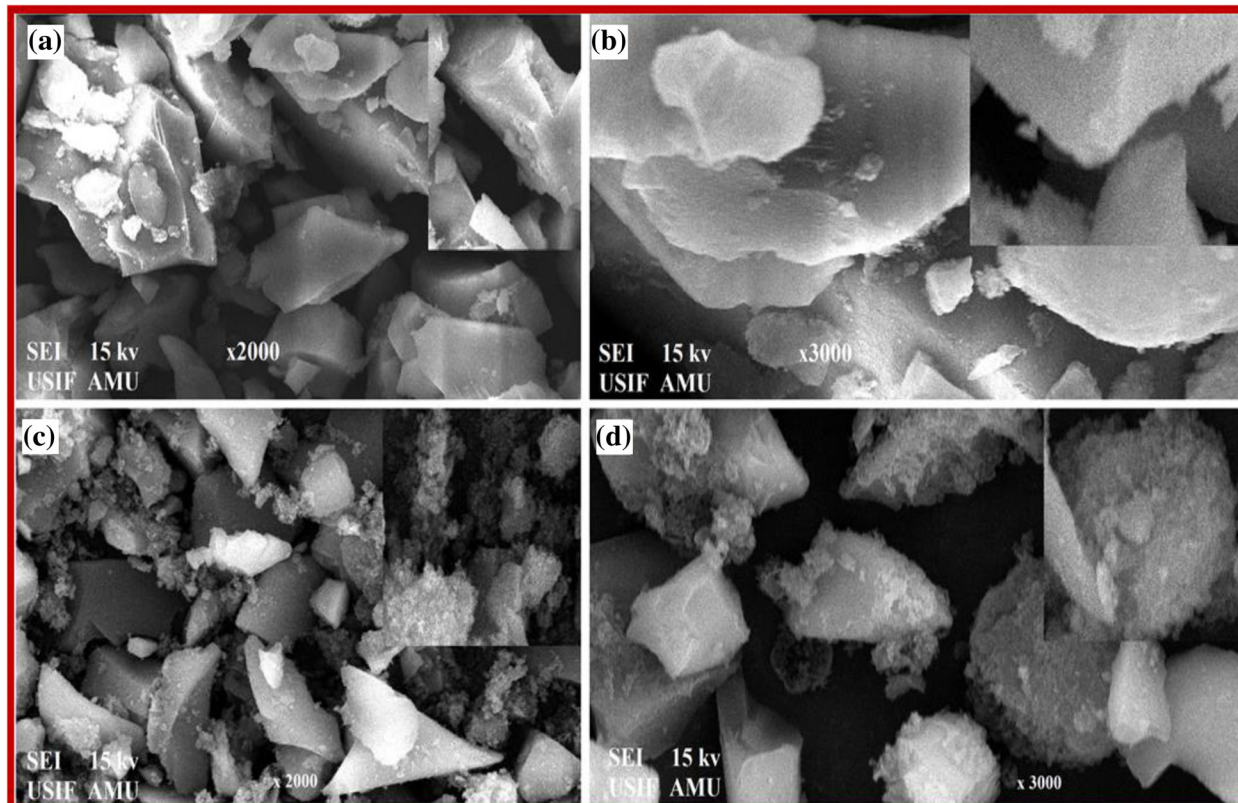


Fig. 3 SEM micrographs of a, b silica gel (S_1) and c, d Pani@SG (ES)- S_2 nanocomposite at different magnifications

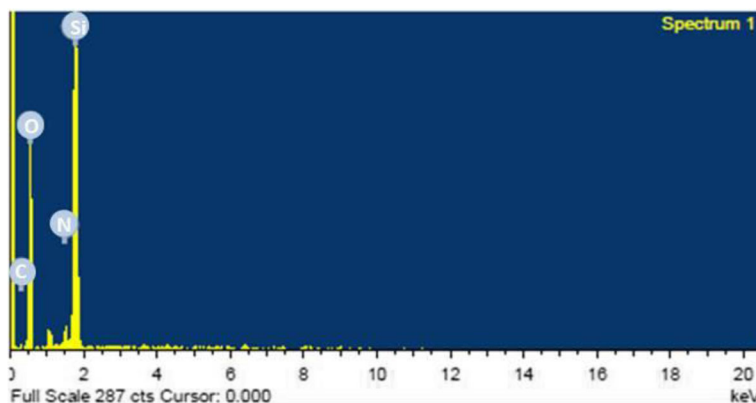


Fig. 4 EDX image of Pani@SG (ES)-S₂ nanocomposite

(AR), xylenolorange (XO) and bromo-cresol purple (BP) were mixed and 0.1 μL of the resultant mixture was spotted on the TLC plates. The plates were developed with selected mobile phase M₃ and stationary phase S₂. The spots were detected and the R_F values of the separated dyes were determined. The R_F values were calculated from the R_L (R_F of leading front) and R_T (R_F of trailing front) values of the spots by taking the average of two values as given below.

$$R_F = (R_L - R_T)/2.$$

For the separation of dye mixture, equal volumes of each dye were mixed and 0.1 μL of the resultant mixture was applied onto the TLC plates of silica gel or polyaniline-modified silica gel. The TLC plates were developed with different mobile phases, the spots were

detected, the R_F values were determined and other studies were carried out on the separated spots of the dyes. The representative TLC chromatogram for the separation of three-component mixture of dyes (tartrazine, alizarin red S and brilliant blue) on Pani@-SIG-ES layer developed with M₃ mobile phase has been presented in Fig. 6.

Effect of different ionic liquids on separation

To understand the separation behaviour of dyes in mobile phases having different concentrations of aqueous ionic liquids (1-methylimidazolium chloride, 1,2,3-trimethylimidazolium methyl sulphate and 1-ethyl 3-methylimidazolium tetrafluoroborate), the stationary phase systems of silica gel S₁ and polyaniline-modified silica gel S₂, S₃ and S₄ were used for the

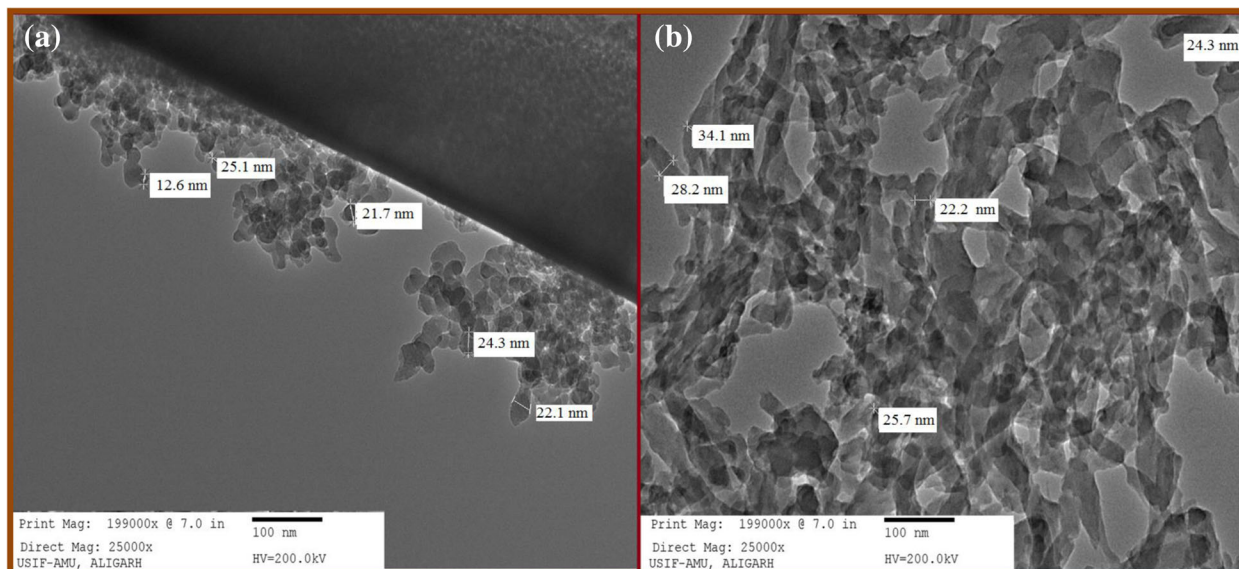


Fig. 5 TEM micrographs of **a** silica gel (S₁) and **b** Pani@SG (ES)-S₂ nanocomposite



Fig. 6 Separation achieved separation (or resolution) of three-component mixture of dyes (tartrazine, alizarin red S and brilliant blue) on Pani@SIG-ES layer developed with M_3 mobile phase

chromatography of dyes. The concentration of ionic liquid was varied from 0.1 to 2.0% (w/v). The R_F values obtained by using these stationary phases were compared with those obtained with S_2 stationary phase in M_3 mobile phase on which better separation was obtained.

Effect of foreign substances

For investigating the interference of metal cations and inorganic anions as impurities on the separation of the mixture, 0.1 μL of the test mixture of dye solutions was spotted on the Pani@SG(ES) TLC plate followed by spotting of 0.1 μL of the metal cations or inorganic anions being considered as impurities. The plates were developed with M_3 and detected, and the R_F values of the separated dyes were calculated.

Limits of detection

The detection limits of the dyes were determined by spotting 0.1 μL of tartrazine, carmoisine, brilliant blue, alizarin red S, xlenol orange and bromo-cresol purple of different concentrations on the Pani@SG(ES) TLC plates which were developed with the selected mobile phase M_3 , and the spots were visualised. This process was repeated by successive reduction of the concentration of dyes until the detection of the colour of dye was not visible by human eye. The amount of dye just detectable was taken as the detection limit.

Results and discussion

Pani@SG stationary phase

SG was modified by in situ oxidative polymerisation of aniline over it. Separations of mixture of organic dyes were more efficiently achieved on Pani@SG in comparison to SG. It may be understood that on modification of silica gel surface, there is a partial conversion of surface silanol groups to new organo-functional groups imparting considerably different sets of properties to the SG surface than the original (Shimada et al. 2003).

The following two types of interactions are supposed to be operative, viz. (i) lone pairs of oxygen of silica gel interacts with polarons of Pani (ES) and (ii) the lone pairs of nitrogen of Pani (EB) interacts with hydrogen of silica (Fig. 7). Thus, after modification of SG with Pani, both the positive and negative centres are developed on the stationary phases which are capable to selectively interact with the dyes in the mixture. The polarons of

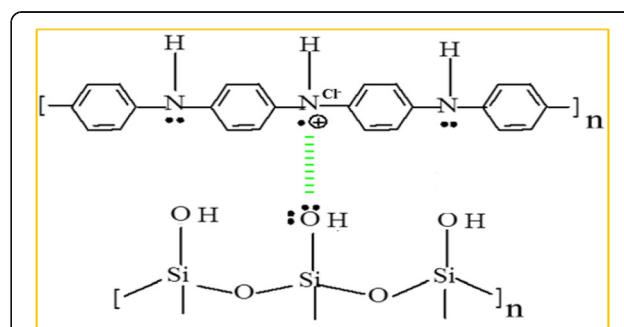


Fig. 7 Schematic presentation of interaction between Pani and silica gel Pani@SG nanocomposite

Pani interact with the oxygen atoms of the silanol groups via electrostatic interaction giving rise to a new organo-functional group with both positive and negative centres (Ahmad et al. 2016). In aqueous medium, dye molecule bears both positively and negatively charged centres along with other groups and hence can interact with the organo-functional groups of the stationary phase via electrostatic interaction. However, different dyes interact differently depending on their molecular structure. This difference in mobility due to different types of interactions of different dyes with organo-functional group of stationary phase eventually leads to their separation. Due to the polar nature of stationary phase, mobile phase and dye molecules, electrostatic interactions between the anionic dye and the polymer, hydrogen bonding (between H, O and N atoms in dye molecule and N and H atoms in polymer) and van der Waals forces (between the aromatic nature of polymeric matrix and the aromatic rings of the dye) are responsible for differential migration of dyes which eventually led to their separations. In the present case, brilliant blue, xylene orange and bromo-cresol purple are strongly retained by the stationary phase exhibiting very low R_F values (R_F ranges 0.02–0.05). It appears that steric hindrance due their bulkiness plays a dominant role to reduce the mobility of the dyes besides the strong electrostatic interaction between the dyes and stationary phase S_2 .

In the case of alizarin red S, the steric hindrance is lesser than that in brilliant blue, xylene orange and

bromo-cresol purple, and therefore, the mobility (R_F –0.26) of this dye was observed to be greater than that of the three dyes. But in the case of tartrazine dye, the steric hindrance and electrostatic interactions are minimal and therefore its R_F (0.55) is greater than the other four dyes leading to a very good separation from the others. The chemical structures of dyes under study are illustrated in Fig. 8.

Thin-layer chromatography of dyes tartrazine, carmoisine, brilliant blue, alizarin red S, xylene orange and bromo-cresol purple was performed on four different stationary phases, viz. (i) silica gel- S_1 , (ii) Pani@SG(ES), (iii) Pani@SG(EB₁) and (iv) Pani@S-G(EB₂) with 15 different mobile phases of ionic liquids for obtaining a novel TLC system for the separation of dyes from their mixtures. It was noticed that the anionic part (chloride, sulphate or tetrafluoroborate) of ionic liquids marginally affects the magnitude of R_F values of dyes. Obtained results tabulated in Tables 3, 4, 5, 6, 7, 8 and 9 and presented in Figs. 7, 8, 9, 10 and 11 are discussed below.

(A) Silica gel (SG) as stationary phase S_1

(a) *1-Methylimidazolium chloride* [M_1 – M_5]: With 10% aqueous 1-methylimidazolium chloride (M_1) on pure silica gel stationary phase (S_1), separation of BB, AR, XO and BP dyes ($R_F = 0.04$ – 0.12) which remained near the point of application due to strong interaction with stationary phase is possible from TZ

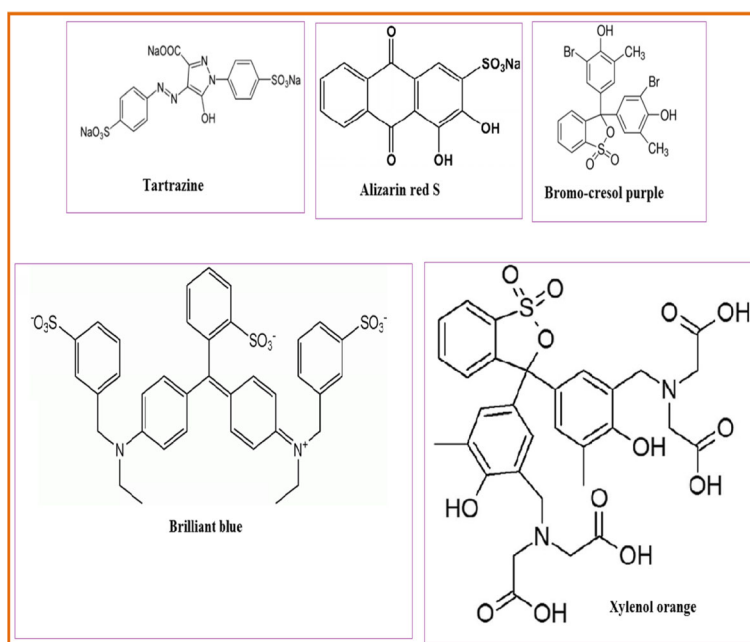


Fig. 8 Chemical structures of the dyes

Table 3 Mobility of dyes in terms of R_F values on stationary phase S_1 with different mobile phases

Mobile phase	R_F values					
	CS	TZ	BB	AR	XO	BP
M ₁	0.20	0.55	0.04	0.05	0.04	0.12
M ₂	0.15	0.35 T	0.05	0.05	0.08	0.15
M ₃	0.33	0.60 T	0.01	0.26	0.27	0.26
M ₄	0.25	0.55 T	0.05	0.13	0.12	0.06
M ₅	0.46 T	0.55 T	0.04	0.35 T	0.45 T	0.25
M ₆	0.12	ND	0.02	0.25	0.12	0.25
M ₇	0.10	0.18	0.01	0.04	0.04	ND
M ₈	0.25 and 0.95 DS	0.20 and 0.97 DS	0.03	0.09	ND	ND
M ₉	0.10	0.15 and 0.93 DS	0.04	0.35 T	0.13 and 0.93 DS	0.16 and 0.85 DS
M ₁₀	0.15 and 0.73 DS	0.15 and 0.97 DS	0.05	0.15	0.12 or 0.85 DS	0.11
M ₁₁	0.20	0.35	0.02	ND	0.10	0.14
M ₁₂	0.21	0.22	0.01	0.02	0.24	0.21
M ₁₃	0.20	0.30	0.01	0.15	0.40 T	0.40 T
M ₁₄	0.15	0.20	0.03	0.1	0.05	0.11
M ₁₅	0.12 and 0.88 DS	0.20 and 0.97 DS	0.02	0.12 and 0.86 DS	0.12	0.20

CS carmoisine, TZ tartrazine, BB brilliant blue, AR alizarin red S, XO xlenol orange, BP bromo-cresol purple, ND not detected, DS double spots, T tailed spot, $R_L - R_T \geq 0.3$

($R_F = 0.55$). At lower concentration of 1-methylimidazolium chloride, e.g. 5–0.1% (M₂, M₅), CS can be separated in the case of M₂, M₃ and M₄ from BB. However, TZ produced tailed spots as shown in Table 3.

(b) 1,2,3-Trimethylimidazolium methyl sulphate [M₆–M₁₀]: At all the concentrations (10–0.1%) of aqueous 1,2,3-trimethylimidazolium methyl sulphate

(M₆–M₁₀), BB remained near the point of application. Some dyes produced tailed spots.

Double spots for TZ with M₈, M₉ and M₁₀ mobile phases were realised; hence, the mobile phase systems (M₆–M₁₀) are not suitable for separation of dyes (Table 3).

(c) 1-Ethyl 3-methyl-imidazolium tetrafluoroborate [M₁₁–M₁₅]: Separation of TZ ($R_F = 0.20$ – 0.35) from BB ($R_F = 0.01$ – 0.02) in M₁₁–M₁₄ mobile phases is possible. In the case of M₁₃, XO and BP showed tailed spots while CS, TZ and AR produced double spots in the case of M₁₅. Thus, no good separations could be achieved (Table 3).

Table 4 Mobility of dyes in terms of R_F values on stationary phase S_2 with different mobile phases

Mobile phase	R_F values					
	CS	TZ	BB	AR	XO	BP
M ₁	0.18	0.55	0.01	0.04	0.04	ND
M ₂	0.12	0.45	0.04	0.04	0.05	0.03
M ₃	0.17	0.55	0.03	0.26	0.05	0.02
M ₄	0.18	0.50 T	0.02	0.05	0.04	0.05
M ₅	0.45 T	0.60	0.01	0.50 T	0.18	0.24
M ₆	0.12	ND	0.01	0.1	0.11	0.06
M ₇	0.05	ND	0.02	0.08	0.07	0.14
M ₈	0.30 T	ND	0.01	0.05	0.05	0.04
M ₉	0.18	0.30	0.01	0.08 and 0.80 DS	0.40 T	0.15
M ₁₀	0.45	0.14	0.03	0.13	0.14	0.06
M ₁₁	0.12	0.25	0.02	0.21	0.20	0.20
M ₁₂	0.10	ND	0.01	0.12	0.11	0.10
M ₁₃	0.40 T	0.13	0.04	0.40 T	0.17	0.14
M ₁₄	0.10	0.18	0.01	0.05	0.05	ND
M ₁₅	0.47 T	0.10 and 0.97 DS	0.04	0.11 and 0.74 DS	0.40 T	0.20

All abbreviations are as in Table 3

(B) Polyaniline-modified silica gel S_2 , S_3 and S_4

(i) Stationary phase S_2

(a) 1-Methylimidazolium chloride (M₁–M₅): The selective separation of TZ from BB, AR, XO and CS is always possible on S_2 stationary phase with M₁–M₃ mobile phases. TZ in M₄ and CS as well as AR in M₅ showed tailed spots on S_2 . The differential migration of dyes (TZ, BB, AR, XO and BP $R_F = 0.55, 0.03, 0.26, 0.05$ and 0.02 , respectively) achieved with M₃ mobile phase on Pani@SG-ES stationary phase, and hence, this TLC system was considered most favourable for ternary separations such as TZ-BB-AR, TZ-AR-XO and TZ-AR-BP (Table 4). This system was selected for further detailed studies. The R_F value of BB remained almost unchanged on variation of concentration of ionic liquid from 0.1 to 10% in aqueous mobile phase.

Table 5 Mobility of dyes in terms of R_F values on stationary phase S_3 with different mobile phases

Mobile phase	R_F values					
	CS	TZ	BB	AR	XO	BP
M ₁	0.05	0.60	0.01	ND	0.05	ND
M ₂	0.12	0.61	0.02	ND	ND	ND
M ₃	0.15	ND	0.05	0.24	0.25	ND
M ₄	0.25	0.47	0.03	ND	0.40	0.01
M ₅	0.60	0.50 T	0.01	ND	0.04	ND
M ₆	0.18	ND	0.02	0.07	0.08	0.18
M ₇	0.15	0.16	0.03	0.08	0.15	0.12
M ₈	0.40 T	0.30	0.01	0.10	0.09	ND
M ₉	0.43 T	0.50 T	0.04	0.15 and 0.84 DS	0.15 and 0.76 DS	0.20
M ₁₀	0.45 T	0.53 T	0.1	0.15 and 0.86 DS	0.13 and 0.73 DS	0.18
M ₁₁	0.18	0.25	0.01	0.14	0.18	0.20
M ₁₂	0.15	0.30	0.02	0.11	0.10	0.14
M ₁₃	0.40 T	0.15	0.03	0.04	0.03	0.03
M ₁₄	0.10	0.12	0.01	0.05	ND	ND
M ₁₅	0.1 and 0.80 DS	0.1 and 0.90 DS	0.04	0.11 and 0.86 DS	0.10 and 0.80 DS	0.15

All abbreviations are as in Table 3

(b) *1,2,3-Trimethylimidazolium methyl sulphate* (M_6 – M_{10}): In M_6 – M_8 mobile phase systems, TZ was not detected and BB, AR as well as XO remained near the point of application on stationary phase S_2 . With M_9 , AR appeared in the form of double spots while XO showed tailed spot. Binary separations such as TZ-BB with M_9 and CS-BB and CS-BP with M_{10} mobile phases are possible (Table 4).

Table 6 Mobility of dyes in terms of R_F values on stationary phase S_4 with different mobile phases

Mobile phase	R_F values					
	CS	TZ	BB	AR	XO	BP
M ₁	0.04	0.60	0.01	0.12	0.12	ND
M ₂	0.14	0.60	0.03	0.08	ND	0.10
M ₃	0.20	0.37	0.05	0.14	0.12	0.14
M ₄	0.14	0.35	0.02	0.17	0.16	0.10
M ₅	0.47 T	0.54 T	0.03	0.40 T	0.42 T	0.22
M ₆	0.18	ND	ND	0.06	0.06	0.13
M ₇	0.12	0.15	0.02	0.11	0.10	0.14
M ₈	0.40 T	0.18	0.03	0.07	0.06	0.08
M ₉	0.05	NS	0.02	0.13	0.15	0.17
M ₁₀	0.10	0.05	0.01	0.10	0.13	0.13
M ₁₁	0.12	0.27	0.01	0.18	0.18	0.17
M ₁₂	0.08	ND	0.02	0.15	0.15	0.16
M ₁₃	0.10	0.15	0.01	0.44 T	0.24	0.21
M ₁₄	0.09	0.1	0.01	0.10	0.11	0.15
M ₁₅	0.45 T	0.11 and 0.96 DS	0.04	0.10 and 0.86 DS	0.40 T	0.18

All abbreviations are as in Table 3

Table 7 Separated dyes on the nature of stationary phases developed with different mobile phases

Mobile phase	Stationary phase	Separation
M ₁	S ₁	TZ-BB, TZ-AR, TZ-XO, TZ-BP
M ₃	S ₁	CS-BB, BB-AR, BB-XO
M ₄	S ₁	CS-BB
M ₆	S ₁	BB-AR, BB-BP
M ₁₁	S ₁	TZ-BB
M ₁₃	S ₁	CS-BB, TZ-BB
M ₁₄	S ₁	TZ-BB, TZ-XO
M ₁	S ₂	TZ-BB, TZ-AR, TZ-XO
M ₂	S ₂	TZ-BB, TZ-AR, TZ-XO, TZ-BP
M ₃	S ₂	TZ-BB-AR, TZ-AR-XO, TZ-AR-BP
M ₅	S ₂	TZ-BB, TZ-XO
M ₉	S ₂	TZ-BB
M ₁₀	S ₂	CS-BB, CS-BP
M ₁₁	S ₂	TZ-BB
M ₁	S ₃	CS-TZ, TZ-BB, TZ-XO
M ₂	S ₃	CS-TZ, TZ-BB
M ₄	S ₃	TZ-BB, TZ-BP, BB-XO
M ₅	S ₃	CS-BB, CS-XO
M ₈	S ₃	TZ-BB
M ₁₂	S ₃	TZ-BB
M ₁	S ₄	CS-TZ, TZ-BB, TZ-AR, TZ-XO
M ₂	S ₄	CS-TZ, TZ-BB, TZ-AR, TZ-BP
M ₃	S ₄	TZ-BB
M ₄	S ₄	TZ-BB
M ₁₁	S ₄	TZ-BB

Table 8 Effect of interference on ΔR_F , separation (α) and resolution (R_S) factors of the separation of ternary mixtures of dyes

	Ternary separations					
	TZ-AR-BB					
	TZ-AR		AR-BB			
	ΔR_F (0.50)	α (10.2)	R_S (35.5)	ΔR_F (0.28)	α (26.3)	R_S (30.4)
Cations						
Cu ²⁺	0.52	10.051	32.5	0.22	29.571	24.44
Zn ²⁺	0.53	10.707	36.55	0.24	17.216	26.66
Mn ²⁺	0.57	13.499	42.222	0.18	23.222	30.00
Ni ⁺	0.39	5.221	26.896	0.32	48.761	35.55
Anions						
CO ₃ ²⁻	0.51	9.588	32.903	0.24	11.958	26.66
NO ₃ ⁻	0.55	11.87	33.33	0.21	27.923	20.00
Br ⁻	0.47	10.038	55.294	0.12	14.793	30.00
Cl ⁻	0.55	12.318	44.00	0.17	21.731	22.66
CH ₂ COO ⁻	0.57	14.571	54.285	0.27	38.499	41.53

(c) *1-Ethyl 3-methyl-imidazolium tetrafluoroborate* (M_{11} – M_{15}): Most of the dyes are not separable with M_{11} – M_{15} mobile phases on stationary phase S_2 . However, TZ-BB separation is possible with M_{11} . TZ and BP are not detected in M_{12} and M_{14} , respectively. While CS showed tailed spots in M_{13} as well as M_{15} , AR produced tailed spots in M_{13} . In M_{15} , double spots for TZ and AR appeared (Table 4).

(ii) Stationary phase S_3

(a) *1-Methylimidazolium chloride* (M_1 – M_5): On stationary phase S_3 , the mobility of CS slightly increases with decreasing concentration of ionic liquid. With mobile phases M_1 – M_2 , TZ ($R_F = 0.60, 0.61$, respectively) can be separated from BB ($R_F = 0.01, 0.02$, respectively) and CS ($R_F = 0.05, 0.12$, respectively). Furthermore, TZ-XO separation with M_1 mobile phase is also possible. AR and BP organic dyes were not detected when TLC plates were developed with M_1, M_2 mobile phases. With M_3 mobile phase, TZ and BP were not detected and AR, XO and CS showed broad peaks and remained BB near

the point of application. On S_3 with M_4 mobile phase, binary separations such as TZ-BP, TZ-BB and BB-XO are possible while AR is not detected as shown in (Table 5). With M_5 mobile phase, CS-BB and CS-XO separations are possible whereas other dyes (AR and BP) could not be detected and TZ showed tailed spots.

(b) *1,2,3-Trimethylimidazolium methyl sulphate* (M_6 – M_{10}): In M_6 and M_7 mobile phases on S_3 stationary phase, CS, XO and BP showed broad spots and both the BB and AR remained near the point of application; hence, no separation possibilities arise. In M_8 mobile phase, TZ can be separated from BB. There are no separation possibilities in most cases due to formation of either tailed spots or double spots of dyes (Table 5).

(c) *1-Ethyl 3-methyl-imidazolium tetrafluoroborate* (M_{11} – M_{15}): In M_{11} – M_{15} mobile phases, CS, TZ, AR, XO and BP dyes showed broad spots with M_{11} on S_3 . Tailed spots in M_{13} of CS and non-detectability of XO and BP in M_{15} hampered the separation possibilities. Double spots were realised for CS, TZ, AR and XO with M_{15} (Table 5).

(iii) Stationary phase S_4

(a) *1-Methylimidazolium chloride* (M_1 – M_5): This TLC system is most suitable for the selective separation of TZ from other food dyes under study with M_1 – M_4 mobile phase system. However, with M_5 tailed spots for CS, TZ, AR and XO on S_4 were noticed (Table 6).

(b) *1,2,3-Trimethylimidazolium methyl sulphate* (M_6 – M_{10}): In M_6 mobile phase on S_4 stationary phase, BB and TZ could not be detected and tailed spot of CS with M_8 mobile phase was observed. From a separate point of view, this TLC system is unsuitable for analysis of dyes (Table 6).

(c) *1-Ethyl 3-methyl-imidazolium tetrafluoroborate* (M_{11} – M_{15}): With M_{11} – M_{14} mobile phases, all the dyes showed little mobility and remained near the point of application. In M_{12} , TZ was not detected and AR showed tailed spot in M_{13} . There was no separation possibility in the case of M_{15} mobile phase; tailed spots of CS and XO and double spots of TZ and AR were obtained as reported in Table 6. There is no possibility of separation of dyes with this TLC system.

Table 9 Identification of tartrazine (in Roscillin[®]) and brilliant blue (in Ambrodil[®]S) according to their R_F values

Dyes	R_F value	
	Standard sample	Drug sample
Brilliant blue	0.03	0.05
Tartrazine	0.55	0.48

From the results listed in Tables 3, 4, 5, 6 and 7, several combinations of stationary and mobile phases are capable to resolve two-component mixtures of dyes which are listed in Table 7. However, the best TLC system was S_2 – M_3 which facilitated the separations of three-component mixtures of dyes (Fig. 9).

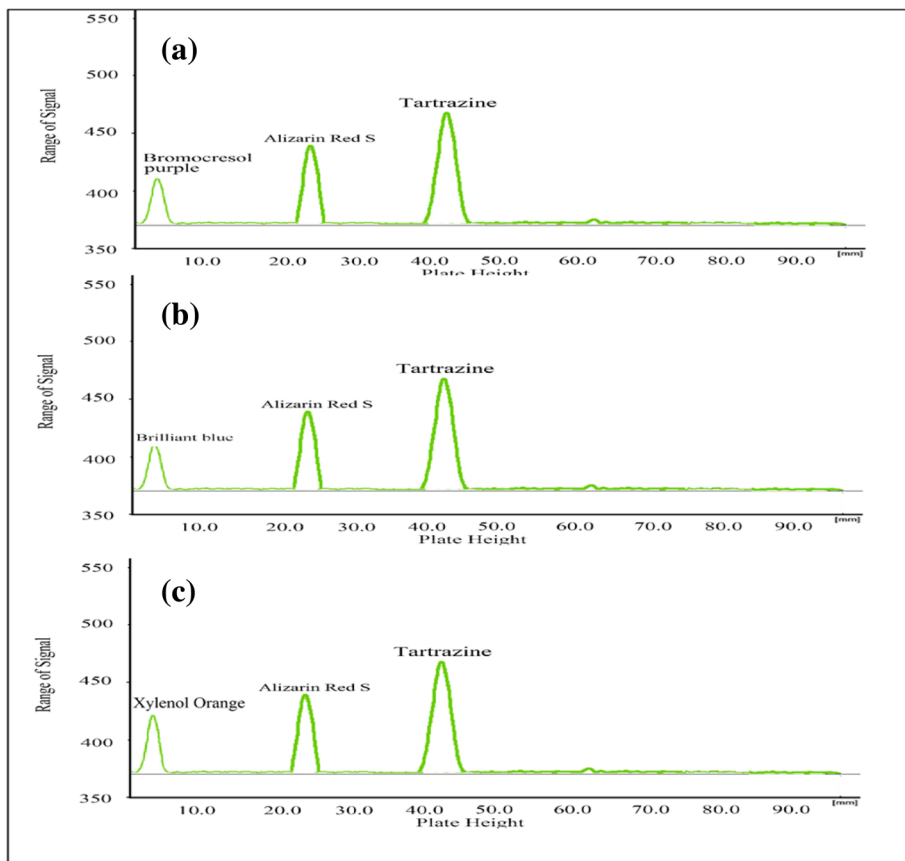


Fig. 9 Densitographic presentation of representative separations of three-component mixtures of dyes achieved with M_3 mobile phase on S_2 stationary phase. **a** TZ-AR-BP. **b** TZ-BB-AR. **c** TZ-AR-XO

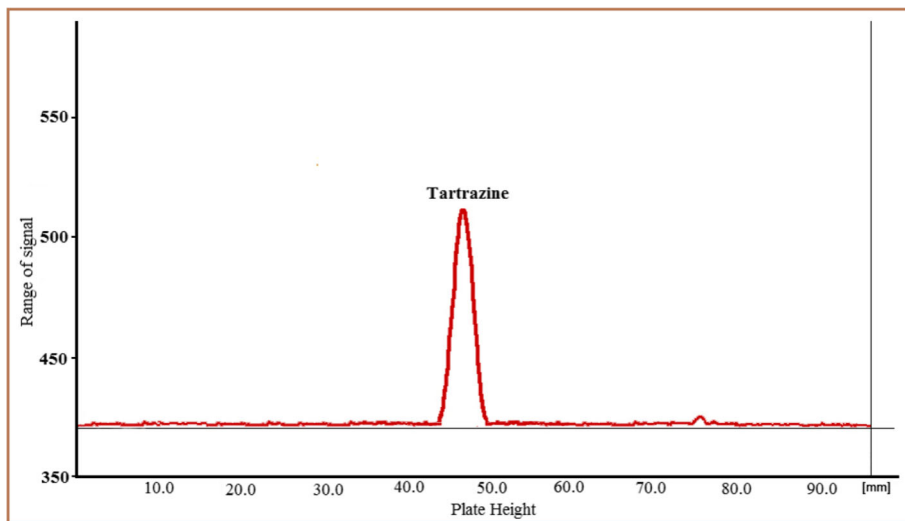


Fig. 10 Densitographic illustration of identification of tartrazine in Roscillin^R syrup with preliminary separation from associated components on S_2 with M_3

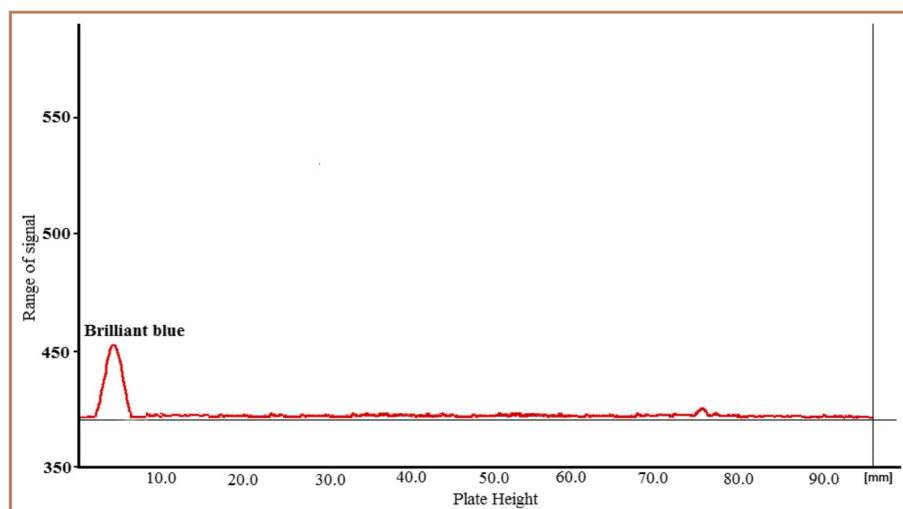


Fig. 11 Densitographic illustration of identification of brilliant blue in Ambrodil[®]S syrup with preliminary separation from associated components on S_2 with M_3

Effect of replacement of silica with modified Pani@SG stationary phase

Modified silica gel was used in place of silica gel with the hope of getting new separations. In the case of Pani@SG (ES), ternary separation was obtained with 2% aqueous 1-methyl-imidazolium chloride (M_3) mobile phase. The separation efficacy of different stationary phases towards dyes was in the order or $S_2 > S_4 > S_1 > S_3$. It appears that the differences in surface area and activity level of these stationary phases influence the separation pattern. Compared to plain (or non-modified) silica gel, Pani-modified silica gel performs better as stationary phase in the separation of dyes.

Effect of interference

Effect of metal cations and anions on the magnitude of separation factor (α), resolution parameter (R_s) and ΔR_F values for separation of three-component mixtures consisting of TZ, AR and BB has been examined, and the results are presented in Table 8. From the results, it is clear that magnitude of these parameters is marginally influenced (increased or decreased) in the presence of these foreign substances, but separation was always possible in each case. The minor change in the value of these parameters was due to the slight increase in spot size of the analyte because of certain interactions of dyes with these foreign substances.

Ageing effect of mobile phase

The stability (ageing effect) of mobile phase (M_3) on the separation was insignificant since slight variation in their R_F values was observed during the separation of dyes from their ternary mixture with the use of freshly prepared mobile phase and use of the same mobile phase

after storing for 24 h. Hence, it can be concluded that the composition of mobile phase (M_3) remains unaltered for several hours, and therefore, it is most suitable for chromatographic analysis.

Limit of detection

The lowest possible detectable amounts ($\mu\text{g}/\text{spot}$) of carmosine, tartrazine and brilliant tartrazine, carmoisine, brilliant blue, alizarin red S, xylenol orange and bromocresol purple on S_3 developed with M_3 (2% aqueous 1-methylimidazolium chloride) were 1.0, 0.75, 1.0, 1.0, 1.25 and 1.0, respectively.

Applications

The proposed thin-layer chromatographic method comprising of polyaniline-modified silica gel Pani@SG(ES) as stationary phase and 2% aqueous 1-methyl-imidazolium chloride (M_3) as mobile phase is applicable for the identification of tartrazine in Roscillin^R and brilliant blue in Ambrodil[®]S syrups (Table 9 and Figs. 10 and 11).

Conclusions

It may be concluded that the use of thin-layer chromatographic system consisting of polyaniline-modified silica gel (S_2) as stationary phase with 2% aqueous 1-methylimidazolium chloride as eco-friendly mobile phase is most favourable for the identification and separation of three-component mixtures of tartrazine, alizarin red S and brilliant blue, bromo-cresol purple and xylenol orange. The chosen TLC system is also applicable for the identification of these food dyes in pharmaceutical products (Roscillin^R and Ambrodil[®]S syrups). The use of aqueous solutions of cationic and ionic liquids as green mobile phase systems makes the proposed TLC systems

as environment friendly and paves the way for the development of green chromatography as a future analytical technique.

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Authors' contributions

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Competing interests

The authors declare that they have no competing interests.

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