

Monoazo disperse dyes based on pyrazolopyrimidinones provide added value

Morsy A. El-Apasery 1* and Mohamed O. Saleh 2

¹Dyeing, Printing and Auxiliaries Department, Textile Industries Research Division, National Research Centre, Cairo

12622, Egypt.

² Departmentof Chemistry, Faculty of Science, Al-Azhar University at Assiut, Assiut 71524, Egypt.

Abstract

We treated the colored polyester texture with scatter colors that we synthesized previously or after the coloring cycle trying to give these fabric functional properties. The light fastness was studied after treating the fabric with zinc oxide ZnO nano particle size NPs., and it was tracked down that this property was extraordinarily improved. The ability of the polyester texture protect against ultraviolet radiation has been evaluated.

Keywords: Disperse dyes, pyrazolopyrimidinones, dye bath reuse.

1. Introduction

It is worth noting that ultraviolet rays have harmful and dangerous effects on human health, so exposure to ultraviolet rays for long periods may lead to serious diseases, such as skin cancer [1-4]. In the past, textiles were used and some modifications were made in the thickness of these textiles in order to help protect against UV damage, such as umbrellas and hats, although these modifications are not sufficient to improve the performance of textiles against UV rays. Therefore, some potential treatments have been studied to improve the performance of textiles in protecting against UV rays, especially on human skin [5-7]. The term ultraviolet protection factor (UPF) appeared, which gives us a real picture of the tissue's ability to reduce damage caused by UV rays [8, 9]. One of the significant elements that influence the protection factor is the fabric itself, just like the kind of fabrics and its capacity to absorb ultraviolet beams. For instance, polyester textures are influenced by ultraviolet beams, as it can able to absorb ultraviolet in UVA (320-400 nanometers) and UVB (290-320 nanometers) [10-14]. Polyester textures have the property of assurance against UV harm, can be treated for certain natural and inorganic synthetic materials and are called blockers. Inorganic blockers are semiconductor oxides like TiO₂ or ZnO. Recently we have mentioned that ZnO has been accounted for as a decent and safe blocker for bright beams as it retains beams well and on a wide reach, so it is prescribed to utilize it as an UV blocker.

2. Materials and Methods

General method for the Synthesis of Disperse Dyes 1-9 which applied in this survey had been annotated in our published study [1].

Fabric

Scoured and bleached 100% polyester fabric was supplied by El-Mahalla El-Kobra Company, Egypt. The fabrics were scoured in aqueous solution having a liquor ratio of 1:50 and containing 2 g/L of nonionic detergent solution (Hostapal; Clariant, Swiss) and 2 g/L of Na₂CO₃ at 50 °C for 30 min to remove waxes and impurities, then rinsed thoroughly in cold tap water, and dried at room temperature.

Dyeing process

Dyeing procedure by using microwave oven had been described in our published study [2]

Color fastness to light

The light fastness test was carried out in accordance with the ISO 105-B02:1988 test method 9, using a carbon arc lamp and continuous light for 35 h. The effect on the color of the tested samples was recorded by reference to the blue scale for color change.

Fabric Treatment with zinc oxide Pre-treatment

The fabric samples were soaked for 10 min. in 10 g/l nonionic detergent solution (Hostapal, Clariant),

*Corresponding author e-mail: <u>elapaserym@yahoo.com</u>.; (**Morsy Ahmed Elapasery**). Receive Date: 27 April 2021, Revise Date: 19 June 2021, Accept Date: 20 June 2021 DOI: 10.21608/EJCHEM.2021.74320.3669

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dispersion of ZnO NPs (0-2.5% w/w) under gentle stirring for 15 min. The fabrics were squeezed to remove the excess dispersion and dried in an oven at 70 °C for 10 min. The fabrics were querying at 140 °C for 3 min. The fabrics were washed in aqueous solution with a liquor ratio1:50 containing 3 g/l nonionic detergent solution (Hostapal, Clariant) at 60 °C for 15 min.

Post-treatment

The fabric samples were soaked for 10 min. in 10 g/l nonionic detergent solution (Hostapal, Clariant), dispersion of ZnO nano particles (0-2.5% w/w) under gentle stirring for 15 min after dyeing. The fabrics were squeezed to remove the excess dispersion and dried in an oven at 70 °C for 10 min. The fabrics were querying at 140 °C for 3 min. The fabrics were washed in aqueous solution with a liquor ratio1:50 containing 3 g/l nonionic detergent solution (Hostapal, Clariant) at 60 °C for 15 min.

UV- blocking measurements of nano ZnO treated polyester fabrics

UV-blocking measurements were performed by measuring transmittance with duple beam UV-Vis. spectrophotometer attached with integrating sphere at National Institute for Standards, Cairo, Egypt [10].

Dye bath waste water treatment

Dye baths which resulting from first reuse of dye baths had been adjusted to pH4.5 then used as a new dye bath in the same conditions of first dyeing and the same for third dying.

3. Results and Discussion

In this manner, figure 1, shows the chemical structure of the pyrazolopyrimidinones disperse dyes that were applied for dyeing the polyester fabrics [1-3].

UV protective properties of untreated and treated polyester fabrics with zinc oxide nano particle size ZnO NPs

It is clear from Table 1 that treatment using zinc oxide nano particle size ZnO NPs has given polyester fabric multiple properties now, for example, the property of protection from ultraviolet rays, where the results indicated that the treatment after the dyeing process was better with all the dyes used except for dye 8, where the results were the opposite, meaning that the treatment before the dyeing process is better than after the dyeing process, and the zinc oxide ratio was 2.5 g/ L, where the UPF value was 12.1. Referring to the treatment after the dyeing process, the ZnO NPs ratio of 1 g/L was the highest for dye 2, dye 5, dye 6 and dye 7 with UPF values of 16.9, 13.2, 17.2 and 11.9. This was followed by a ZnO NPs ratio of 1.5 g/L which is the highest for dye 1, dye 3 with UPF values of 15.1 and 12.7. Finally, the ZnO NPs ratio of 2.5 g/ L is the highest for dye 4 and dye 9, with UPF values of 17.1 and 15.3. In general, we can say that the treatment after the dyeing process is much better than the treatment before the dyeing process, and it is preferable that the ZnO NPs ratio be 1 g/L.

Treatment of dyeing waste water through Dye baths reuse for second time

The results in Table 2 show that the dye baths resulting from the first dyeing process can be treated by reusing them again. In our previous study [3], dyeing baths were used after the first dyeing process, and the results were satisfactory, but we found that the same dyeing baths can also be used for dyeing once. Others are for the purpose of treating wastewater before the process of disposal, and this reflects positively on the environment, as well as obtaining dyed fabrics without much cost.

Table 2 shows that reusing the dye baths can remove a large amount of dye from the dyeing baths, as the fabric has very good color intensity compared to the first dyeing process except dye **1** and dye **5**.



Figure 1. Chemical structure of the disperse dyes

Table 1. UPF of untreated and treated polyester fabrics with ZnO NPs

Dye No	Treatment	ZnO %	AATCC Test Method 183 - UPF	AATCC - UVA Trans.	AATCC - UVB Trans	AATCC test method183 - UVA	AATCC test method183 - UVB
	Untreated		7.7				
		0.5	10.1	19.3	7.1	80.7	92.9
		1.0	10.0	19.7	7.3	80.3	92.7
	Pre-treated	1.5	9.7	19.9	7.6	80.1	92.4
		2.0	10.0	20.0	7.2	80.0	92.8
(1)		2.5	9.6	21.1	7.5	78.9	92.5
		0.5	12.5	11.7	6.5	88.3	93.5
		1.0	12.9	11.6	6.3	88.4	93.7
	Post-treated	1.5	15.1	9.3	5.5	90.7	94.5
		2.0	12.2	13.5	6.4	86.5	93.6
		2.5	14.3	10.4	6.7	89.6	94.8
	Pre-treated	0.5	12.0	11.4	<i>с</i> 1	00.6	02.6
		0.5	12.8	11.4	6.4	88.6	93.6
		1.0	12.0	12.2	6./	87.8	93.3
		1.5	11.9	12.1	6.9	87.9	93.1
		2.0	12.2	12.0	6.6	88.0	93.4
(2)		2.5	12.7	11.5	6.3	88.5	93.7
	Post-treated	0.5	16.5	6.7	5.5	93.3	94.5
		1.0	16.9	6.3	5.5	93.7	94.5
		1.5	15.2	7.8	5.8	92.2	94.2
		2.0	15.3	7.2	5.9	92.8	94.1
		2.5	16.6	6.9	5.4	93.1	93.4
		0.5	11.8	15.5	6.2	84.5	93.8
	Pre-treated	1.0	10.4	17.0	7.2	83.0	92.8
(3)		1.5	10.8	16.6	6.8	83.4	93.2
		2.0	10.6	16.9	6.9	83.1	93.1

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		2.5	11.5	16.2	6.3	83.8	93.6
		0.5	11.3	15.2	6.6	84.8	93.4
		1.0	12.3	13.0	61	87.0	93.9
	Doct treated	1.0	11.2	14.6	6.8	85.4	03.2
	1 Ost-treated	1.5	11.2	14.0	6.1	85.4	93.2
		2.0	12.5	12.9	0.1	07.1	95.9
		2.3	12.7	12.0	0.0	07.4	94.0
		0.5	0.5	25.2	11.0	100.1	12.0
		0.5	8.5	25.3	11.2	- 180.1	- 43.2
	_	1.0	11.0	10.31	10.5	- 41.2	95.0
	Pre-treated	1.5	12.5	11.4	6.7	91.6	93.2
		2.0	13.2	11.4	6.1	-92.3	83.2
(4)		2.5	11.5	15.1	14.5	67.3	47.3
		0.5	14.1	8.1	6.4	91.9	93.5
		1.0	14.6	7.5	6.4	92.6	93.6
	Post-treated	1.5	15.6	7.2	5.9	92.8	54.1
		2.0	15.0	5.9	4.9	91.8	35.3
		2.5	17.1	6.6	5.4	93.5	94.5
		0.5	10.4	19.5	6.9	80.5	93.1
		1.0	10.3	20.5	6.8	79.5	93.2
	Pre-treated	1.5	10.0	22.7	6.9	77.3	93.1
		2.0	11.2	18.7	6.4	81.3	93.6
(5)		2.0	0.0	20.9	7.4	79.1	92.5
(3)		2.5	10.7	15.7	7.4	94.2	92.3
		0.5	10.7	13.7	1.2	04.3	92.0
	De et tree te d	1.0	15.2	12.7	5.9	07.5	94.1
	Post-treated	1.5	11.4	10.5	0.4	83.3	93.0
		2.0	11.6	15.2	6.6	84.8	93.4
		2.5	12.4	13.1	6.3	86.9	93.7
		7.0.4/	A AMOOM A				
Dve	Treatment	ZnO %	AATCC Test	AATCC -	AATCC -	AATCC test	AATCC test
No			Method 183 -	UVA Trans.	UVB Trans	method183 -	method183 -
			UPF			UVA	UVB
		0.5	11.0	12.4	12.0	02.1	01.2
				1.1.4	1211	V / I	ui :)
		0.5	11.9	12.4	13.0	03.1	91.2
		1.0	13.2	11.2	13.0	82.1	93.8
	Pre-treated	1.0 1.5	11.9 13.2 14.2	12.4 11.2 11.9	13.0 13.0 5.8	83.1 82.1 88.1	93.8 84.3
	Pre-treated	1.0 1.5 2.0	11.9 13.2 14.2 13.9	12.4 11.2 11.9 11.1	13.0 13.0 5.8 6.8	83.1 82.1 88.1 89.8	93.8 84.3 91.1
(6)	Pre-treated	1.0 1.5 2.0 2.5	11.9 13.2 14.2 13.9 12.2	12.4 11.2 11.9 11.1 11.1	13.0 13.0 5.8 6.8 7.1	83.1 82.1 88.1 89.8 81.1	93.8 93.8 84.3 91.1 97.6
(6)	Pre-treated	$ \begin{array}{r} 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ \underline{2.5} \\ 0.5 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14,6	12.4 11.2 11.9 11.1 11.1 8.2	13.0 13.0 5.8 6.8 7.1 6.9	83.1 82.1 88.1 89.8 81.1 91.8	93.8 93.8 84.3 91.1 97.6 98.0
(6)	Pre-treated	$ \begin{array}{r} 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14,6 17.2	12.4 11.2 11.9 11.1 11.1 8.2 5.9	13.0 13.0 5.8 6.8 7.1 6.9 5.2	83.1 82.1 88.1 89.8 81.1 91.8 93.1	91.2 93.8 84.3 91.1 97.6 98.0 94.0
(6)	Pre-treated Post-treated	$ \begin{array}{r} 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ \underline{2.5} \\ 0.5 \\ 1.0 \\ 1.5 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8
(6)	Pre-treated Post-treated	$ \begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ \underline{2.5} \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2
(6)	Pre-treated Post-treated	$ \begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \overline{0.5} \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0
(6)	Pre-treated Post-treated	$ \begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0
(6)	Pre-treated Post-treated	$ \begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 0.5 \\ \end{array} $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5
(6)	Pre-treated Post-treated	$0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 0.5 \\ 1.0 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.5 \\ 1.0 $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1 10.0	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 94.0 93.5 92.7
(6)	Pre-treated Post-treated	$0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1 10.0 10.5	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 94.2 94.0
(6)	Pre-treated Post-treated Pre-treated	$0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 1.5 \\ 1.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 $	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.2 93.3
(6)	Pre-treated Post-treated Pre-treated	$\begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline \end{array}$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1	93.8 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1
(6)	Pre-treated Post-treated Pre-treated	$\begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 0.5 \\ \hline 0.5 \\ 0.5 \\ \hline 0$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9 7.0	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2	93.8 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.2 93.3 93.1 93.0
(6)	Pre-treated Post-treated Pre-treated	$\begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 1.0 \\ \hline \end{array}$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9 7.0 6.2	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2	93.8 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8
(6)	Pre-treated Post-treated Pre-treated	$\begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 1.0 \\ 1.5 \\ 0.5 \\ 0.5 \\ 1.0 \\ 0.5$	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9 7.0 6.2 6.2	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6	93.8 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.2 93.3 93.1
(6)	Pre-treated Post-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ \hline 0.5\\ 1.0\\ 1.5\\ 0.5\\ \hline 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.4	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3 17.4 17.0	$ \begin{array}{c} 13.0\\ 13.0\\ 5.8\\ 6.8\\ 7.1\\ 6.9\\ 5.2\\ 6.2\\ 5.8\\ 6.6\\ \hline 6.4\\ 7.3\\ 6.8\\ 6.7\\ 6.9\\ \hline 7.0\\ 6.2\\ 6.2\\ 6.5\\ \hline \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8
(6)	Pre-treated Post-treated Pre-treated	$\begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 1.5 \\ 1.5 \\ 2.0 \\ 2.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 1.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.5 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\ 1.0 \\$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 1.1 1.1 1.2 1.2 1.2 1.2 1.	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4 17.0 16.2	$ \begin{array}{c} 13.0\\ 13.0\\ 5.8\\ 6.8\\ 7.1\\ 6.9\\ 5.2\\ 6.2\\ 5.8\\ 6.6\\ \hline 6.4\\ 7.3\\ 6.8\\ 6.7\\ 6.9\\ \hline 7.0\\ 6.2\\ 6.2\\ 6.2\\ 6.2\\ 6.5\\ 6.6\\ \hline \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 82.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.5 93.5 93.5 93.5
(6) (7)	Pre-treated Post-treated Pre-treated Post-treated	$\begin{array}{r} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 0.5\\ 0.5\\ 1.0\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0$	$ \begin{array}{c} 11.9\\ 13.2\\ 14.2\\ 13.9\\ 12.2\\ 14.6\\ 17.2\\ 14.3\\ 15.2\\ 14.5\\ 14.5\\ 10.5\\ 10.5\\ 10.8\\ 10.5\\ 10.2\\ 11.9\\ 11.4\\ 11.1\\ 11.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0$	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3 17.4 17.0 16.2	$ \begin{array}{c} 13.0\\ 13.0\\ 5.8\\ 6.8\\ 7.1\\ 6.9\\ 5.2\\ 6.2\\ 5.8\\ 6.6\\ \hline 6.4\\ 7.3\\ 6.8\\ 6.7\\ 6.9\\ \hline 7.0\\ 6.2\\ 6.2\\ 6.2\\ 6.5\\ 6.8\\ \hline 6.5\\ \hline 6.8\\ \hline 6.8\\ \hline 6.8\\ \hline 6.5\\ \hline 6.8\\ \hline 6.8\\ \hline 6.5\\ \hline 6.8\\ \hline 6$	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 81.4	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.8 93.8
(6)	Pre-treated Post-treated Pre-treated Post-treated	$\begin{array}{r} 0.3 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ \hline 0.5 \\ 0.5 \\ 0.5 \\ \hline 0.5 \\ 0.5 \\ \hline 0.5 \\$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.3 15.2 14.5 10.5 10.5 10.2 11.9 11.4 11.1 10.0 8.8	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4 17.0 16.2 27.4	$ \begin{array}{c} 13.0\\ 13.0\\ 5.8\\ 6.8\\ 7.1\\ 6.9\\ 5.2\\ 6.2\\ 5.8\\ 6.6\\ \hline 6.4\\ 7.3\\ 6.8\\ 6.7\\ 6.9\\ \hline 7.0\\ 6.2\\ 6.2\\ 6.2\\ 6.5\\ 6.8\\ \hline 7.7\\ \hline 6.8\\ 7.7\\ \hline 6.8\\ \hline 7.7\\ \hline 6.9\\ \hline 7.0\\ \hline 6.2\\ 6.2\\ \hline 6.5\\ \hline 6.8\\ \hline 7.7\\ \hline 6.8\\ \hline 7.7\\ \hline 6.8\\ \hline 7.7\\ \hline 6.9\\ \hline 7.0\\ \hline 6.2\\ \hline 6.2\\ \hline 6.5\\ \hline 6.8\\ \hline 7.7\\ \hline 7.8\\ \hline 7.8\\ \hline 7.7\\ \hline 7.8\\ \hline 7.7\\ \hline 7.8\\ \hline 7.8\\ \hline 7.7\\ \hline 7.8\\ \hline 7.8\\$	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.1 93.0 93.8 93.8 93.8 93.8 93.5 93.2 93.2 93.2 93.2
(6)	Pre-treated Post-treated Post-treated	$\begin{array}{r} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ \hline 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ \hline 1.0\\ \hline 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ \hline 1.0\\ \hline 0.5\\ 1.0\\ 1.5\\ 1.0\\ 0.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0$	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4	$12.4 \\ 11.2 \\ 11.9 \\ 11.1 \\ 11.1 \\ 8.2 \\ 5.9 \\ 8.3 \\ 7.9 \\ 8.4 \\ 17.8 \\ 19.2 \\ 18.6 \\ 18.1 \\ 18.9 \\ 15.3 \\ 17.4 \\ 17.0 \\ 16.2 \\ 27.4 \\ 28.6 \\ 18.1 \\ 18.9 \\ 15.3 \\ 17.4 \\ 17.0 \\ 16.2 \\ 27.4 \\ 28.6 \\ 100 $	$ \begin{array}{c} 13.0\\ 13.0\\ 5.8\\ 6.8\\ 7.1\\ 6.9\\ 5.2\\ 6.2\\ 5.8\\ 6.6\\ \hline 6.4\\ 7.3\\ 6.8\\ 6.7\\ 6.9\\ \hline 7.0\\ 6.2\\ 6.2\\ 6.5\\ 6.8\\ \hline 7.7\\ 8.1\\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4	93.8 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.5 93.2 93.2 92.3 91.9
(6)	Pre-treated Post-treated Post-treated Post-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ \hline \end{array}$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9 7.0 6.2 6.5 6.8 7.7 8.1 8.2	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.8 93.8
(6)	Pre-treated Post-treated Post-treated Post-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 0.5\\ 1.0\\ 0.5\\ 1.0\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9 7.0 6.2 6.5 6.8 7.7 8.1 8.2 8.4	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.8 93.5 93.2 92.3 91.9 91.8 91.6
(6)	Pre-treated Post-treated Post-treated Post-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline \end{array}$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0 22.2	13.0 13.0 5.8 6.8 7.1 6.9 5.2 6.2 5.8 6.6 6.4 7.3 6.8 6.7 6.9 7.0 6.2 6.5 6.8 7.7 8.1 8.2 8.4 5.5	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8	93.8 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.8 93.5 93.2 92.3 91.9 91.8 91.6 94.6
(6) (7) (8)	Pre-treated Post-treated Post-treated Post-treated	$\begin{array}{r} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ \hline 0.$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0 22.2 24.5	$ \begin{array}{r} 13.0 \\ 13.0 \\ 5.8 \\ 6.8 \\ 7.1 \\ 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.4 \\ 7.3 \\ 6.8 \\ 6.7 \\ 6.9 \\ \hline 7.0 \\ 6.2 \\ 6.5 \\ 6.8 \\ 7.7 \\ 8.1 \\ 8.2 \\ 8.4 \\ 5.5 \\ 7.4 \\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.5 93.2 92.3 91.9 91.8 91.6 94.6 92.6
(6) (7) (8)	Pre-treated Post-treated Post-treated Post-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 1.0\\ \hline 0.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0$	11.9 13.2 14.2 13.9 12.2 14,6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3 9.8	$12.4 \\ 11.2 \\ 11.9 \\ 11.1 \\ 11.1 \\ 8.2 \\ 5.9 \\ 8.3 \\ 7.9 \\ 8.4 \\ 17.8 \\ 19.2 \\ 18.6 \\ 18.1 \\ 18.9 \\ 15.3 \\ 17.4 \\ 17.0 \\ 16.2 \\ 27.4 \\ 28.6 \\ 28.2 \\ 28.0 \\ 22.2 \\ 24.5 \\ 24.6 \\ 12.2 \\ 24.5 \\ 24.6 \\ 12.2 \\ 24.6 \\ 12.2 \\ 24.6 \\ 12.2 \\ 24.5 \\ 24.6 \\ 12.2 \\ 12.2 $	$ \begin{array}{c} 13.0\\ 13.0\\ 5.8\\ 6.8\\ 7.1\\ 6.9\\ 5.2\\ 6.2\\ 5.8\\ 6.6\\ \hline 6.4\\ 7.3\\ 6.8\\ 6.7\\ 6.9\\ \hline 7.0\\ 6.2\\ 6.2\\ 6.5\\ 6.8\\ \hline 7.7\\ 8.1\\ 8.2\\ 8.4\\ 5.5\\ \hline 7.4\\ 6.8\\ \hline $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5 75.4	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.5 93.2 92.3 91.9 91.8 91.6 94.6 92.6 93.2
(6) (7) (8)	Pre-treated Post-treated Pre-treated Pre-treated Pre-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ \hline 1.0\\ 1.5\\ \hline 0.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.5\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0\\ 1.0$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3 9.8 9.9	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0 22.2 24.5 24.6 24.2	$ \begin{array}{r} 13.0 \\ 13.0 \\ 5.8 \\ 6.8 \\ 7.1 \\ 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.4 \\ 7.3 \\ 6.8 \\ 6.7 \\ 6.9 \\ 7.0 \\ 6.2 \\ 6.5 \\ 6.8 \\ 7.7 \\ 8.1 \\ 8.2 \\ 8.4 \\ 5.5 \\ 7.4 \\ 6.8 \\ 6.8 \\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5 75.4 75.8	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.5 93.2 92.3 91.9 91.8 91.6 94.6 92.6 93.2 93.2
(6) (7) (8)	Pre-treated Post-treated Post-treated Pre-treated Post-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 0.5\\ 1.0\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3 9.8 9.9 9.0	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0 22.2 24.5 24.6 24.2 27.0	$ \begin{array}{r} 13.0 \\ 13.0 \\ 5.8 \\ 6.8 \\ 7.1 \\ 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.4 \\ 7.3 \\ 6.8 \\ 6.7 \\ 6.9 \\ 7.0 \\ 6.2 \\ 6.5 \\ 6.8 \\ 7.7 \\ 8.1 \\ 8.2 \\ 8.4 \\ 5.5 \\ 7.4 \\ 6.8 \\ 6.8 \\ 7.5 \\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5 75.4 75.8 73.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.5 93.2 93.3 93.5 93.2 92.3 91.9 91.8 91.6 94.6 92.6 93.2 93.2 93.2 93.2 93.2 93.2 93.2
(6) (7) (8)	Pre-treated Post-treated Post-treated Pre-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3 9.8 9.9 9.0 11.0	$\begin{array}{c} 12.4 \\ 11.2 \\ 11.9 \\ 11.1 \\ 11.1 \\ \hline \\ 8.2 \\ 5.9 \\ 8.3 \\ 7.9 \\ 8.4 \\ \hline \\ 17.8 \\ 19.2 \\ 18.6 \\ 18.1 \\ 18.9 \\ \hline \\ 18.9 \\ 15.3 \\ 17.4 \\ 17.0 \\ \hline \\ 18.9 \\ 15.3 \\ 17.4 \\ 17.0 \\ \hline \\ 27.4 \\ 28.6 \\ 28.2 \\ 28.0 \\ 22.2 \\ 24.5 \\ 24.6 \\ 24.2 \\ 27.0 \\ 24.0 \\ \hline \end{array}$	$ \begin{array}{r} 13.0 \\ 13.0 \\ 5.8 \\ 6.8 \\ 7.1 \\ 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.4 \\ 7.3 \\ 6.8 \\ 6.7 \\ 6.9 \\ 7.0 \\ 6.2 \\ 6.2 \\ 6.5 \\ 6.8 \\ 7.7 \\ 8.1 \\ 8.2 \\ 8.4 \\ 5.5 \\ 7.4 \\ 6.8 \\ 6.8 \\ 7.5 \\ 5.9 \\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5 75.4 75.8 73.0 76.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.5 93.2 92.3 91.9 91.8 91.6 94.6 92.6 93.2 93.2 92.5 94.1
(6) (7) (8)	Pre-treated Post-treated Post-treated Pre-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline \end{array}$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.8 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3 9.8 9.9 9.0 11.0	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0 22.2 24.5 24.6 24.2 27.0 24.0	$ \begin{array}{r} 13.0 \\ 13.0 \\ 5.8 \\ 6.8 \\ 7.1 \\ 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.4 \\ 7.3 \\ 6.8 \\ 6.7 \\ 6.9 \\ 7.0 \\ 6.2 \\ 6.2 \\ 6.2 \\ 6.5 \\ 6.8 \\ 7.7 \\ 8.1 \\ 8.2 \\ 8.4 \\ 5.5 \\ 7.4 \\ 6.8 \\ 7.5 \\ 5.9 \\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5 75.4 73.0 76.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.5 93.2 92.3 91.9 91.8 91.6 94.6 92.6 93.2 93.2 92.5 94.1
(6) (7) (8) (9)	Pre-treated Post-treated Pre-treated Pre-treated Pre-treated Pre-treated Pre-treated	$\begin{array}{c} 0.3\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ \hline 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 2.0\\ 0.5\\ 1.0\\ 1.5\\ 0.5\\ 1.0\\ 0.5\\ 1.0\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0$	11.9 13.2 14.2 13.9 12.2 14.6 17.2 14.3 15.2 14.5 11.1 10.0 10.5 10.2 11.9 11.4 11.1 11.0 8.8 8.4 8.3 8.3 12.1 9.3 9.8 9.9 9.0 11.0 10.1	12.4 11.2 11.9 11.1 11.1 8.2 5.9 8.3 7.9 8.4 17.8 19.2 18.6 18.1 18.9 15.3 17.4 17.0 16.2 27.4 28.6 28.2 28.0 22.2 24.5 24.6 24.0 20.9	$ \begin{array}{r} 13.0 \\ 13.0 \\ 5.8 \\ 6.8 \\ 7.1 \\ 6.9 \\ 5.2 \\ 6.2 \\ 5.8 \\ 6.6 \\ \end{array} $ $ \begin{array}{r} 6.4 \\ 7.3 \\ 6.8 \\ 6.7 \\ 6.9 \\ 7.0 \\ 6.2 \\ 6.5 \\ 6.8 \\ 7.7 \\ 8.1 \\ 8.2 \\ 8.4 \\ 5.5 \\ 7.4 \\ 6.8 \\ 6.8 \\ 7.5 \\ 5.9 \\ 7.0 \\ \end{array} $	83.1 82.1 88.1 89.8 81.1 91.8 93.1 91.7 92.1 91.5 82.2 80.8 81.4 81.9 81.1 81.2 84.2 82.6 82.0 83.3 72.6 71.4 71.8 72.0 77.8 75.5 75.4 75.8 73.0 76.0	91.2 93.8 84.3 91.1 97.6 98.0 94.0 93.8 94.2 94.0 93.5 92.7 93.2 93.3 93.1 93.0 93.8 93.8 93.8 93.8 93.8 93.8 93.5 93.2 93.2 93.2 92.3 91.9 91.8 91.6 94.6 94.6 92.6 93.2 93.2 93.2 93.2 93.2 93.2 93.2 94.1

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MONOAZO DISPERSE DYES BASED ON PYRAZOLOPYRIMIDINONES PROVIDE	
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	1.0	9.8	21.0	7.3	79.0	92.7
	1.5	9.9	20.7	7.3	79.3	92.7
	2.0	9.2	22.5	7.8	77.5	92.2
	2.5	10.1	20.9	7.0	79.1	93.0
	0.5	11.2	17.3	6.5	82.7	93.5
	1.0	10.9	17.2	6.8	82.8	93.2
Post-treated	1.5	11.2	16.8	6.6	83.2	93.4
	2.0	10.7	18.1	6.7	81.9	93.3
	2.5	15.3	13.5	4.8	86.5	95.2

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Table 2. Reusing of dye bath waste water in dyeing process

Dye	K/S	K/S	L*	<i>a</i> *	b*	<i>C</i> *	h^*
No	First dyeing	Second Dye baths reuse					
1	10.69	2.53	71.07	9.59	41.00	42.10	76.83
2	18.53	12.23	65.32	20.22	67.79	70.74	23.18
3	7.71	3.56	74.11	4.01	27.32	27.62	81.64
4	18.73	12.27	70.96	3.20	72.38	72.45	87.46
5	14.54	0.96	76.20	- 3.32	24.44	24.66	97.75
6	2.87	2.84	74.73	- 5.57	45.78	46.11	96.94
7	4.71	1.93	72.70	8.36	38.26	39.16	77.67
8	2.53	1.30	73.19	5.15	30.06	30.50	80.28
9	1.75	0.69	76.32	- 1.25	18.86	18.90	93.80

Table 3. Light fastness of the untreated and treated polyester fabrics with ZnO NPs.

Dye	Treatment	ZnO %	Light	Dye	Treatment	ZnO %	Light	Dye	Treatment	ZnO %	Light
No.			fastness	No.			fastness	No.			fastness
	Pre-treated	Untreated	2	-		Untreated	4			Untreated	3
		0.5	2			0.5	6			0.5	3
		1.0	2		Pre-treated	1.0	4		Dra traatad	1.0	3
		1.5	2			1.5	5		rie-tieateu	1.5	3-4
		2.0	2			2.0	5			2.0	4
1		2.5	2-3	4		2.5	5	7		2.5	3
		0.5	3			0.5	4			0.5	3
		1.0	4			1.0	4		Dest	1.0	3
	Post-treated	1.5	3		Post-treated	1.5	4		Post-	1.5	3-4
		2.0	4			2.0	4		treated	2.0	4
		2.5	3			2.5	3			2.5	3-4
		Untreated	2			Untreated	2			Untreated	3-4
		0.5	4			0.5	2		Pre-treated	0.5	3
	Pre-treated	1.0	3-4	5	Pre-treated	1.0	2-3	8		1.0	4
		1.5	4			1.5	3			1.5	3
		2.0	3			2.0	2			2.0	3
2		2.5	4			2.5	2-3			2.5	3-4
	Post-treated	0.5	2		Post-treated	0.5	2-3		Post- treated	0.5	3
		1.0	3			1.0	4			1.0	5
		1.5	2			1.5	3			1.5	4
		2.0	5			2.0	3			2.0	3-4
		2.5	3-4			2.5	3			2.5	3-4
		Untreated	2-3			Untreated	3-4			Untreated	2-3
		0.5	4	-		0.5	5		Dra tracted	0.5	2-3
	Dra traatad	1.0	3		Dra traatad	1.0	3-4			1.0	3
	Fie-treated	1.5	3-4		Fle-treated	1.5	4		Fle-treated	1.5	2-3
		2.0	3	6		2.0	4			2.0	2-3
3		2.5	3			2.5	3-4	9		2.5	2-3
		0.5	3			0.5	3			0.5	2-3
		1.0	3			1.0	3-4		Post-	1.0	3-4
	Post-treated	1.5	2		Post-treated	1.5	3-4			1.5	3
		2.0	3-4			2.0	4		ucated	2.0	3
		2.5	3			2.5	3			2.5	3

It is clear from Table 3 that treatment using zinc oxide nano particle size ZnO NPs has given polyester fabric multiple properties now, for example, improved light fastness, where the results indicated that the treatment after the dyeing process was better with all dyes used except dye 3, dye 4 and dye 6, which was the opposite, this means that the treatment before the dyeing process is better than after the dyeing process, and the proportion of zinc oxide was 0.5 g/L, where the light fastness values become 4, 6 and 5, where the light fastness values of the fabrics improved as these were 2-3, 4 and 3-4. Referring to the treatment after the dyeing process, the ZnO NPs ratio of 1 g/L was the highest for dye 1, dye 5, dye 8 and dye 9 with light fastness values 4, 4, 5 and 3-4, where the light fastness property of the fabrics was improved as these were 2, 2, 3.4 and 2-3. This was followed by the ZnO NPs ratio of 2 g/L which is the highest for dye 2 and dye 7, the light fastness values become 5 and 4, where the light fastness property of the fabrics was improved as it was 2 and 3. In general, we could say that the treatment after the dyeing process is much better than the treatment before the dyeing process, and it is preferable that the ZnO NPs ratio be 1 g/L.

4. Conclusions

In summary, we would like to point out that these prepared disperse dyes provided an added value as the polyester fabric dyed with these dyes gave good results against ultraviolet rays that harm the skin, in addition to that the light-fastness property improved when the fabrics were treated with zinc oxide nano particle size ZnO NPs.

5. Conflicts of interest

There are no conflicts to declare.

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