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Union dyeing of cotton/nylon blended fabric by plasma-nano chitosan treatment

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Abstract

Current union dyeing processes rely on one or two dye baths with one or two dyes for cotton/nylon blend fabrics. For 50:50 cotton/nylon fabrics, cotton is dyed first under alkaline condition with reactive dyes and then the nylon is dyed with acid dyes under acidic condition. Atmospheric plasma- nano Chitosan treatment as an environmentally friendly method was employed to modify surface properties of cotton/nylon blend fabrics to develop union dyeing with acid dyes. Cellulose fibers when immersed in water produce a negative electro-kinetic potential. The negative charge on the fiber repels the anionic dye ions and consequently the exhaustion of the dye bath is limited. When the fabric is treated with chitosan, the primary hydroxyl groups of cellulose is partially modified into amide groups, which intern leads the cellulose to act like as polyamide fiber. Experimental work was carried out on finding the possibility of one bath dyeing of plasma- chitosan pretreated cotton/nylon fabric with acid dyes. Plasma treated cotton/nylon surface characteristics were evaluated using FTIR. The surface activation using air plasma introduces different functional groups in cotton/nylon blend fabric. The effect of plasma-nano chitosan pretreatment on dye ability, fastness, and few physicochemical properties has been investigated, and results are presented. The cotton/nylon sample treated with 0.3% of chitosan nanoparticles had higher K/S values, washing, and crocking fastness. New method of union dyeing showed good fastness properties and offers the option of eco-friendly.

Keywords: Acid dyes, Colour strength, Amino groups, Antibacterial, Fastness

Background

Dyeing of fabric blends such as Cotton/Nylon (C/N) is presently dyed by two-bath or one-bath two-step dyeing. Good solidity of hue and depth is more critical in 50:50 blends and in union fabrics, such as nylon warp stretch fabrics, containing cotton or nylon/cotton wefts for swim wear and narrow fabrics, crimped nylon warp/viscose filament dress wear, or cotton warp/nylon weft constructions for uniforms, rain wear or work wear. Cotton/nylon is also used in socks. Nylon being a polyamide contains many amide groups in its structure. It also contains free amine groups at the ends of its polymeric chains, although the number of these free amine groups is less than the number of carboxylic groups, and the fiber possesses a negative charge unless in the appropriate pH region (Haji et al. 2014). These amine groups provide excellent electrostatic and hydrogen bonding sites and are the main factors contributing to the substantively of the dye molecules. Acid dyes have very

little affinity for cotton, but cationic cotton can be dyed readily with acid dyes. The ammonium groups act as dye sites (Run-ling 2010).

Also, a variety of cationic agents with amino, ammonium, sulfonium, phosphonium and other groups has been employed to modify cellulose fabrics (Varma and Kulkarni 2002). However, some disadvantages, such as high cost, inadequate reactivity, fabric yellowing, excessive fabric tendering and toxicity, were observed with these substances, preventing their industrial application. Chitosan has the same backbone with cellulose except for its acetamide group instead of a hydroxyl group. Chitosan is naturally presenting ß-1, 4-linked linear polysaccharides, and most of its glucopyranose residues are 2, 2-deoxy-b-D-glucopyranos (Yang and Wang 2010). Chitosan can easily adsorb anionic dyes, such as direct, acid and reactive dyes, by electrostatic attraction due to its cationic nature in an acidic condition. The dye enhancement activity of Chitosan nanoparticles was seldom reported. Unique characters of nanoparticles for their small size and quantum size effect supposedly promised Chitosan nanoparticles to exhibit superior dye ability improvement (Rinaudo 2006).

Plasma treatment of textiles has been investigated as an alternative wet chemical fabric treatment and pre-treatment processes. It would result in desirable surface modification including but not limited to surface etching, activation, cross linking, chain scission, decrystallisation and oxidation (Kang and Sarmadi 2004; Vaananen et al. 2010; Voher et al. 1988). Glow discharge plasma of oxygen, nitrogen, ammonia etc. introduces functional groups like hydroxyl, peroxides, and amines on polymer surface. The technique of plasma treatment is an effective surface modification method to save processing costs and to avoid environmental pollution (Shahidi et al. 2007; Wakida et al. 1988). Atmospheric air plasma was used for oxidation of cotton/nylon fiber in the preparatory process with chitosan nanoparticles to produce aminised cotton/nylon fiber. The facility to attain high wet fastness standards on nylon/cellulosic blends by a one-bath technique at mildly acidic pH is a substantial advantage over the two-bath or two-stage. Meanwhile, this phenomenon gives a possibility to one-bath dyeing for blended fabrics, using aminised cotton and nylon fabric. The main objective of this research is to explore the possibilities of union dyeing of cotton/nylon fabric with acid dyes by introducing amino group in plasma treated cotton/nylon interwoven fabric using chitosan nano-particles.

Method

Materials

Ready for dyeing 50/50 Cotton/Nylon blended fabric with the weights of 150 g/m^2 was used. Chitosan (Degree of deacetylation 92.5%, MV 1,000 kD) and Acid Red 138 (CI 18073) were used respectively for pretreatment and dyeing. All other reagents are commonly used laboratory reagent grade.

Low temperature plasma treatment

The cotton fabric was treated with glow discharge plasma operated at a pressure of 0.5 mbar (Hydro pneo Vac). The distance between electrodes is 0.2 cm. The samples were placed between electrodes and treated on both sides, each side for 60 s (60 s × 2). In all treatments, a uniform glow discharge plasma system operating under atmospheric condition with air used as a processing gas. Due to interactions between air and activated

surface, plasma treated fabric was conditioned for 24 h at standard atmospheric condition accordingly to ISO 139 test method.

Preparation of chitosan nanoparticles

Chitosan was dissolved in a dilute aqueous acetic acid solution of 0.5% (w/v) under microwave irradiation. Aqueous ammonia was then dropped into the chitosan solution to precipitate the chitosan. The obtained gel-like swollen chitosan was washed to neutral with DI water, and was then transferred into a 25 ml volumetric flask. The total volume of liquid was added to 25 ml with DI water. An ultrasound processor with a 6 mm probe was used and it was put into the volumetric flask. Ultrasound treatment was conducted under an ice-water bath. Finally, a milky nano-emulsion chitosan was obtained.

Pretreatment with nano-chitosan

Pre-washed cotton/nylon blend fabrics were soaked for 15 min at in chitosan nano-emulsion at five different concentrations separately 0.01, 0.05, 0.1, 0.3 and 0.5% (w/v). The padding processes were then completed with pick up weight of around 80%. All padded samples were dried at 100°C for 3 min, cured at 150°C for 3 min and finally rinsed with warm water (40°C) for 1 min. Finally fabric rinsed with running cold water and dried again.

Union dyeing with acid dyes

Dyeing of the pretreated blend fabrics were carried out in the laboratory dyeing machine by exhaust method. Fabrics were dyed with 3% (owf) Acid Red 138 in a bath containing 9% of Ammonium acetate, and 3% hydrochloric acid of 10%, with a liquor ratio of 1:20. Firstly, salt and acid were added to water and the dyeing bath was warmed at 60°C, then the samples were immersed in the dyeing bath and the dyeing continued for 15 min, followed by adding dye solution and the dyeing continued for 15 min., then the temperature was raised to 80°C through 20 min, the dyeing was continued at this temperature for 30 min, finally the dyeing was stopped and the dyeing bath was cooled. Dyed samples were thoroughly rinsed with running cold water, then washing with a solution containing 4 g/l ECE detergent and 1 g/l sodium carbonate at 40°C for 15 min. Washing carried out for three more times to ensure good washing fastness and finally rinsing with hot and cold water then air dried. A washed sample was kept in standard atmospheric conditioned for 1 h.

Evaluation of the dyed sample

The reflectance of dyed samples and colour coordinates CIE L*, a*, b* values were measured on X-rite spectrophotometer, colour-eye 5000 equipped with integrated using illuminate D65. Colour strength (K/S) of the dyes samples were calculated using according to Kubelka- Munk equation.

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

where R is the Decimal fraction of the reflectance of dyed samples, K is the Absorption coefficient, S is the scattering coefficient.

Fourier transform-infrared analysis

Fourier Transform-infrared measurements carried out using a Nicolet 670 instrument (Thermo scientific). An average of 20 scans was recorded in the attenuated total reflection (ATR-Smart Endurance) mode.

Antibacterial efficiency

AATCC100-2012 modified test method was used to analyze the antibacterial activity of the treated cotton fabrics. The organisms taken for this study were Staphylococcus aureus (ATCC No. 6538) and Escherichia coli (ATCC No. 8739). The incubated test culture in a nutrient broth is diluted with a sterilized 0.5 mM phosphate buffer (pH 5.2) to give a concentration of 1.3×10^5 CFU/ml (working dilution). 1 g of fabric is transferred to flask containing 50 ml of the working dilution then capped flask shaken for 1 h at 250 rpm. After a series of dilutions of the bacterial solutions using the DI water, 1 ml of the solution is plated in nutrient agar. The inoculated plates are incubated at 37°C for 24 h and surviving cells are counted. The antimicrobial activity is expressed in % reduction of the organisms after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control. The percentage reduction is calculated using the following equation:

$$\text{Reduction \% (CFU/ml)} = (\text{B} - \text{A/B}) \times 100$$

where A are the surviving cells (CFU/ml) for the flasks containing the treated substrate after the specified contact time and B are "0" contact time CFU/ml for the flasks used to determine A before the addition of the treated substrate.

Results and discussions

Effect of plasma treatment on fabric properties

The FTIR spectra of the untreated and plasma treated cotton/nylon samples were taken to determine the chemical changes that could have occurred as a result of a plasma treatment. Figure 1 shows these spectra. The absorption peaks for amine stretching at 3,296 cm^{-1}, amide carbonyl at 1,534 cm^{-1}, and carboxylic acid at 1,634 cm^{-1} were normalized with respect to that of C–H stretching at 2,932 cm^{-1}. It could be seen from Table 1 that the value of the normalized peak intensity for –NH2 and –CONH groups increased significantly for the plasma-treated sample. Possibly, the presence of oxygen in air plasma promoted the formation of amide groups over the amine groups during the plasma treatment. On plasma treatment, an increase in the value of normalized peak intensity for the –C=O groups was observed. The increase in –C=O groups, which indicates the formation of more –COOH groups, may be due to the reaction of oxygen with generated radicals on the plasma-treated surface. These functional groups were produced on the fabric by the reaction between the active species induced by the plasma in the gas phase and the fabric surface.

Morphology of treated sample

The chitosan nano-emulsion consisted of positive charged nanoparticles with average size of 250 nm as determined by laser scan. The emulsions had zeta potentials of +25 mV and pH values around 6.7. Figure 2 shows the profile of the spherical nanoparticles from

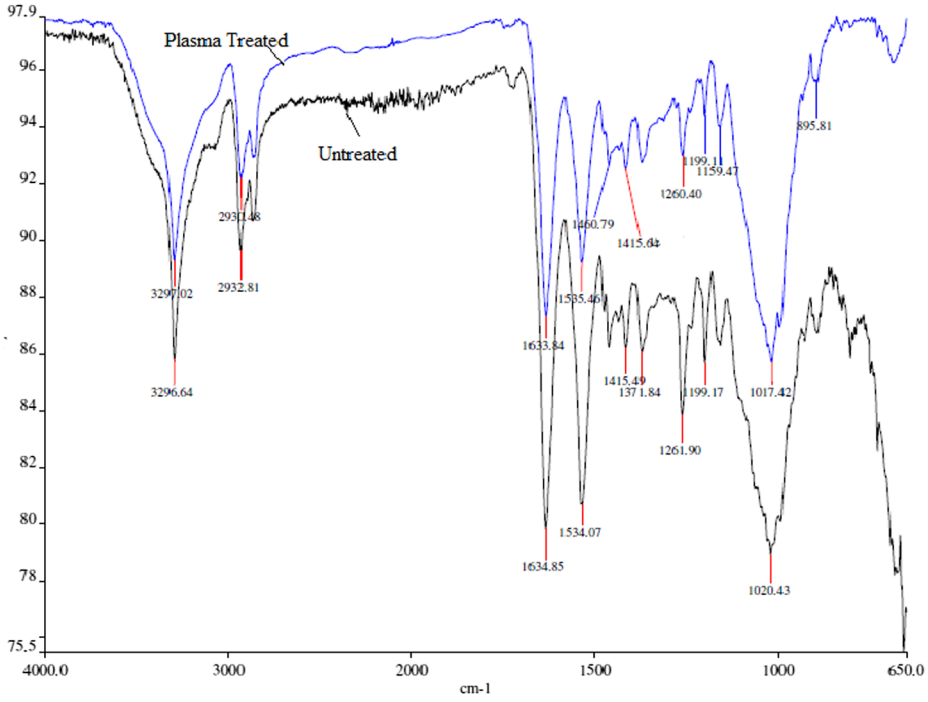


Figure 1 FTIR spectra of untreated and plasma treated cotton/nylon Fabric.

Table 1 Characteristic of FTIR Transmission

Frequency (cm−1)	Bond	Untreated fabric (% T)	Plasma treated (% T)
3,296	N–H stretch	85.6	89.2
2,932	C–H stretch	89.0	92.3
1,634	N–C=O stretch	79.2	86.9
1,261	C–O stretch	83.4	92.2

filtrated emulsion with 0.45 μm nylon membrane. These nanoparticles were believed to adhere onto the surface of cotton/nylon fibers by electrostatic and physical interactions. The Chitosan nanoparticles in the emulsion accumulated onto the surface of cotton/nylon aggregated together during drying and finally formed a rough film, promising a huge surface area that could be useful in the dyeing process. Chitosan has the same backbone with cellulose except for its acetamide group instead of a hydroxyl group. The PH of the emulsion of the nanoparticles is more favorable for the carboxyl groups to confer negative charge, which attracted more positive charged chitosan nanoparticles to form a thicker film. More spaces were included in the structure as revealed in the SEM images (Figure 3).

Colour strength

K/S value of a dyed material has a close relationship to the amount of dye absorbed by the fabric. K/S values of cotton/nylon dyed samples with acid dyes are shown in Table 2. It was observed that the color measurements of untreated cotton/nylon fabric have the

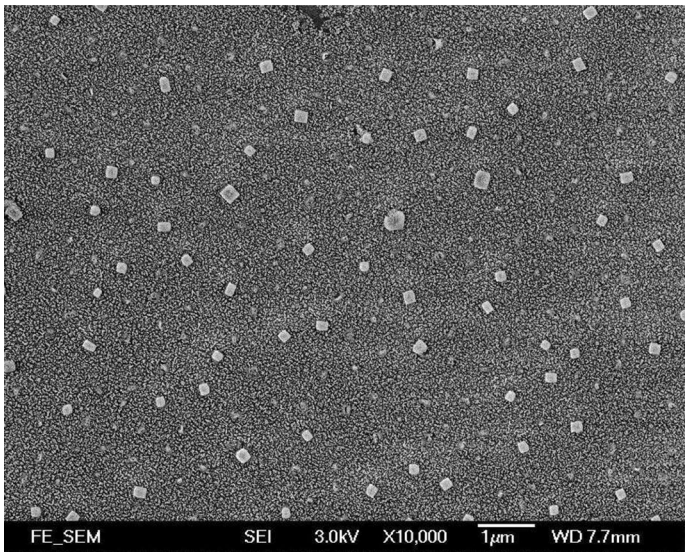


Figure 2 SEM image of chitosan nanoparticles from filtrated emulsion with 0.45 μm membrane.

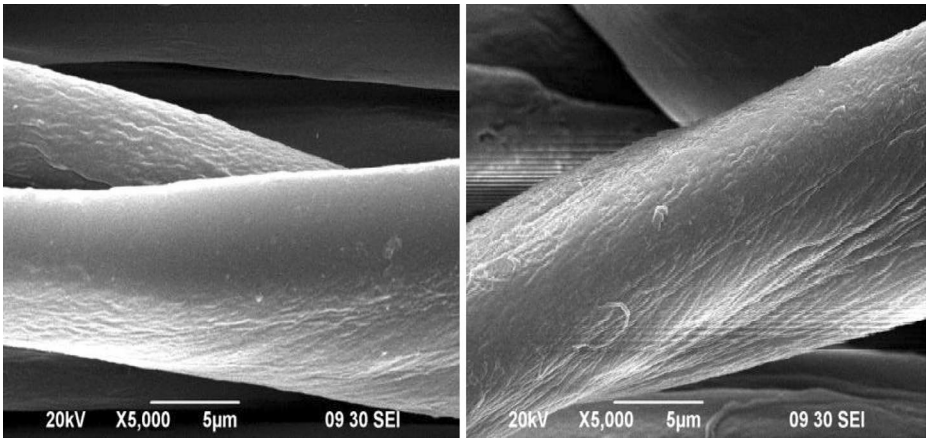


Figure 3 SEM images—*left* untreated sample and *right* treated sample.

Table 2 K/S Values of dyed sample

Dyes	Chitosan concentration (%)	ΔE	K/S
Acid Red 138	0	–	2.246
	0.01	0.956	2.865
	0.05	1.209	3.054
	0.1	1.429	3.204
	0.3	1.790	3.699
	0.5	1.789	3.692

lowest values. This was because cotton fibers when immersed in water produce a negative zeta potential. The negative charge on the fiber repels the acid dye ions and consequently the exhaustion of the dye bath was limited which lead to the decrease of the

color measurements. The color measurements of cotton/nylon blends increased with the plasma- nano chitosan pretreatment, it can be concluded that the K/S values of chitosan treated dyed fabrics are higher than that of untreated sample. This enhancement in K/S values of chitosan treated cotton/nylon fabrics shows that the chitosan has an incremental effect in dyeing processes. The improved dye ability is related to the presence of amine groups available from the chitosan. Increasing the number of active functional groups due to plasma activation in the cotton/nylon surface enabled the adsorption of higher amounts of chitosan and, consequently, a higher amount of amino groups responsible for dyeing.

It has to be pointed out that several past researches showed that, in some cases, when chitosan interacts with non-activated cellulose, adsorption could also be irreversible (Cakara et al. 2009). That irreversible adsorption of chitosan onto weakly acidic cotton fabric is, under present conditions, predominately driven by a non-electrostatic attraction. Myllyte et al. (2009) evidenced a non-electrostatic interaction between chitosan and cellulose. This may be attributed to specific structural interaction between chitosan and cellulose (H-bonds and hydrophobic interactions). Under acidic condition, protonation of the carbonyl group oxygen atom of amide groups generates new cationic sites for dye adsorption. The higher amount of amino groups in plasma activated nano chitosan treated samples increased the probability that a protonated amino group met electrostatic bond with acid dye anions under acidic conditions. Once a dye anion with moderate substantively adsorbs onto an ammonium ion site in the cotton nylon, it is quite resistant to displacement. The dye–fiber interaction must involve forces other than the attraction of oppositely charged ions. Obviously, dipole–dipole and hydrophobic interactions between the dye and nylon molecules play an important role in determining the high substantively and good washing fastness of acid dyes.

Colour fastness properties

Table 3 shows the colour fastness properties of untreated and plasma-nano chitosan treated samples dyed with acid dyes. Samples dyed after plasma-nano chitosan treatment showed better wash fastness, which may be due to ionic and physical attraction between newly formed functional groups on the plasma-nano chitosan treated of cotton/nylon fabrics and acid dyes. There is no considerable difference between the colour fastnesses to light of the samples, but the crocking fastness is still lower in the case of the low concentration of chitosan treated fabrics. As mentioned before, plasma enhances chitosan absorbance, but, because of the nature of plasma treatment, the chemical modification made by plasma

Table 3 Colour fastness properties

Dyes	Chitosan concentration (%)	Wash fastness			Wet crocking fastness	Light fastness
		Colour change	Staining on cotton	Staining on nylon		
Acid Red 138	0	3–4	3–4	2–3	3	4
	0.01	4	3–4	3–4	3	4
	0.05	4	4	3–4	3–4	4
	0.1	4	4	4	3–4	4
	0.3	4	4	4	4	4
	0.5	4	4	4	4	4

processes is restricted to the surface of the material. Therefore, some of the dye molecules are adsorbed to the near-surface layers of the plasma-nano chitosan treated fibers and can be removed easily when subjected to a crocking test. However at high chitosan concentration, non-electrostatic interaction between chitosan nanoparticles and individual cellulose fiber bring in more chitosan throughout fibers which makes adequate ionic bonding with dye molecules. The fastness values of all such dyed samples are quite improved whereas untreated sample shows poor washing and crocking fastness properties.

Physical properties

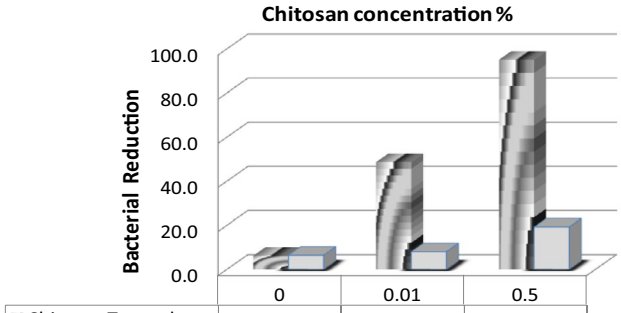
Pretreated cotton/nylon samples were tested for fabric properties such as air permeability and, tensile strength. Plasma-nano chitosan treated fabric performance was compared with control sample i.e. untreated fabric. It is inferred from the Table 4 that there was a change in air permeability of the plasma- nano chitosan treated cotton fabric as compared to the untreated one. There are some factors affecting the air permeability of the fabric, e.g., the fabric structure, thickness, and surface characteristics, etc. The fabric thickness has a significant effect on the air permeability values of the fabric, as the air permeability tends to decrease as the thickness increased. It is postulated that the plasma treatment induces a certain degree of roughness on the fiber surface which increases the fabric thickness and changes the fabric surface characteristics. Etched fiber changes act as a boundary to hinder the air flow through the fabric, thus resulting in a reduction of the air permeability of the fabric. Plasma has a permanent effect on air permeability as air is kept inside the plasma-treated fabric and cannot escape easily. Also reduction of air permeability was speculated from a slight thickening of the fibers due to a layer of nanoparticles. All these factors contribute towards the lower air permeability. But nonetheless, nanoparticles of chitosan incorporated on the individual fiber surface by electrostatic and other physical forces not the inter-fiber voids in the fibrous network. The slight significant losses of air permeability in the pretreated fabrics have not affected intact breathability of the cotton/nylon fabrics. It is also obvious from Table 4 that tensile strength loss slightly significant after the process. The slight loss of strength is mainly due to the oxidation and stiffening of the molecular backbone after cross-link formation.

Antibacterial activity

The antibacterial activities of cotton/nylon fabrics have been tested with prepared specimens for each analysis and Figure 4 represents reduction values. Data shows that nano-chitosan treated fabrics had bacterial reduction. The antibacterial activity of treated sample was significantly decreased after dyeing due to the bonding of the available amino

Table 4 Physical Properties of dyed samples

Dyes	Chitosan concentration (%)	Tensile strength-warp (N)	Vertical wicking (cm in 5 min)	Air permeability ($l/m^2/s$)
Acid Red 138	0	459.5	3.5	350.5
	0.01	439.5	5.5	286.5
	0.05	434.6	6.2	280.7
	0.1	432.6	6.9	276.2
	0.3	429.0	7.4	271.9
	0.5	428.5	7.9	269.7



	0	0.01	0.5
Chitosan Treated Sample	6.2	48.6	95.0
Chitosan Treated Sample with Acid Red 138	6.4	8.0	19.2

Figure 4 Graphical representations of antibacterial activity results.

groups of the chitosan by dye molecules. The reduction values exhibited by dyed fabrics are slightly higher than un-dyed samples.

Conclusions

This paper described the ability to dye cotton/nylon blend fabric in one step, one dyeing bath with shortened time. It was found that the treatment of cotton/nylon fabrics with plasma-nano chitosan enhanced the dye uptake of cotton/nylon fabrics compared with untreated fabric. The improved dye ability of cotton to acid dye is postulated due to the presence of amine groups available from the chitosan. Based on the depth of shade values, it was found that by increasing chitosan nanoparticles concentration up to 0.3% (w/v), there was significant improvement of color strength. Moreover, colorfastness properties to washing and wet crocking of the treated samples were improved at higher chitosan concentration. Union dyeing of cotton/nylon fabrics with acid dyes using biodegradable modification agent such as chitosan is an environmental friendly approach in textile dyeing industry.

Authors' contributions

KK and RT conceived and designed the experiments. KK performed the experiments, analyzed the data in consultation with RT. All authors read and approved the final manuscript.

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Compliance with ethical guidelines

Competing interests

The authors declare that they have no competing interests.

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