A salt-free, zero-discharge and dyebath-recyclable circular coloration technology based on cationic polyelectrolyte complex for cotton fabric dyeing

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Research Article

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Abstract

Textile industry is one of the most polluting industries due to the large quantities of dyeing wastewater it generates and discharges. Herein, we report an eco-friendly and sustainable circular coloration technology based on cationic polyelectrolyte complex to realise salt-free, zero-effluent-discharge circular dyeing for cotton fabrics with a recyclable dyebath by using a typical cationic polyelectrolyte polyhexamethylene biguanide (PHMB) bonded with anionic dyes. The cotton fabrics were first treated with PHMB and then dyed with three commercial acid dyes. Colour measurements show that the colour strength is controllable by adjustment of concentrations of both PHMB and the dyebath. The dyed fabric samples were found to have good/excellent colour levelness (< 0.49), and the colour fastness (Grade 3 ~ 5) was basically satisfactory and acceptable. The dyebath was proved to be recyclable for circular dyeing occurring at room temperature, which greatly reduces consumption of both water and heat energy for textile dyeing. Meanwhile, the dyed fabrics showed antimicrobial activity, particularly for the gram-positive S. aureus, which may help reduce the healthcare-associated infections that transmit through textiles. These results suggest that cationic polyelectrolyte-based circular dyeing could provide a promising and practicable strategy to address the pollution issue caused by wastewater generated in dyeing process in the textile industry.

Introduction

The dyeing of textiles is widely considered as one of the most polluting industry sectors due to the volume and composition of effluents it discharges (Khatri et al. 2015). Apart from a variety of synthetic dyestuffs, textile dyeing also consumes huge volumes of water, energy, and auxiliaries, e.g., salts, electrolytes, acids, alkali/bases, levelling agents, penetrating agents and dispersing agents, which can and does lead to large effluent discharge and causes serious environmental burden and health issues (Burkinshaw and Salihu 2019; Ozturk et al. 2020). It has been reported that the annual consumption of reactive dyes for cellulosic fibres dyeing exceeds 400, 000 tons, and up to 50% of that is discharged into the environment in the form of unutilised or hydrolysed dye, resulting in highly polluting effluents with high oxygen demand and salt load (Xie et al. 2016; Nallathambi and Venkateshwarapuram 2017; Mu et al. 2019). The presence of dyes in aquatic environment is not only aesthetically undesirable but it also causes toxic and carcinogenic effects on living organisms, thereby severely threating the aquatic ecological environment (Zhao et al. 2020).

In order to eliminate effluents and reuse water, numerous studies have been conducted to develop a wide variety of techniques and methodologies for removal of dye from wastewater (Dasgupta et al. 2015; Wang et al. 2021). Examples include adsorption by adsorbents, oxidation, photocatalytic degradation, biological treatment, ozonation, electrochemical treatment, membrane filtration and chemical coagulation/flocculation, etc. (Cai et al. 2021; Ahmad et al. 2015; Vikrant et al. 2018; Yagub et al. 2014; Furlan et al. 2010). Among them, chemical coagulation and flocculation have been widely employed for pretreatment of dyeing wastewater by using cationic polyelectrolyte complex due to its low capital cost and the tailorability (Wilts et al. 2018; Sun et al. 2016). Cationic polyelectrolytes for coagulation and flocculation such as cationic polyacrylamides, chitosan and poly(diallyldimethyl ammonium chloride, PDDA) are water-soluble polymers with positively charged moieties on each repeating unit which allow interaction with anionic dye molecules (Meka et al. 2017; Song et al. 2018). Cationic polyelectrolytes have the tendency to form polyelectrolyte complexes with negatively charged ions predominated by the electrostatic interactions, leading to phase separation and formation of stable and insoluble precipitation in most common solvents (Zahrim et al. 2011). Meanwhile, it is the theoretical basis for the spectrophotometric method to quantify quaternary ammonium compounds using a low-molecular anionic dye such as bromophenol blue (Auerbach 1943; Sakai 1983). The anions of aqueous salts of bromophenol blue initially reacts with cationic polyelectrolytes via ion-ion bonding at ambient temperature to form a stable and water-insoluble dye, which is then extracted by chlorinated solvents and thus spectrophotometrically determined (Nand and Ellwood 2018).

On the other hand, cationic polyelectrolytes also find wide applications as cationic agents such as chitosan and PDDA in cationisation of cellulosic fibres to improve dyeability and reactivity by changing the fibre surface charge and thus enhancing dye adsorption (Fang et al. 2015; Correia et al. 2020). Therefore, utilisation of reactive dyes is enhanced while the use of organic salts is reduced or eliminated, thereby contributing to alleviation of pollution resulting from effluent discharge (Arivithamani and Giri Dev 2018; Ma et al. 2020). For example, Dong and coworkers (2020) successfully grafted 2-(N, N-dimethylamino) ethyl methacrylate on the surface of cotton fabrics, and the dyeing showed excellent colour strength, dye uptake, fixation yield and levelness in a low-salt dyeing process by using reactive dye. Acharya et al. (2014) utilised a typical cationic agent, i.e., (3-chloro-2-hydroxylpropyl)trimethylammonium chloride (CHPTAC), to treat cotton fabrics by the exhaustion method, and found that the colour strength and dye uptake with reactive dyes in salt-free dyeing was greatly increased. Fang and colleagues (2013) cationised cotton fabric with the cationic agent acrylamide and improved utilisation of the reactive dyes in salt-free dyeing. Compared with the traditional dyeing process, the dyeing mechanism for cationised cotton fabric with reactive dyes remains unchanged, and it still involves diffusion, penetration, and adsorption of dye molecules onto the fibre. In essence, cationisation of cellulosic fibres functions as inorganic salts (sodium sulphate or sodium chloride) used in traditional cotton dyeing process to promote dye adsorption by reducing the charge repulsion. Actually, even though the researchers claimed that salt-free dyeing process with reactive dyes was performed for the dyeing of cationised cotton fabrics, they still utilised another inorganic salt—sodium carbonate to enhance the dye fixation (Acharya et al. 2014; Fang et al. 2013). Moreover, it is impossible to realise zero discharge of dye wastewater and 100% utilization of dyes via cationic modification of cotton fabric. The dyebath after dyeing is non-recyclable and needs to be discharged into the environment. Consequently, it is essential to develop an ecologically sustainable and economical dyeing technology to address the pollution issue associated with effluent discharge in textile dyeing.

Additionally, another widespread application of cationic polyelectrolytes in textile industry is used as antimicrobial agents such as polyhexamethylene biguanide (PHMB) due to its high biocidal ability, hypotoxicity and reasonable cost (Simoncic and Tomsic 2010; Wang and Kan 2020). Blackburn and coworkers (2006) demonstrated that the adsorption mechanism of PHMB on cellulosic fibre follows the

Langmuir isotherms at low concentrations with the formation of monomolecular layer, whereas at higher concentrations it shows the characteristics of the Freundlich isotherms, leading to stacking of multilayer PHMB molecules via electrostatic interaction and hydrogen bond. Moreover, owing to the small molecule diameter (22 Å), PHMB molecules can diffuse into the inner pores of the cellulose fibres (80 Å) (Wågberg and Hägglund 2001; Blackburn et al. 2006). This could be responsible for the strong affinity of PHMB molecules to cellulosic fibres and the good durable properties of PHMB treated cellulosic fabrics in resistance to abrasion during wearing and household washing (Cao et al. 2020; Chen-Yu et al. 2007). Bhaskara et al. (2021) studied the kinetics of adsorption and desorption of PHMB on cotton fabrics and concluded that nearly zero desorption PHMB was observed from the surface of cotton fabrics at low concentrations. The underlying reason may consist in both the electrostatic interaction and diffusion of PHMB molecules into the inner cores of cellulose fibres.

Based on our previous findings (Wang and Kan 2020; Wang et al. 2021), we are motivated to develop an environment-friendly dyeing method with recyclable dyebath and zero effluent discharge (Fig. 1), considering the stable and insoluble precipitation stoichiometrically formed between anionic dyes and cationic polyelectrolytes at room temperature. The dyeing heavily depends on the stoichiometric reaction predominated by electrostatic force between positively charged polyelectrolytes and negatively charged dye molecules and can occur at room temperature without addition of inorganic salts, which enables the dyebath to be completely recyclable without being discharged into the environment. As shown in Fig. 1, the cellulosic fabric is initially treated with cationic polyelectrolytes and then dyed with anionic dyes at room temperature; after first dyeing, the dyebath is recycled for the second and/or third dyeing. The dyebath is replenished for circular dyeing if concentration of dyebath becomes too low after serial dyeings.

This study aims to explore feasibility and applicability of the above proposed proof-of-concept. The representative antimicrobial agent PHMB was selected as the model cationic polyelectrolyte to treat cotton fabrics, which were then dyed with three commercial anionic acid dyes commonly used to dye wool and silk that contain many cationic sites (protonated -NH_2 groups). The dyed fabric samples were evaluated by a series of analytical techniques in terms of colour strength, colour levelness and dyebath recyclability for circular dyeing.

Experimental

Materials

Desized and scoured plain-woven 100% cotton fabric (fabric weight 175 g/m^2) was used for this study. Polyhexamethylene biguanide (PHMB) was procured from Breakthrough Textiles Co., Ltd (Taipei City, Taiwan) as a 20% w/v aqueous solution. C13-oxoalcoholethoxylates (7EO) used as nonionic detergent was supplied by SDC Enterprises Limited, Holmfirth, UK. Three model anionic dyes C.I. Acid Red 127, C.I. Acid Blue 83 and C.I. Acid Black 172 were obtained from Shanghai Anoky Group Co., Ltd. (China). Chemical structures of PHMB and the three anionic acid dyes are given in Fig. 2.

PHMB coated onto cotton fabrics

Cotton fabric specimens (20×30cm) were initially exhausted in prediluted PHMB solutions (0.2% and 0.4% w/v) for 5 minutes to achieve uniform deposition, and then padded in a laboratory-scale horizontal roller with a wet uptake of 80%. Afterwards, the samples were dried at 90 ^{o}C for 2 minutes, followed by curing for 1 minute at 140 ^{o}C. The specimens prepared with PHMB solutions of 0.2% and 0.4% (w/v) were labelled as PH02 and PH04, respectively.

Dyeing

The dyebath (300 mg/L, 500 mg/L) of three model acid dyes was prepared before dyeing. PHMB-coated cotton fabrics (PH02, PH04) were directly dipped in the dyebath (liquor ratio 50:1) at ambient temperature for 1 hour. Then, the dyed fabrics were withdrawn and washed with copious running water to remove the unfixed dyes. Afterwards, the dyed cotton fabrics were dried in air. Suffixes − 300 and − 500, related to 300 mg/L and 500 mg/L dye concentration respectively, distinguish the PH02 and PH04 samples in the following discussion, i.e., PH02-300, PH02-500, PH04-300, and PH04-500.

Recycled dyebath for circular dyeing

To validate the reusability of recycled dyebath (circulating dyeing), the 500 mg/L dyebath of three acid dyes after first dyeing of PH02 was collected and reused for circular dyeing (Fig. 1). The samples were named PH02-1, PH02-2 and PH02-3 for first, second and third dyeing processes (with the same bath) in Fig. 1, respectively. After the third dyeing, the dyebath was replenished to maintain original concentration for circular dyeing, i.e., PH02-4. The conditions for dyeing remained unchanged, and the concentration of dyebath was spectrophotometrically determined after each dyeing.

Fourier transform infrared (FTIR) analysis

FTIR analysis was carried out to validate the presence of PHMB on the cotton fabrics after being treated with PHMB by using Spectrum 100 FT-IR Spectrometer (Perkin Elmer, USA).

Dye uptake

A calibration curve of each dye was established in advance. After dyeing, the concentration of residual dyebath was determined by using a UV-visible double-beam spectrophotometer (UH5300, Hitachi, Tokyo, Japan) at λmax of each dye. The dye uptake was calculated according to Eq. (1).

$$\text{Dye uptake}(\%) = (1-C_1/C_0) \times 100 \quad (1)$$

Where C_0 and C_1 are the dyebath concentrations before and after dyeing, respectively.

Colour strength evaluation

The colour strength, or colour yield of the dyed fabrics, i.e., so-called K/S value, was evaluated by using a spectrophotometer (GretagMacbeth Color Eye 7000A) based on the Kubelka-Munk equation (Eq. (2)), where K, S, and R denote the absorption coefficient, the scattering coefficient, and the reflectance value of the coloured samples, respectively. The testing was conducted and averaged at three different locations on the surface of each specimen after it was folded twice.

$K/S = (1-R)^2/2R$ (2)

Colour levelness properties

The relative unlevelness index (RUI), developed by Chong et al. (1992), is the most frequently used method to evaluate the colour levelness of dyed fabrics. By this method, the lower the RUI value, the better the colour levelness is. It means excellent visual levelness if RUI value is less than 0.2; the colour levelness is regarded as good if RUI ranges from 0.2 to 0.49; the rating of visual levelness is poor if RUI ranges from 0.5 to 1.0; while bad visual levelness is graded if RUI value exceeds 1.0.

Fastness assessment

Colour fastness to rubbing of the dyed samples were examined in accordance with AATCC TM8-2016e, and the colour fastness to laundering was evaluated by the standard method of AATCC TM61-2013 (Test No. 1A) with a slight amendment by using the nonionic detergent C13-oxo alcohol ethoxylates in place of the proposed anionic detergent in order to minimize the potential impacts.

Antimicrobial activity evaluation

The antimicrobial behaviour of fabric samples against the gram-positive *Staphylococcus aureus* (*S. aureus*) and the gram-negative *Klebsiella pneumoniae* (*K. pneumoniae*) before and after dyeing with acid dyes were qualitatively evaluated by using AATCC TM 147–201, as reported in previous publication (Wang and Kan 2020). The average width of the inhibition zone was obtained according to Eq. (3).

$W = (T-D)/2$ (3)

Where W, T, and D represent the width of inhibition zone in mm, the total diameter of the specimen and inhibition zone in mm, and the diameter of the specimen in mm, respectively.

Results And Discussion

Surface analysis

The change in chemical structure of surface of cellulosic fibres after being coated with PHMB was assessed by FTIR analysis. As expected, a strong absorbance with a sharp peak at 1543 cm^{-1} is observed in Fig. 3(a). This is attributed to the characteristic absorption of imine group (–C = N–) of PHMB molecule (Gao et al. 2011). The wide double absorption bands at 3175 cm^{-1} and 3304 cm^{-1} are due to stretching vibration of amine groups (–NH– and $–NH_2–$), whereas another double peak observed at 2856 cm^{-1} and 2930 cm^{-1} results from the asymmetrical and symmetrical stretching vibration of $–CH_2$ group (Worsley et al. 2019). Compared with the control sample, i.e., untreated cotton fabric, the characteristic absorption band at 1544 cm^{-1} and the double peak at 2850 cm^{-1} and 2917 cm^{-1} are observed on the samples after being treated with PHMB, indicating the existence of PHMB after coating on the surface of fabric samples. Moreover, the band shift of PHMB results from electrostatic attraction between PHMB and cellulose molecules.

Cellulosic fabrics are generally dyed with reactive dye and direct dyes, whereas acid dyes are commonly used to dye wool and silk that contain many cationic sites (protonated $-NH_2$ groups) by hydrogen bonding, Van der Waals' forces or ionic bonding. Therefore, dyeing of cotton fabrics with acid dyes provide further evidence that PHMB was successfully coated onto the fabrics (Fig. 3b). Moreover, the colour shade not only depends on concentration of PHMB for treating cellulosic fibres, but also relates to concentration of the dyebath. The reason could be the stoichiometric reaction between anionic dye molecules and cationic polyelectrolyte, which suggests that the colour shade is controllable. Figure 3c displays the underlying dyeing mechanism between anionic dye molecules and cationic polyelectrolyte, which markedly differs from the traditional cotton dyeing methods involving diffusion, penetration, and adsorption of dye molecules. The stoichiometric reaction between anionic dye molecules and cationic polyelectrolyte makes it possible to reuse the dyebath for circular dyeing, thereby achieving zero effluent discharge. Furthermore, this reaction can occur at room temperature, which implies that heat energy is not a necessity for textile dyeing.

Colour measurement of dyed samples

The reflectance value of a colour depends on its ability to reflect the visible light, which means that the reflectance value varies inversely with the colour strength. Figure 4 shows the reflectance values of PHMB modified cellulosic fibres dyed with three model acid dyes. Clearly, a similar tendency was obtained in the reflectance curves of dyed samples for each dye, and there is not any band shift, which means that the colour shade for all the three acid dyes remained unchanged. The lowest reflectance value for acid red is 510 nm, while values for acid blue and acid black are 590 nm and 580 nm, respectively.

For C.I. Acid Red 127 (Fig. 4(a, b)), the sample PH02-300 presents the maximum reflectance value, which indicates that PH02-300 is the lightest in terms of colour depth. As concentration of the dyebath grew from 300 mg/L to 500 mg/L, reflectance value of the sample (PH02-500) declined. Similar trends are also observed in PH04-300 and PH04-500 samples, which indicates that the reflectance is dependent on dyebath concentration. Compared to PH02-300, PH04-300 has a lower reflectance value, whereas this value for PH04-300 is higher than that of PH04-500. This demonstrates that the value of reflectance varies inversely with the concentration of PHMB attached on the cotton fabric. Similar results were also achieved in C.I. Acid Blue 83 (Fig. 4(c, d)) and C.I. Acid Black 172 (Fig. 4(e, f)).

Colour strength of dyed samples can be calculated from the reflectance curves, according to Eq. (1). Table 1 shows the maximum K/S value for each sample, which corresponds to the minimum reflectance value. A higher K/S value means the more dye bonded with the cationic polyelectrolyte. Clearly, for all the samples, the value of K/S shows a positive relationship with dyebath concentration; it increases with an increase in the concentration of dyebath from 300 mg/L to 500 mg/L, which suggests that the sample dyed with 500 mg/L dyebath had a darker shade than that dyed with 300 mg/L dyebath. This could be due to the fact that a higher concentration of dyebath offers more anionic dye molecules that bond with cationic sites. Comparing PH02 and PH04, the latter presented a higher K/S value for the same concentration of dyebath, indicating that the colour strength is positively associated with the content of cationic polyelectrolytes coated onto cellulosic fibres. These results agree with those observed in Fig. 3b.

Table 1

Colour strength (K/S value) of PHMB treated cotton fabrics after dyeing with three acid dyes at different concentrations

Samples **Dyebath**	**PH02-300**	**PH02-500**	**PH04-300**	**PH04-500**
C.I. Acid Red 127	1.86	2.29	2.40	2.67
C.I. Acid Black 172	2.49	3.13	3.34	3.63
C.I. Acid Blue 83	2.44	2.67	3.03	3.34

Next, we evaluated the colour levelness which is commonly used for describing the dyeing quality by using the relative unlevelness index (RUI). Table 2 displays that all the dyed fabric samples with acid dyes show good and excellent visual uniformity, which suggests that the nonuniformity of colour shade is imperceptible to the naked eye and is merely detectable by specialised equipment under close inspection. Actually, since dyeing principally occurs between acid dye molecules and the cationic polyelectrolyte PHMB, evenness of deposition of PHMB on the cellulosic fabric is of high importance and dominates the levelness of the dyed fabrics. At high concentration, PHMB molecules may form multilayer adsorption via layer-by-layer assembly on the surface of cellulosic fibres (Blackburn et al. 2006), which may impede bonding of dye molecules resulting from steric hindrance effect and lead to colour unlevelness. Meanwhile, this explains why we used low concentrations of PHMB to modify cellulosic fabric via exhaustion, the purpose of which is to deposit PHMB uniformly onto the cellulosic fibres.

Table 2
RUI value of cotton fabrics coated with PHMB after dyeing with three acid dyes at different concentrations

Sample		RUI	Rating
C.I. Acid Red 127	PH02-300	0.27	Good levelness
	PH04-300	0.23	Good levelness
	PH02-500	0.17	Excellent levelness
	PH04-500	0.19	Excellent levelness
C.I. Acid Black 172	PH02-300	0.06	Excellent levelness
	PH04-300	0.49	Good levelness
	PH02-500	0.25	Good levelness
	PH04-500	0.127	Excellent levelness
C.I. Acid Blue 83	PH02-300	0.13	Excellent levelness
	PH04-300	0.28	Good levelness
	PH02-500	0.05	Excellent levelness
	PH04-500	0.29	Good levelness

Recycled dyebath for circular dyeing

Based on the above discussion, we investigated reusability of the dyebath for the proposed circular dyeing in the following experiments. Contents of the dyebath of 500 mg/L after first dyeing of PH02 were reused for second and third dyeing and were then replenished for the next round of dyeing. Spectrophotometric method was employed to determine the concentration of dyebath after dyeing and the corresponding dye uptake. Figure 5(a) exhibits that the maximum absorption peaks are at 500 nm and 569.8 nm, respectively, for C.I. Acid Red 127 and C.I. Acid Black 172, while C.I. Acid Blue 83 shows double absorption peaks in visible spectra, i.e., 590 nm and 630 nm. Based on the maximum absorption, standard calibration curves of the three dyestuffs were established according to the Beer-Lambert's law, all of which show high correlation ($R^2 > 0.99$) Fig. 5(b).

Figure 5(c) shows colour strength (K/S value) obtained in circular dyeing of PH02 in 500 mg/L dyebath. Clearly, for three acid dyes, there was a slight decrease in colour strength after the second and third dyeing using the recycled dyebath. This could be related to the decrease in concentration of dyebath after dyeing. After first dyeing, the dye uptake for C.I. Acid Black 172, C.I. Acid Red 127, and C.I. Acid Blue 83 was around 16%, 21%, and 25%, respectively (Fig. 5d). This implies that the dyebath concentration was reduced to 420 mg/L,395 mg/L, and 375 mg/L, respectively, from the original 500 mg/L after first dyeing. These dyebaths were collected for circular dyeing, and dye uptake increased to 40%, 45% and 57% for C.I. Acid Black 172, C.I. Acid Red 127 and C.I. Acid Blue 83, respectively, after using the dyebath thrice.

Accordingly, concentration of dyebath declined to 300 mg/L, 275 mg/L and 215 mg/L for C.I. Acid Black 172, C.I. Acid Red 127 and C.I. Acid Blue 83, respectively. Then, the dyebath was replenished to maintain the concentration at 500 mg/L for the next round of dyeing, i.e., PH02-4, the fourth dyeing (Fig. 5c). For three acid dyes, there is no significant difference between colour strength in the circular dyeing and the K/S value of PH02-4 was very close to that of PH02-1, PH02-2 and PH02-3, which demonstrates that the dyebath is recyclable.

Fastness properties

Colour fastness is a term used for measuring and describing ability of the colour to withstand fading and staining when in use. In the present study, we investigate two of the most representative colour fastness measures, i.e., rubbing fastness and washing fastness (Table 3). Regarding the rubbing fastness, clearly, all the fabric samples showed excellent fastness to dry rubbing, reaching Grade 5. However, it was found that the wet rubbing fastness was slightly poorer, with the Grade above 3. For the fastness to laundering, it denotes the resistance of coloured fabrics against colour fading during household washing. In the present study, the colour change and staining of dyed fabrics after laundering were evaluated. Clearly, colours of all samples show a slight variation after washing, with Grade rating of above 4, while the colour staining was of rating 5. This demonstrates that the dyed samples have satisfactory and acceptable colour fastness properties, which implies that cationic polyelectrolyte-based dyeing strategy could be a practicable alternative and circular dyeing without effluent discharge is feasible. This may help mitigate the pollution caused by textile dyeing wastewater.

Table 3
Colour fastness of PHMB treated cotton fabrics after dyeing with three acid dyes

Dyebath (mg/L)			Acid Red		Acid Black		Acid Blue	
Colour fastness			300	500	300	500	300	500
Rubbing fastness	PH02	Dye	5	5	5	5	5	5
		Wet	3−4	3−4	3−4	3−4	3−4	3−4
	PH04	Dye	5	5	5	5	5	5
		Wet	3−4	3−4	3−4	3	3−4	3−4
Wash fastness	Colour change	PH02	4	4	4	4	4	4
		PH04	4	4	4	4	4	4
	Colour staining	PH02	5	5	5	5	5	5
		PH04	5	5	5	5	5	5

Antimicrobial efficacy

Next, the antimicrobial activities of cotton fabrics coated with PHMB were qualitatively evaluated after dyeing with acid dyes against two selected model bacteria, i.e., *S. aureus* and *K. pneumoniae*, as shown in Fig. 6. Table 4 presents the inhibition zone (mm). Clearly, the cotton fabrics coated with PHMB exhibit a stronger inhibition against gram-positive *S. aureus*, with the inhibition zone going up to 0.58 mm, as compared with the pristine control sample. By contrast, *K. pneumoniae* shows an obvious resistance to PHMB, and the inhibition zone was merely at 0.05 mm, far less than that of *S. aureus*. After dyeing with C.I. Acid Blue 83, the inhibition zone against *S. aureus* was reduced to 0.47 mm, whereas regarding C.I. Acid Red 127 and C.I. Acid Black 172, the inhibition zone against *S. aureus* dropped to 0.33 and 0.06, respectively. Regarding *K. pneumoniae*, inhibition zone for the three acid dyes declined to zero. Despite this, the growth of *K. pneumoniae* traversing the fabric samples was inhibited. This indicates that dyeing can weaken the antimicrobial activities of PHMB-treated cotton fabrics. The reason is closely associated with the strong ion-ion bonding between positively charged PHMB molecules and negatively charged dye molecules, which neutralises PHMB and thus diminishes its bactericidal action.

Table 4

The inhibition zone (mm) of cotton fabrics treated with PHMB after dyeing with three acid dyes in inhibiting *S. aureus* (*SA*) and *K. pneumoniae* (*KP*)

Samples		Control	PH04	PH04-500		
				Red	Black	Blue
Inhibition zone/mm	SA	0	0.58	0.33	0.06	0.47
	KP	0	0.05	0	0	0

Conclusions

Textile industry discharges large quantities of wastewater generated in dyeing which results in severe pollution issues since there are substantial quantities of water and chemicals. The studies on ecologically sustainable and clean dyeing technology have aroused great interest among researchers and practitioners since the need to cut down generation and discharge of effluents from textile dyeing has become an important concern. The present study investigates the applicability and feasibility of cationic polyelectrolyte-based circular dyeing method using the typical cationic antimicrobial agent PHMB and anionic acid dyes. FTIR analysis confirms the presence of PHMB attached onto the surface of cellulosic fibres, as validated by the dyeing with acid dyes. The colour measurement shows that the colour strength is not only dependent upon the concentration of dyebath, but also relies on the content of PHMB coated on the fibres, suggesting the controllability of colour depth. PHMB treated fabric samples after dyeing have good/excellent colour levelness, and the colour fastness is basically satisfactory and acceptable. It was found that the dyebath is recyclable for circular dyeing, which implies that cationic polyelectrolyte-based dyeing method may provide a practicable and promising strategy for ecologically sustainable dyeing to address the pollution issue of effluents discharged by the textile industry. Moreover, the dyeing can occur at room temperature which would greatly reduce consumption of heat energy in textile dyeing.

Meanwhile, the bacteriostatic ability of dyed fabrics may be conducive to elimination or reduction of healthcare-associated infections that transmit through textiles. Based on the present study, the pilot-scale experiments are expected to be conducted to promote the industrial application of cationic electrolyte complex based circular coloration technology with recyclable dyebath.

Declarations

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Conflicts of interest

The authors declare they have no financial interests.

Author contributions

Conceptualizaiton: Wen-Yi Wang, Chi-Wai Kan; Methodology: Wen-Yi Wang, Jia-Chi Chiou, Wan-Xue Chen, Jia-Li Yu; Formal analysis and investigation: Wen-Yi Wang, Chi-Wai Kan; Writing- original draft preparation: Wen-Yi Wang; Writing- review and editing: Chi-Wai Kan; Funding acquisition: Chi-Wai Kan; Resources: Chi-Wai Kan, Jia-Chi Chiou; Supervision: Chi-Wai Kan

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Figures

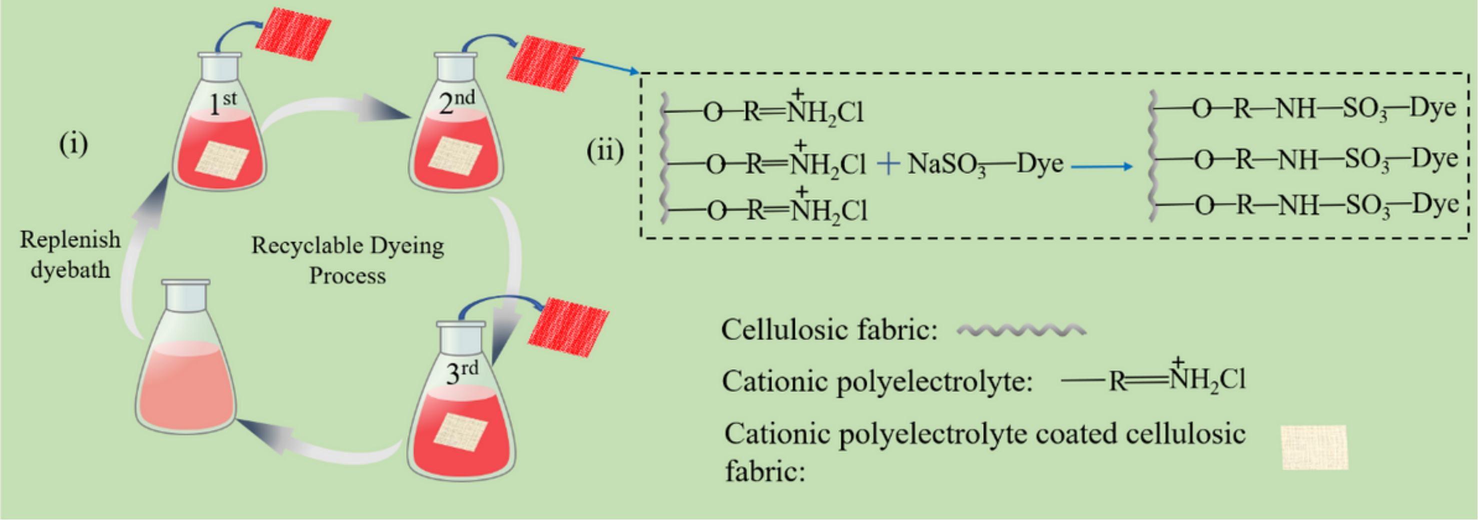

Figure 1

(i) Schematic diagram of the proposed recyclable dyeing process based on cationic polyelectrolyte; and (ii) The dyeing mechanism between anionic dye molecules and cationic polyelectrolyte treated cellulosic fabric

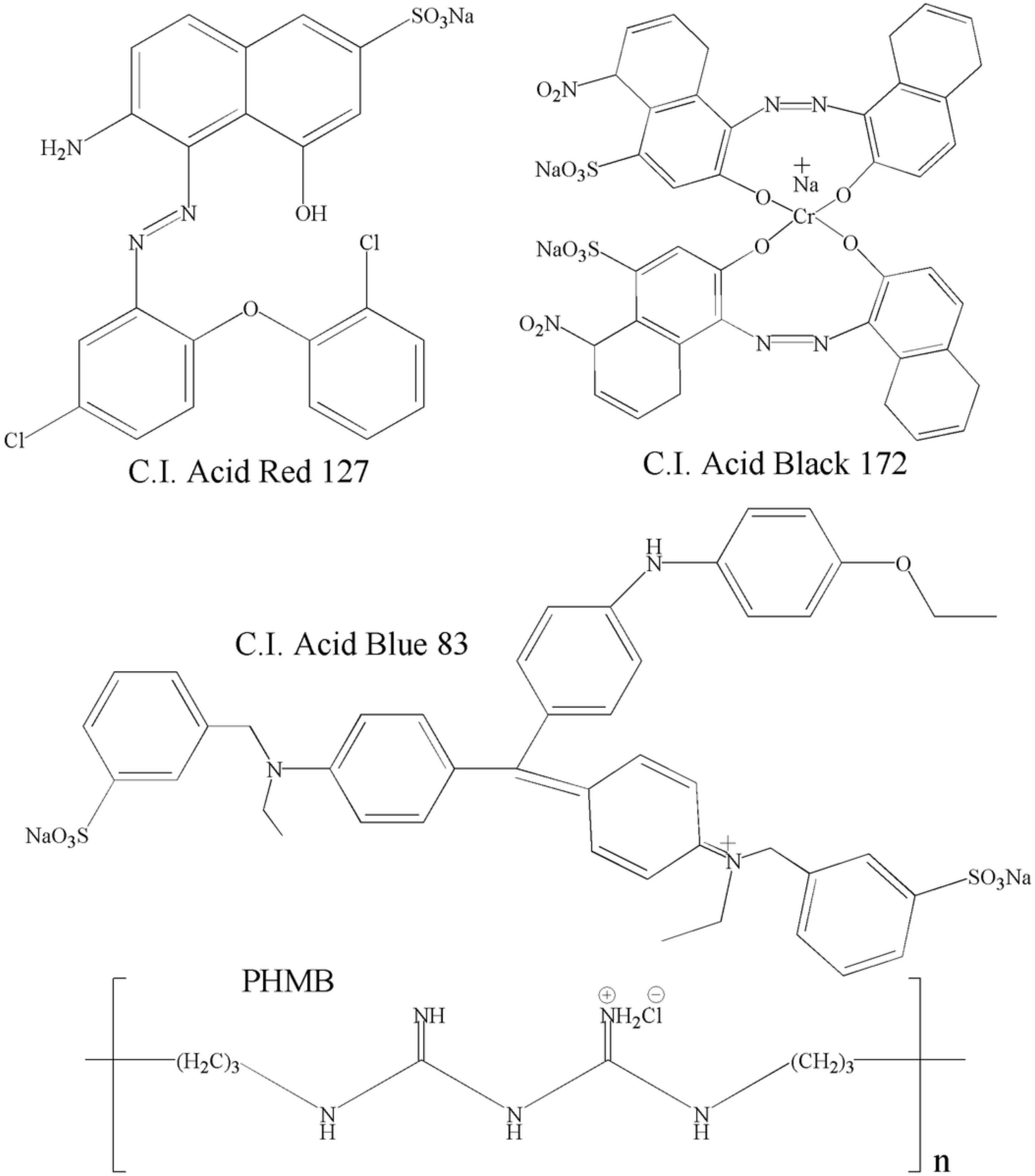

Figure 2

Chemical structures of C.I. Acid Red 127, C.I. Acid Black 172, C.I. Acid Blue 83 and PHMB

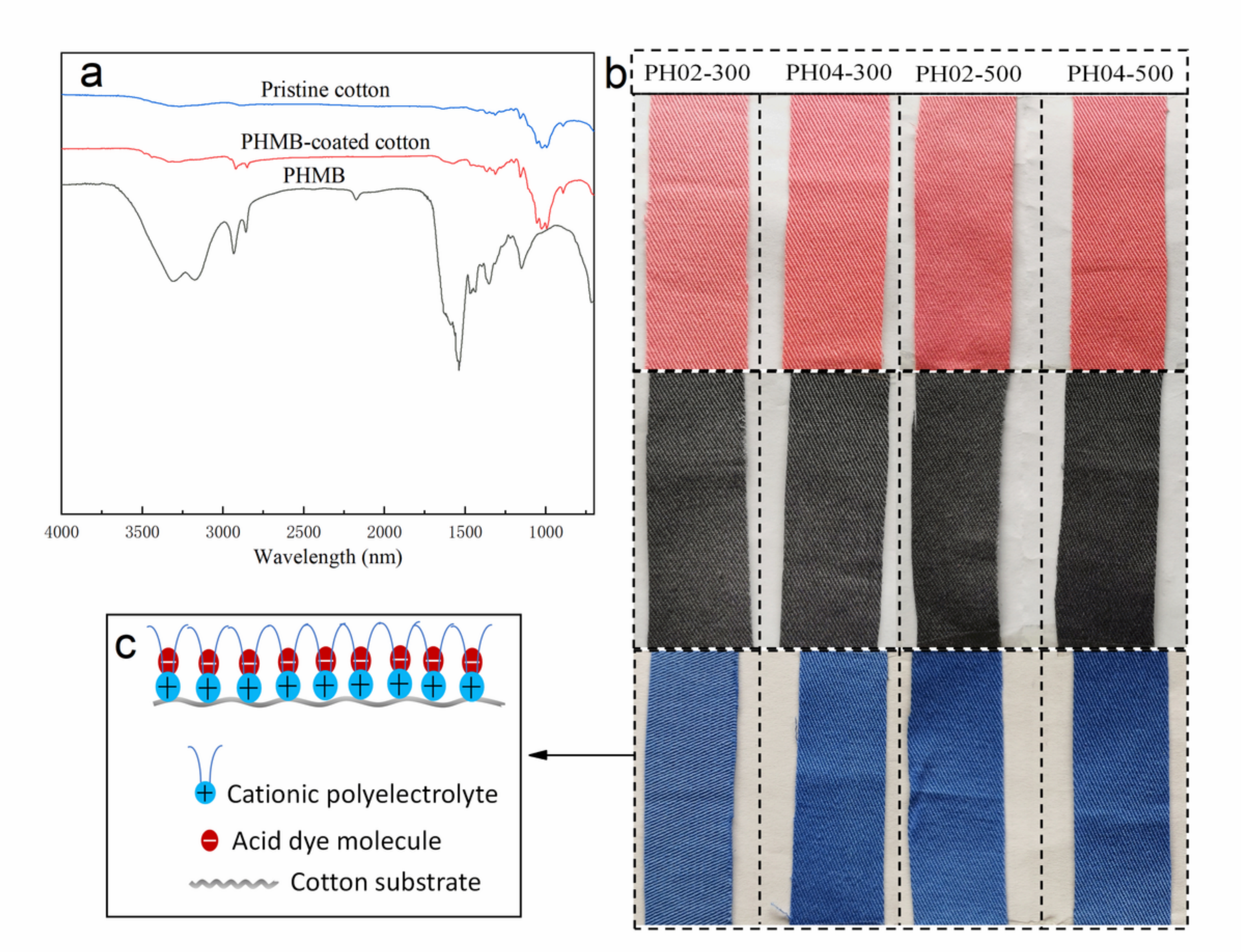

Figure 3

(a) FTIR spectra of pristine cotton fabric, PHMB, and the cotton fabric treated with PHMB; (b) colour shades of PHMB treated cotton fabric dyed with C.I. Acid Red 127, C.I. Acid Black 172 and C.I. Acid Blue 83, respectively; and the underlying dyeing mechanism between acid dye molecules and PHMB-coated cotton fabric (c)

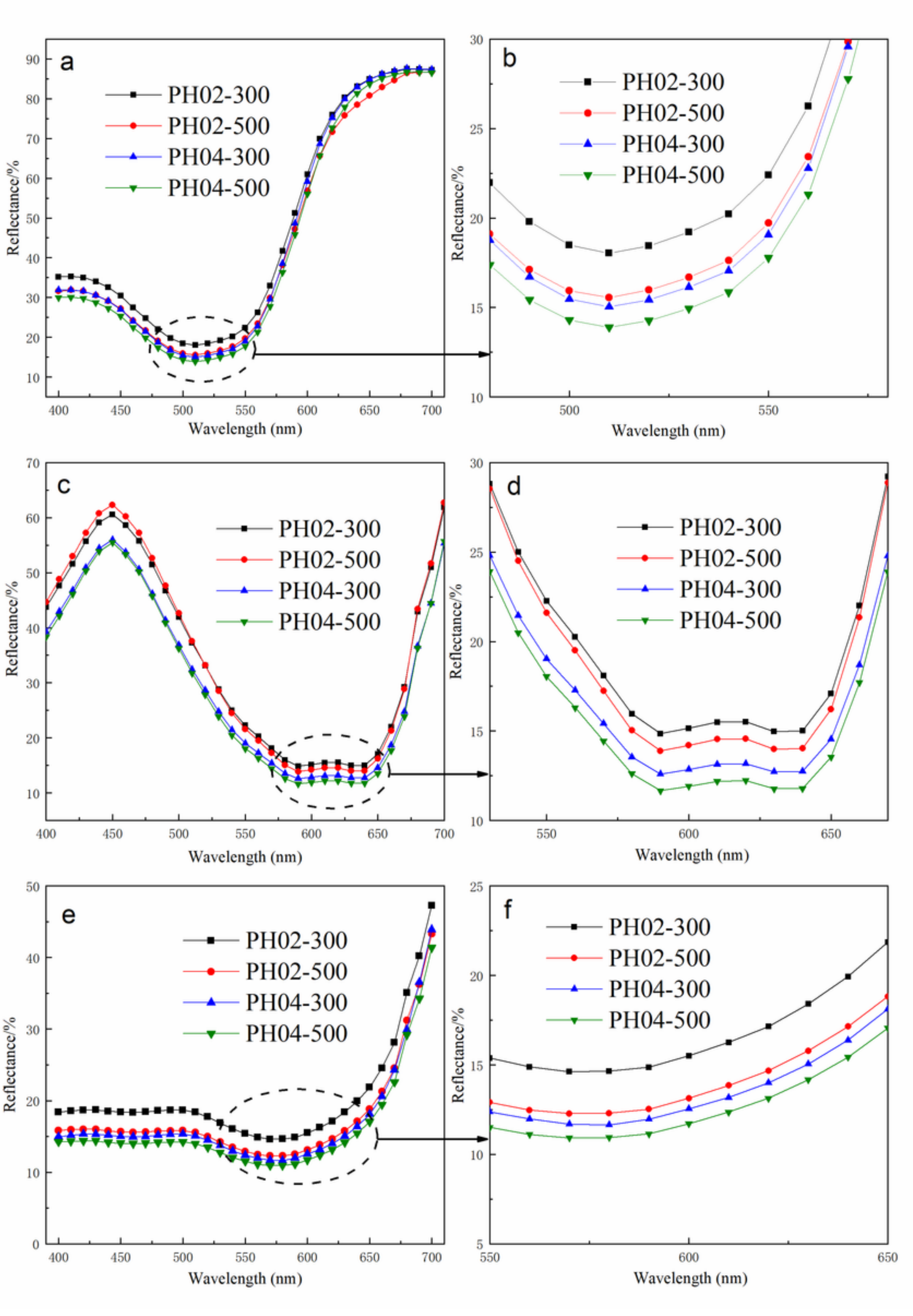

Figure 4

The reflectance curves of PHMB treated cellulosic fabrics dyed with C.I. Acid Red 127 (a); C.I. Acid Blue 83 (c); and C.I. Acid Black 172 (e); and the corresponding enlarged maximum adsorption peaks (b, d, f), respectively

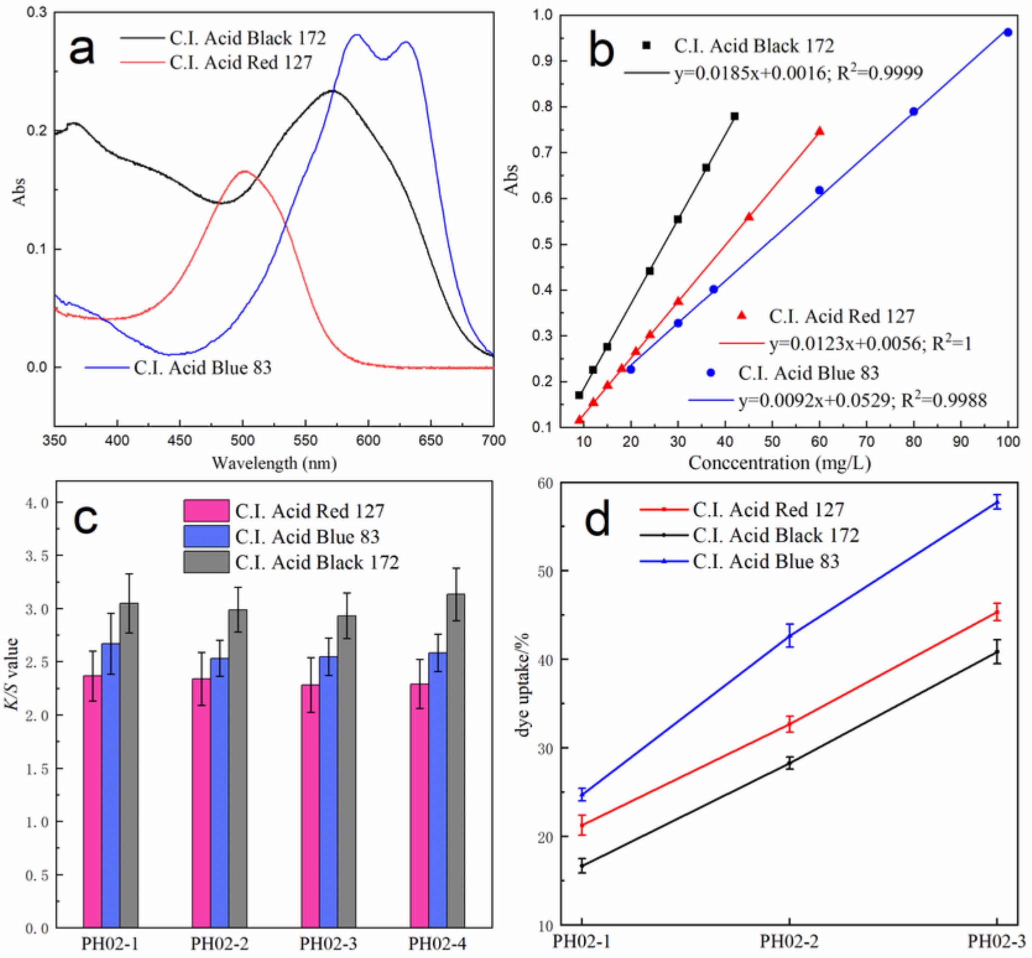

Figure 5

Absorbance curves of the three model acid dyes in aqueous solution in the range of UV–visible spectrum (a); the corresponding calibration curves established at maximum absorption peaks (b); (c) displays colour yields of PHMB treated cotton fabrics after being dyed with recycled dyebaths; and dye uptake of three model acid dyes after being dyed with recycled dyebaths (d)

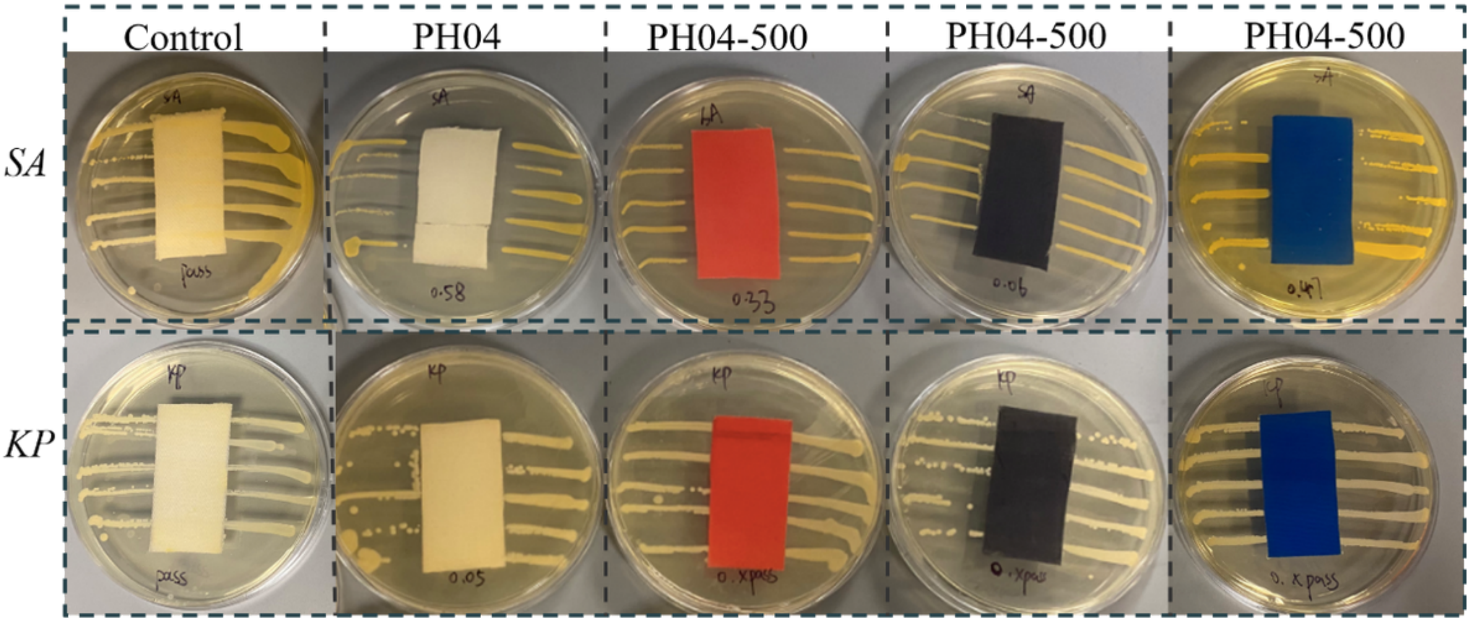

Figure 6

Antimicrobial activities against S. aureus (SA) and K. pneumoniae (KP) of cotton fabrics treated with PHMB after dyeing with three acid dyes