



Assessment of Reactive Dyeing of Cotton using Seawater

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Abstract

This study investigated the effects of auxiliary chemicals on reactive dyeing of cotton fabric using seawater as an alternative to freshwater. The study involved dyeing of 100% cotton fabric with reactive blue 21 using both fresh and seawater. The effects of Na_2SO_4 , NaCl and Na_2CO_3 auxiliaries were assessed on dye exhaustion, fixation and colour strength. Reactive dyeing using seawater with a pH 9 which contained Na^+ (882.4 mg/L), Cl^- (938 mg/L), Ca^{2+} (1200 mg/L), CO_3^{2-} (3000 mg/L), Mg^{2+} (1030 mg/L) and alkalinity (4615 mg/L), resulted in exhaustion rate of 54%, colour strength of 0.098 and fixation rate of 44%. While dyeing using freshwater gave exhaustion rate of 34%, colour strength of 0.026 and fixation rate of 34%. When auxiliaries were added, the exhaustion, colour strength and fixation for freshwater dyeing were 66%, 0.199 and 84%, respectively. In contrast for seawater dyeing, the corresponding results were 56% for exhaustion, 0.53 for colour strength, and 76% for fixation. These results showed that seawater's natural electrolytes reduced the need for additional chemicals but also led to excessive auxiliary concentrations that hindered dye performance. Freshwater dyeing, by contrast, showed higher dye exhaustion, colour strength, and fixation when auxiliaries were added. Given the rising demand for freshwater and the high-water consumption in textile dyeing, particularly with reactive dyes, the seawater could be a viable substitute. Therefore, seawater is a feasible alternative for textile dyeing, provided chemical adjustments are made to optimize dye exhaustion and fixation.

Key words: Seawater; Reactive dyeing; Auxiliary chemicals; Exhaustion; Fixation

Introduction

Water is an essential material for domestic, agricultural and industrial activities. Water is an environmentally friendly and cost-effective industrial solvent and raw material. Globally, the development in manufacturing industrial sector is rising, hence increased industrial water consumption (Ramin et al. 2024). Textile industry is among the manufacturing sectors which consumes high amount of water especially for the wet processes such as scouring, bleaching, mercerization, dyeing and finishing (Kumar and Pavithra 2019, Muthu 2018). Freshwater

sources are the main water supply for agricultural, domestic and industrial consumption despite the large volume of seawaters. This is due to the fact that, seawater contains high amount of salts hence rich in ions such as Na^+ , Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} and K^+ (Wright and Colling 2013). These salts make seawater not suitable for some uses unless purified. On the other hand, purification of seawater is costly, which results in increased in the manufacturing operational expenses. For that reason, the demand of freshwater is high. In addition, the negative climatic change has led into

shortage of rainfall and consequently into the scarcity of freshwater (Karimi et al. 2024, Jain and Singh 2023). Therefore, it is crucial to minimize freshwater consumption for the activities that are not affected by salts through utilizing seawater instead.

Dyeing is one of the largest water consuming among the wet processes in textile industry. Reactive dyes are the most preferred dye type for cellulosic fibres such as cotton due to the fact that the dyes form covalent bond, high exhaustion rates, high fastness and can be dyed in wider colour shades. However, reactive dyes require use of high amount of auxiliary chemicals for dyeing efficiency and performance of the dyed substrates. Some of the important auxiliary chemicals for reactive dyeing of cotton include alkali (Na_2CO_3) and electrolytes (NaCl , Na_2SO_4) are present in seawater. Alkali provides alkaline media and enhance fixation of dye into fibre (Varadarajan and Venkatachalam 2016). Electrolytes neutralise the electronegativity of the fibre surface and improve the affinity of dyestuff towards the fibre and enhance the exhaustion of dyes from the dye bath onto the fabric leading to more dye uptake and deeper shades.

Therefore, the use of seawater for reactive dyeing can potentially serve as a sustainable alternative by reducing the pressure on freshwater resources. Though, this shift requires careful consideration of the chemical interactions between seawater and reactive dyes, as well as managing the salinity and the amount of auxiliaries present in seawater. This is due to the fact that, higher or lower amount of auxiliaries have negative effect on dye exhaustion, fixation and colour strength hence dye performance. For instance, excessive amount of electrolyte decreases dye solubility and increases aggregation which hinder the exhaustion, dye uptake, and affect the dye performance (Burkinshaw and Salihu 2019). Several studies have reported on the use of seawater for textile dyeing (Karim et al. 2021, de Souza Ferreira et al. 2021). However, the reported studies did not assess the effects of auxiliary chemicals on dyeing of textiles using seawater. In this study the effects of auxiliary chemicals on reactive

dyeing of cotton fabric using seawater was investigated. Specifically cotton fabrics were dyed using seawater and freshwater with and without the auxiliary chemicals then the dye exhaustion, colour strength and fixation were investigated.

Materials and Methods

Materials

Fabric used in this study was scoured and bleached 100% cotton with 152 g m⁻² supplied by 21st Century Textiles Limited, Tanzania. The seawater was collected from Indian ocean, Dar es Salaam, Tanzania. Water from Indian Ocean was selected because the ocean is the only source of seawater in Tanzania. Analytical grade Reactive dye 21, NaCl , Na_2CO_3 , Na_2SO_4 and non-ionic detergent were purchased from Sigma Aldrich, Tanzania.

Methods

Analysis of seawater

The quality of the seawater used in this study was analysed in Water Resources Laboratory, College of Engineering and Technology, University of Dar es Salaam. The analysis focused on the parameters which affect reactive dyeing. The parameters analysed included pH, hardness, total dissolved solids, Na^+ , Cl^- , Ca^{2+} , CO_3^{2-} , Mg^{2+} , alkalinity, salinity and electric conductivity.

Reactive dyeing of cotton fabric

In order to dye the fabric using freshwater, cotton fabric (5 g) was dyed with reactive blue 21 (2%, on the weight of fabric (o.w.f)) at a liquor ratio of 20:1. The amount of NaCl , Na_2SO_4 and Na_2CO_3 was 40, 75 and 15 g L⁻¹, respectively. The reactive dye (0.1 g) was dissolved in freshwater (100 mL) at room temperature followed by exhaustion of the cotton fabric (5 g) in the dye solution then temperature was raised to 60 °C. After 10 minutes, half of the NaCl was added into the dye bath, and the rest of the NaCl was added in the next 10 minutes. This controlled addition of NaCl prevents abrupt change in concentration that could lead to poor dye uptake. After 30 minutes, the temperature was raised to 80 °C at 2 °C min⁻¹, then the Na_2CO_3 and Na_2SO_4 was added into the dye

bath. The dyeing process was maintained for an additional 30 minutes. Then the dye bath was left to cool to room temperature and the dyed cotton fabric was rinsed before treatment with acetic acid (0.8 g L⁻¹) at 55 °C for 10 minutes at a liquor ratio of 1:20.

Similar procedure was repeated for seawater dyeing.

To assess the effect of auxiliary chemicals, different dye bath containing reactive blue 21 (2% o.w.f) and auxiliary chemicals were prepared as summarized in Table 1.

Table 1: Dye bath containing different auxiliaries

Procedure	Auxiliary chemicals added in freshwater dye bath	Auxiliary chemicals added in Seawater dye bath
1	NaCl, Na ₂ SO ₄ and Na ₂ CO ₃	NaCl, Na ₂ SO ₄ and Na ₂ CO ₃
2	NaCl and Na ₂ CO ₃	NaCl and Na ₂ CO ₃
3	Na ₂ SO ₄ , Na ₂ CO ₃	Na ₂ SO ₄ , Na ₂ CO ₃
4	No added auxiliary	No added auxiliary
5	Na ₂ CO ₃	Na ₂ CO ₃

Soaping process

Soaping was done to remove unfixed or loosely attached dye molecules from the surface of the fabric and reduce dye bleeding. The unfixed reactive dyes were washed off during the soaping processes in a rotary dyeing machine at a liquor ratio of 50:1 for 15 minutes at 100 °C using non-ionic detergent (1 g L⁻¹). After washing, the samples were dried in an oven at 60 °C for 120 minutes.

Measurement of Exhaustion, Colour Strength and Fixation

Exhaustion, colour strength, and fixation are interrelated parameters that significantly influence the quality, efficiency, and sustainability of textile dyeing processes. Optimizing these factors leads to better product performance.

Exhaustion

For accurate and reliable results, the absorbance values of the dye bath at the maximum absorption wavelength (λ_{max}) were measured using Ultraviolet visible spectrophotometer. The percentage exhaustion (E) was calculated using equation (1).

$$E = \left(1 - \frac{A_2}{A_1}\right) \times 100 \quad (1)$$

Where:

A₁= absorbance values at λ_{max} of the dye bath solution before the dyeing process.

A₂ = Absorbance values at λ_{max} of the remaining dye bath solution after dyeing plus washings.

Colour Strength

The colour strengths (K/S values) of the dyed samples were measured using a Dacolor International Spectroflash 600 spectrophotometer. The instrument was calibrated using black and white tiles and the maximum aperture size was used for all measurements. Each K/S value was recorded on a piece of fabric that had been folded over twice, so as to provide four layers of fabric, and each measurement was carried out three times.

Fixation

The percentage fixations (F) of the reactive dye blue 21 onto cotton fabrics were calculated using equation (2).

$$F = \left(\frac{\left(\frac{K}{S}\right)_1}{\left(\frac{K}{S}\right)_2}\right) \times 100 \quad (2)$$

where $\left(\frac{K}{S}\right)_1$ and $\left(\frac{K}{S}\right)_2$ represent the colour strengths of the dyed samples after and before the soaping process, respectively.

Results and Discussions

Water Quality

The water quality analysis results show that, seawater is highly saline, alkane and contains higher amount of dissolved solids, electrolytes than freshwater (Table 2). Similar results were reported by de Souza Ferreira et al. (2021) and Karim et al. (2021). Reactive dyeing with freshwater typically requires an alkaline medium and the addition of electrolytes as auxiliaries to enhance

exhaustion, fixation, and colour strength. In contrast, the results from seawater dyeing suggest that remarkably less or even no

auxiliaries and alkali are needed due to the natural presence of these substances in seawater.

Table 2: Quality of water used for dyeing

S/N	Parameters	Unit of Measurement	Seawater	Freshwater
1	pH	-	9	7.3
2	Hardness	ppm	5454	3.8
3	Total Dissolved Solids	ppm	29850	10
4	Sodium	mg/L	882.4	0.5
5	Chloride	mg/L	938	3.0
6	Calcium	mg/L	1200	1.4
7	Carbonate	mg/L	3000	NIL
8	Magnesium	mg/L	1030	1.0
9	Alkalinity (Na ₂ CO ₃)	mg/L	4615	NIL
10	Salinity	%	29.7	0.2
11	Electric Conductivity at 25 °C	µs/cm	45700	19.4

Effects of Auxiliary Chemicals on Dye Exhaustion

Exhaustion measurement parameter indicates how effectively a dye has been absorbed by the fabric during the dyeing process. High exhaustion rates indicate efficient dye uptake. Comparing exhaustion of freshwater and seawater dye baths by changing addition of auxiliaries (Figure 1) shows that the dye exhaustion on reactive dyeing using freshwater depends on the added auxiliary chemicals. Additionally, using comparable types and quantities of auxiliary chemicals leads to higher dye exhaustion in freshwater (66%) than seawater dyeing (56%). On the other hand, dyeing without addition of auxiliaries gave higher exhaustion (54%) in seawater than in freshwater dyeing (34%). This could be due the fact that, the concentration of auxiliaries

naturally present in the seawater boosted exhaustion, while the added amount was high which resulted into excessive. Excessive concentration of electrolytes leads to increased ionic strength in the dye bath, which neutralize the charges on the fibre surface. The neutralization reduces the fibre's ability to attract and hold onto the anions, resulting in lower dye exhaustion rates. Also, if auxiliary agents are present in excessive amounts, they can occupy a significant number of binding sites, limiting the amount of dye molecules that can adhere to the fibre (Hu et al. 2023, Aysha et al. 2022). This suggests that for improved exhaustion of reactive dyeing with seawater, analysis of the presence of type and quantity of exhaustion agent is important so as to establish any need for additional chemicals.

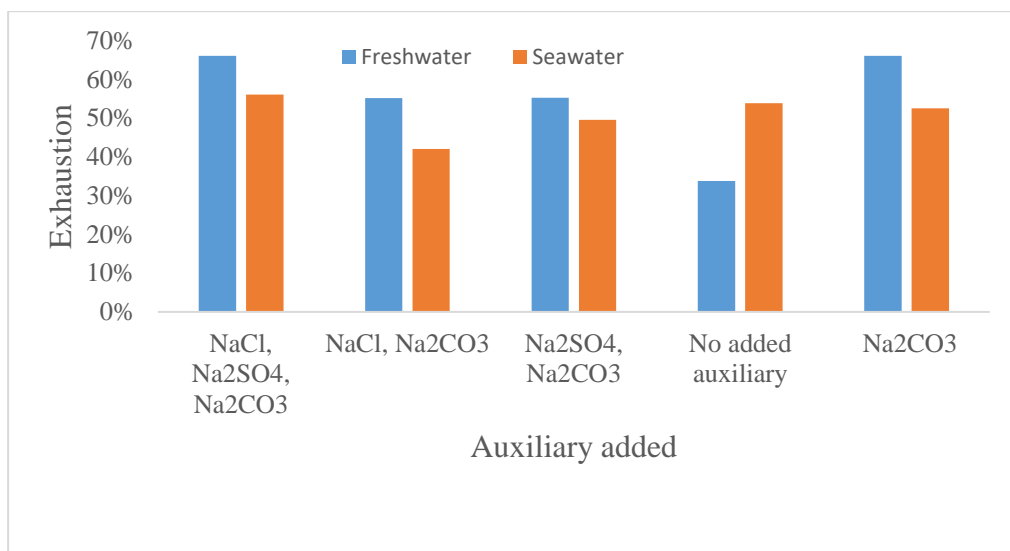


Figure 1: Effect of auxiliary chemicals for cotton reactive blue 21 dyeing using seawater and freshwater on exhaustion

The effects of Auxiliary Chemicals on Colour Strength

Colour strength quantifies the intensity or depth of colour achieved on the fabric after dyeing, high colour strength indicates vibrant and rich colours. Findings on the effects of auxiliary chemicals on the colour strength as measured by K/S values indicate that, the colour strength for freshwater dyeing depends on addition of auxiliary chemicals. Addition of equal amount and similar type of auxiliary chemicals in seawater and freshwater dye baths, resulted into higher colour strength (0.199) in freshwater than seawater (0.153). While, on reactive dyeing without addition of auxiliaries gave higher colour strength in seawater (0.098) than in freshwater (0.026)

(Figure 2). This implies that, the auxiliary chemicals have improved the colour strength during both seawater and freshwater reactive dyeing. However, the improvement is more remarkable on the freshwater dyeing. This could be due to the fact that, the added auxiliary chemicals in seawater dye bath made excessive which resulted into reduced colour strength due to dye and chemical aggregation which retarded dye-fibre interaction (Dong et al. 2019). The natural auxiliaries in the seawater can partially enhance colour strength. However, for achieving performance similar to freshwater dyeing, a controlled addition of these chemicals is recommended.

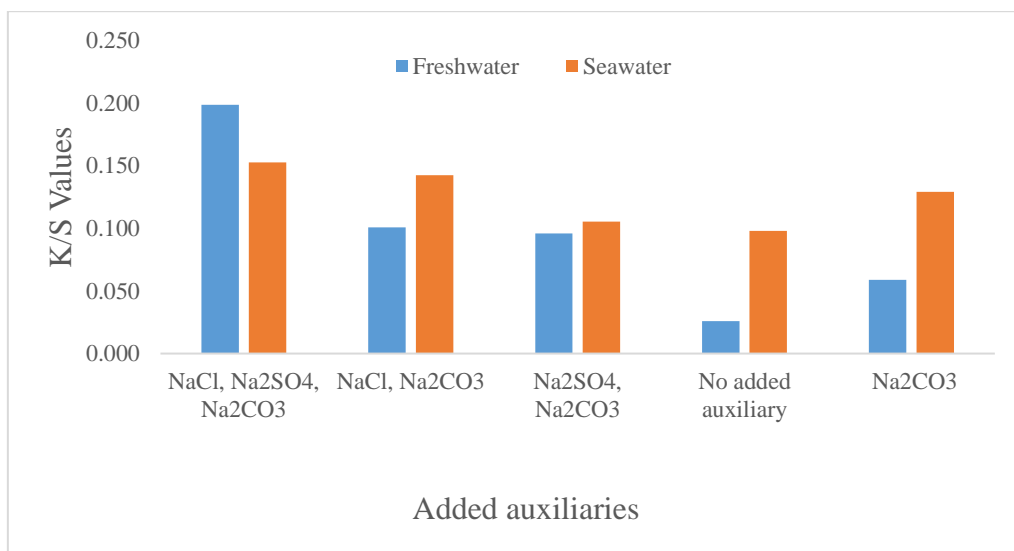


Figure 2: Effect of auxiliaries for cotton reactive blue 21 dyeing using seawater and freshwater on colour strength

Effects of Auxiliary Chemicals on Fixation

Fixation quantifies the percentage of dye that chemically bonds with the fibre. Alkaline environment is necessary for the reaction between the reactive dye and the hydroxyl groups present in cellulose fibres. The hydroxyl groups are weakly acidic and can easily dissociate in the presence of the hydroxide ions forming cellulosate ions that can react with the dye. While alkali facilitates fixation, it can also lead to hydrolysis of the dye if present in excessive amount. Hydrolysis produces a form of the dye that cannot bond with the fibre, thus reducing fixation efficiency. Therefore, maintaining an optimal level of alkali is critical; too much can hinder fixation by increasing hydrolysis rates. Also, the presence of electrolytes stabilizes the dye bath environment, making it more conducive for effective fixation. The concentration of electrolytes must be carefully managed. Insufficient electrolyte levels can lead to poor fixation rates, while excessive amounts can complicate interactions within the dye bath. Findings (Figure 3) on the effects of alkali and electrolytes indicated that when no auxiliary

chemicals added, seawater dyeing had higher fixation (44%) than freshwater dyeing (34%). Also, for the dye baths which contained NaCl and Na₂CO₃, Na₂CO₃ and Na₂SO₄; and Na₂CO₃ only, gave higher fixation for seawater than freshwater. This implies that, the presence of inherent auxiliary in seawater improved the dye fixation. On the other hand, addition of NaCl, Na₂CO₃ and Na₂SO₄, resulted into fixation of 86% for freshwater and 76% for seawater dyeing. Similar trends were reported by de Souza Ferreira et al. (2021). This show that while seawater has inherent electrolytes, they are not present in concentrations adequate for effective dyeing. Therefore, supplementary amounts are required to reach levels comparable to those found in freshwater dye baths. However, addition of similar amount of auxiliaries in seawater as in freshwater dye bath resulted into poor fixation due to the excess amount. Therefore, the added amount of auxiliary chemicals in seawater dyeing should be controlled to top-up the deficit.

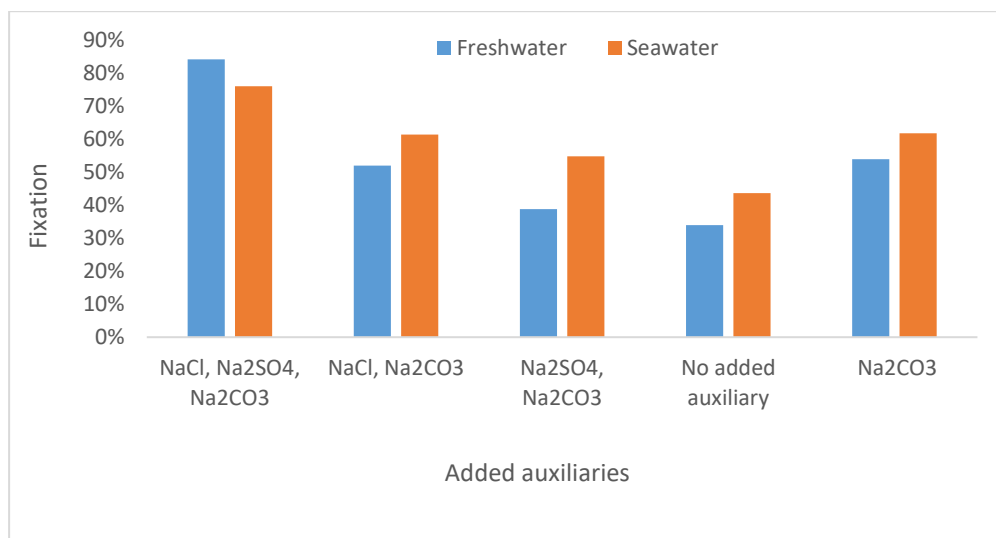


Figure 3: Effect of auxiliaries for cotton reactive blue 21 dyeing using seawater and freshwater on fixation

Conclusion

This study investigated the effects of auxiliary chemicals on the reactive dyeing of cotton using seawater. The findings revealed that reactive dyeing without the addition of auxiliary chemicals resulted in higher dye exhaustion, colour strength, and fixation in seawater compared to freshwater. This suggests that seawater naturally contains some auxiliary substances beneficial for reactive dyeing; however, their concentrations are insufficient to achieve optimal levels of exhaustion, colour strength, and fixation. Conversely, when equal amounts of auxiliary chemicals were added, the parameters measured were significantly higher in freshwater. This may be attributed to the excess concentration of auxiliaries in seawater caused by the added amount. This

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highlights that, seawater can be used for reactive dyeing as an alternative for freshwater. However, there is a need for establishing adequate concentrations of auxiliaries to enhance dye performance effectively. Overall, the research emphasizes the critical role of auxiliary chemicals in both freshwater and seawater dyeing processes to improve dye performance. While seawater presents a viable alternative for dyeing, careful adjustments to the concentrations of auxiliary chemicals are essential to optimize the exhaustion, colour strength, and fixation of reactive dyes on cotton fabrics.

Declaration of Competing Interest

The author declares that there is no conflict of interest regarding this work.

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