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Silver Nanoparticle Elecrocatalyst Embedded onto Indium Tin Oxide Electrodes for Degradation of Azo Dyes

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ABSTRACT

The research was conducted to establish the effectiveness of silver nanoparticles embedded in indium tin oxide (ITO) thin film conducting material in causing the textile azo dye effluent degradation. The percentages of azo dye degradation were as follows: 68.4%, 72.5% and 93.1% using electrocoagulation, ITO and ITO-AgNPs coupled electrodes, respectively. The results obtained from the two-factor ANOVA with replication indicated a significant difference ($p = 0.0024$) when the silver nanoparticles embedded on indium tin oxide electrodes were utilised in the degradation of these azo dyes in the effluent samples. The colour removal was 99.97% showing that the optimised process was effective and efficient in the degradation of these azo dyes in the textile wastewaters.

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INTRODUCTION

Another international problem is industrial effluents that contaminate the aquatic environment with dyes, which are more prevalent in the developing world (Bafana et al., 2011a). This pollution has been reported to not only affect the aquatic life but also reduce the quality of the water to be used by human beings (Lee et al., 2021). Instead, organisations such as: World Health Organization (WHO), the Environmental Protection Agency (EPA) in the USA and in Kenya, the Water Resource Authority (WRA) and many others in other countries have come up with policies governing the discharge of effluents into the water masses by the textile factories (Chung, 2016a). The world is extremely insistent on enhanced innovations and technologies, which contribute to the removal of industrial water pollutants (Saidu et al., 2020). Many innovations have been introduced in other industries that have been involved in the eradication of azo dye and other related chemicals, Osemba, Martin, & Maghanga, Justin. (2025).

The azo dyes are considered one of the most relevant components of industrial effluent (Hodaifa et al., 2019), as they are one of the most popular types of dyes in industries (Qiao et al., 2010). No less than 15 percent of total organic dyes are predominantly azo group that is lost, and they become components of effluents during the manufacturing and use process OSEMBA, 2019). Not only are unique water properties a major and central part of the life support system, but also of its ecological and chemical predisposition determination as well (Hodaifa et al., 2019). Most of them can be attributed to its capacity to develop hydrogen bonding and the polar framework of its molecules (Venkatadri and Peters, 1993).

The dielectric constant of water is the highest among other common liquids. Chemical phenomena of water are also reported to be high compared to any other liquid except ammonia, whose maximum capacity occurs when it exists in the liquid state at 40.0^0C. Basically, chemical phenomena of water do not occur in solutions past, but rather react with other phases like solutes that exist in water molecules (Sharma et al., 2021). An example of this is the redox reaction that will take place in the cells of bacteria, which is claimed to reduce the dissolved oxygen (DO). This is one of the effects induced by the chemical and/or biochemical oxygen demand of the cell Mutuku (Diana *et al.*, 2025). Through such decay mechanisms, the majority of hazardous organic substances tend to be emulsified and reduced into small particle suspensions, which contribute significantly to the total wastes dissolved by water (Wac lawek et al., 2019).

The transformation of sedimentary to aquatic ecosystems using physical or chemical media also infiltrates with waste compounds with harmful consequences that should be addressed as an emergency (Hashemi & Kaykhaii, 2022). The general belief is that the textile industries are the major producers of wastewater pollutants in the world (Bafana et al., 2011b). The waste is generated by their large volumes of water quantity demands in an effort to streamline the processes involved in the dyeing of the substrates (Almeida & Corso, 2019). The depositions alter the chemistry of the water they are deposited in due to the inclusions of composites such as polymers, organic, inorganic and total dissolved solids (M. Osemba et al., 2024). The major problem with the non-biodegradable synthetic dyes used in textile industries is that they exhibit high temperature and daylight (Bafana et al., 2011c). These factors make it quite challenging to destroy synthetic dyes that mostly belong to the azoic grouping with the use of conventionally developed treatment procedures that are already operational (Zhou et al., 2021).

Moreover, the by-products that are emitted during such industrial processes in the degradation process are extremely toxic in nature due to the fact that they are not completely removed through the current degradation methods that are being used, including the electrocoagulation and electrochemical mineralisation (Masomboon et al., 2009). The azo dyes of the textile effluents are not light stable, heat and oxidant stable, and cannot be easily biodegraded (Peng et al., 2021). Dyes can be made in the laboratory or can be obtained naturally (de Campos Ventura-Camargo and Marin-Morales, 2013a). Synthetic have found extensive uses over the last couple of decades as colouring agents in most industries, including textile, pulp and paper, leather tanning, pharmaceutical, paint, cosmetics, printing, plastic and food industries (Brown and De Vito, 1993a).

There are other applications where these dyes are applied in photographic activities, indicators, inks, body arts, biomedical, biological strainers, gasoline and many more. These are all causes of discharge of industrial wastes to the waters and the land areas (Z. Duan et al., 2020).

The lowest levels of the pollution of the industrial dye are also easy to detect below 1mgL-1 (Turgay et al., 2011). Their presence, even at the extremely low level of concentrations that are below1mg L-1, reduces the penetration of light and oxygen, which contributes to coloured water, biological attack on the dissolved substance and inhibits photochemical reactions (Lellis et al., 2019). It is noted that some of the products created by the textile dye effluent pollutant in water bodies are carcinogens and/or mutagens (de Campos Ventura-Camargo & Marin-Morales, 2013b). One of the largest constituents of industrial affluent is made from hydrocarbons, which are produced with the use of coal tar. The hydrocarbons in coal tar include naphthalene, anthracene, benzene, xylene and toluene and are non-biodegradable and stable (de Campos Ventura-Camargo & Marin-Morales, 2013a). The textile finishing sector produces wastes in huge amounts, and these wastes are synthetic dyes in coloured form (Brown and De Vito, 1993b). The polyacrylic substrates are washed a few times with a lot of water to remove all the unattached dyes (Chung et al., 2016b).

The fact that most of the dyes that were not completely utilised in the fixation process get deposited in the industrial effluent discharged to water bodies causes this accumulation to mean that a lot of wastewater in terms of volume is a product of the process (Kavoosi et al., 2014). Studies have also estimated that more than 15 percent of the synthetic dyes that are used in the production of fabrics end up in the form of effluents (Solis et al., 2012). Aryl amines, among other toxic metabolites, not only possess complicated structures but also complicate the bio-degradation of the emitted effluent (M. O. Osemba, Ojwang, et al., 2024).

The existence of a chance to get a job makes the textile industries beneficial to the economic growth of any nation or country in the world (Shy et al., 2021). However, the biggest challenge that is closely related to textile industries is the generation of large quantities of water-based effluents. They are especially referred to as having such dyes as vat, direct, reactive, disperse blue, and reactive deep components (Shindhal et al., 2021). Such dyes and especially azo dyes are difficult to degrade, which is a chronic health hazard to various organisms that may inhabit such environments (Y. Liu et al., 2022a).

One of the main parameters that must be considered when investigating a wastewater situation is TDS, which increases due to the use of common salt and the utilisation of Glauber salt, therefore, leading to high levels of osmotic imbalance in waters (Mei et al., 2023). As it was reported in the study in Bangladesh, in the year 2016, the presence of high and low concentrations of total dissolved solids (TDS) in water may affect the osmotic balance that leads to the appearance of bulged or dehydrated organisms in water (Mohtashim et al., 2021). The analysis conducted in India has shown that the textile industries consume a lot of water and generate almost equal and corresponding volumes of effluents because of the processes they undertake (Aparna et al., 2016).

Innocent and Padikasan (2023) claim that these dyes were present in the water bodies of some of the Turkish textile factories, and could be seen in small amounts of less than 0.1 gL-1 by the human eye. It is an environmental pollutant which is leading to scarcity of fresh water for domestic consumption and aquatic organisms (OSEMBA, M. O., 2019). The report also showed that a large percentage of causes of cancer cases reported in Turkey along disposed effluent waterways may be attributed to their over-consumptive use of foodstuffs and water tainted with azo dyes, Innocent & Padikasan (2023).

The textile dye effluents in Haiti, which in their untreated forms release the organic colored chromophores formed in high concentrations and cast to the water masses, are not only considered pollutants to the environment, but also affect the health condition of the people and other organisms found in the areas (Sundaram et al., 2013). The various kinds of bathing processes entail a slight heating process and even result in increased concentration of salts above 60 g/L that are discharged to the nearby water course, contributing to additional inorganic and organic pollutants to the effluent (Ramachandran et al., 2013).

The effluents released by textile and industries are still affecting living organisms in East African states such as Kenya, Tanzania and Uganda (Yehuala et al., 2022). Chai et al have affirmed that most of the effluents of textile industries in Tanzania are toxic (Chai et al., 2021a). Arusha has been reported to have contaminated the leaves of the green vegetation, which is a byproduct of extracellular respiration, with textile dyes. These toxins form the potential carcinogens, toxins, and mutagens, which are likely to react with the digestive systems of living things in the areas (Osemba et al., 2024).

Rivatex Textile Industry in Kenya is not an exception in its discharge of such hazardous dye effluents and applies vast amounts of it in the dissolution of chemicals in wet-processing the textile (Ding et al., 2020). The deposition of several recalcitrants was due to the fact that the government re-launched the Rivatex industry in 2018 (Othmani et al., 2020). An analysis of the Rivatex industry released waste water to the location by the Uasin Gishu County quality assurance showed that there was a tremendous increase in the use of synthetic chemical dyes due to the Buy Kenya Build Kenya initiative (Osemba, M. O., 2019). The project also facilitated an overuse of the azo dyes in a bid to meet the high and ever-rising demands of the home-made fabrics, and consequently, large volumes of effluents began to be emitted to the local rivers such as Sosani and Kesses.

The ill effects of these untreated effluents, which are deposited into the nearby water bodies, affect the well being and the general health of the residents, the animals and aquatic organisms (Allabakshi *et al.,* 2023). It requires 1 kg of the most popular cotton, 60g of reactive dye material, 150L and 800g of NaCl (Masarbo et al., 2022). However, the 3g/L of the total amount of dye used will not be fixed to the substrate utilised but will be released to the nearest water bodies (Song et al., 2023). The premise behind these claims is that, as carcinogenic and harmful, textile effluents must undergo some treatment or degradation before they can be released to the environment (Belal et al., 2021). It is the most important process of the degradation of textile effluents using azo dyes to reduce hazard levels before the effluent is discharged to the immediate environment (Haghighi et al., 2016).

The degradation is the process involving the disintegration of the complex bond structure of the toxic azo dyes in the effluent by using various physical and chemical treatments to ensure the toxicity and decolourisation of the complex azo dyes (Hussain et al., 2021). Nevertheless, the degradation of these dyes in textile effluents has not been fully attained since these dyes have coloured components in the textile effluents have an effect on the visibility and the quantity of the dissolved oxygen (Ramesh et al., 2021). The dye bio-degradation is challenging due to the complex structure of aromatic hydrocarbon compounds of phenyl, naphthalene, anthracene, and toluene molecules that are contained in them (Ghoreishi et al., 2016).

It is also reported that azo dye-containing textile effluents are highly recalcitrant to degradation due to high levels of concentrations of alkalinity in them, which are attributed to the presence of basic compounds of sodium carbonate and sodium chloride (NaCl), which raise the solution pH up to 10 and extremely high temperature levels of about 40.5 °C (Shehata et al.,2016). The structures of these dyes are aromatic, and this characteristic results in a high stability and low biodegradability (Ali et al., 2016). The existing degradation techniques like electrocoagulation, adsorption and flocculation contain several failures and inefficiencies, including over-polarisation and dye removal (Mahy et al., 2023). It necessitates research on improved physicochemical degradation plans with synthesised and characterised silver nanoparticles (AgNPs) electrocatalyst on ITO, In4Sn3O12 electrodes. The nanoparticles are very critical when degrading the textile azo dyes because they have a wide spectrum and are also antimicrobial (Haque et al., 2021). Decreasing agents like Indium Tin Oxide can also be applied in the textile effluent Catalytic degradation processes involving silver nano-catalysts or nano-particles, which can be illustrated with the assistance of an electron transfer mechanism (Baur et al., 2022).

This research was to address the impacts of this new technology of ITO- NPs thin film electrode on the quality of the effluent and its effectiveness in removal and treatment of the Azo dyes on the textile wastewater before it can be released to various water bodies.

EXPERIMENTAL

Loading Silver Nanoparticles on the Electrodes

Silver nanoparticles to indium tin oxide electrodes were embedded by the drop casting technique. The diameter and concentration ratio of the silver nanoparticles dispersed in the solution were varied to electrify the electrode. Direct modification of the nanoparticles using the assistance of the selected sensors on the working electrode. The thin film conducting material was deposited in a homogeneous way in the form of a flower-like structure at a current density of 0.2 mA cm^{-2}.

Electrochemical Degradation of Azo Dyes

The electrochemical cell performance of the electrolysis process involves the use of a configuration of a scheme shown in the photo diagram of scheme 1 below. The list of equipment that was used included the following: - power supply, AC-DC multimeter, rheostat, hot plate, magnetic stirrer, connecting wires, and the electrodes. The instrument cell was utilised in enhancing the breakdown of the azo dyes of the textile effluent that was put in the 250 mL glass beaker. All the textile dyeing effluent samples were treated with PAC (Analytical Reagent Grade) coagulating agent.

Scheme 1: Electrochemical Cell Setup for Azo Dye Degradation, a Photo Taken from Pwani University Chemistry Laboratory

Samples of 100 mL were placed into a 250 mL glass beaker. Indium tin oxide thin conductive materials coated with silver nanoparticles were suspended to create an inter-electrode distance using an insulator. The ITO electrodes were suspended in the solution and connected in series with an ammeter and rheostat. Potential difference was applied using an AC–DC converter, and current, time and absorbance were recorded at the end of electrolysis. Power consumption was calculated using the relationship;

$$P = Vit \qquad \text{Eq 1}$$

The reaction will continue to complete the removal of colour while recording current. Measurements of absorbance were taken at an interval to monitor colour removal progress. This was repeated using stainless steel electrodes. The electrodes were mechanically polished underwater with abrasive paper, cleaned in 0.2 M HCl solution for 2 minutes and rinsed with distilled water to eliminate any interference and ensure surface reproducibility during EC.

The absorbance was then measured using a UV-V is spectrophotometer. The percentage of colour removal was calculated using the following equation:

$$\% \text{ of color removal} = \frac{A_0 - A_f}{A_0} \text{ x } 100\%$$

Eq 2

Where A_o and A_f are the initial and final absorbance of the effluent, respectively.

The specific energy consumption of the four samples, each from Rivatex and Mombasa Textiles, were determined at the effluent pH of 4.0, 6.0, 7.0 and 8.0 respectively. They were then allowed to settle for about 30 minutes. The solution was then filtered. All these tests were performed at a temperature of 30°C because this temperature is a fundamental parameter for the concentration and viscosity of textile effluent solution (Koulini *et al*., 2022)

RESULTS AND ANALYSIS

Findings of loading silver nanoparticles to indium tin oxide electrodes. The drop casting method was used to embed silver nanoparticles on the indium tin oxide electrodes (G. Duan et al., 2023). The diameter of the drop and the level of the silver nanoparticles suspended in the solution varied the indium tin oxide electrode (Song et al., 2023). The direct modification of the nanoparticles was possible through the assistance of the selected sensors onto the working electrode (J. Shi et al., 2023). The thickness of the thin film conducting material was also covered using homogeneous flower-like structures at a current density of 0.2 mA cm-2. Plate 1 below and plate 2 respectively were pictures of the ITO electrode before and after embedding AgNPs under the Motic light microscope. This research has demonstrated the same results as those reported by Milanovic (Milanovic et al., 2021).

Plate 1: Image of ITO Electrode before Embedment of AgNPs Using Motic Light Microscope

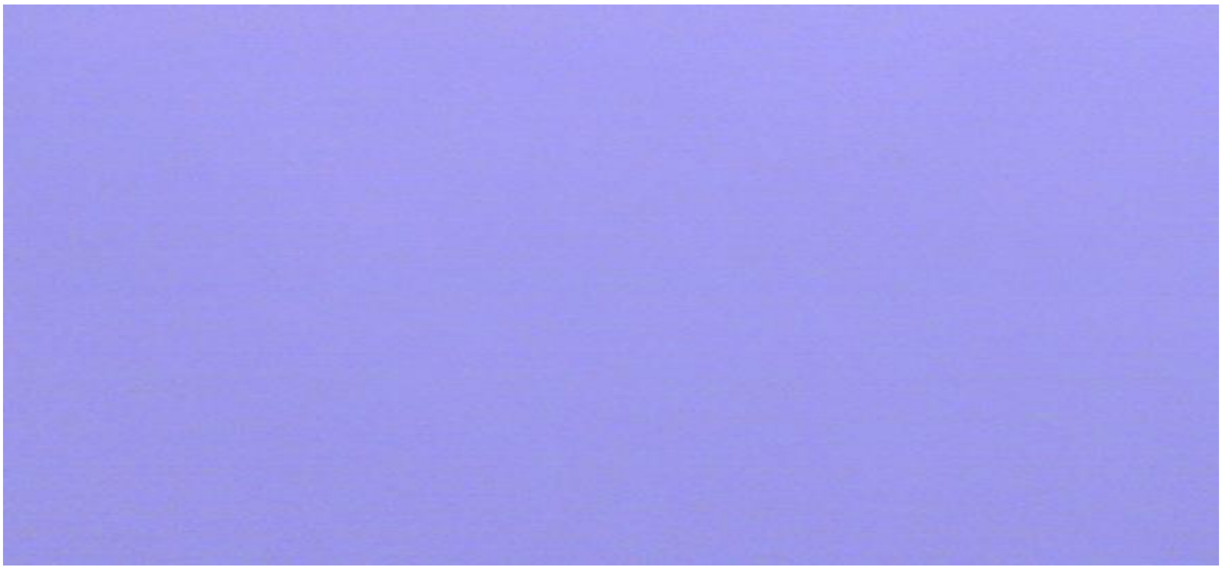
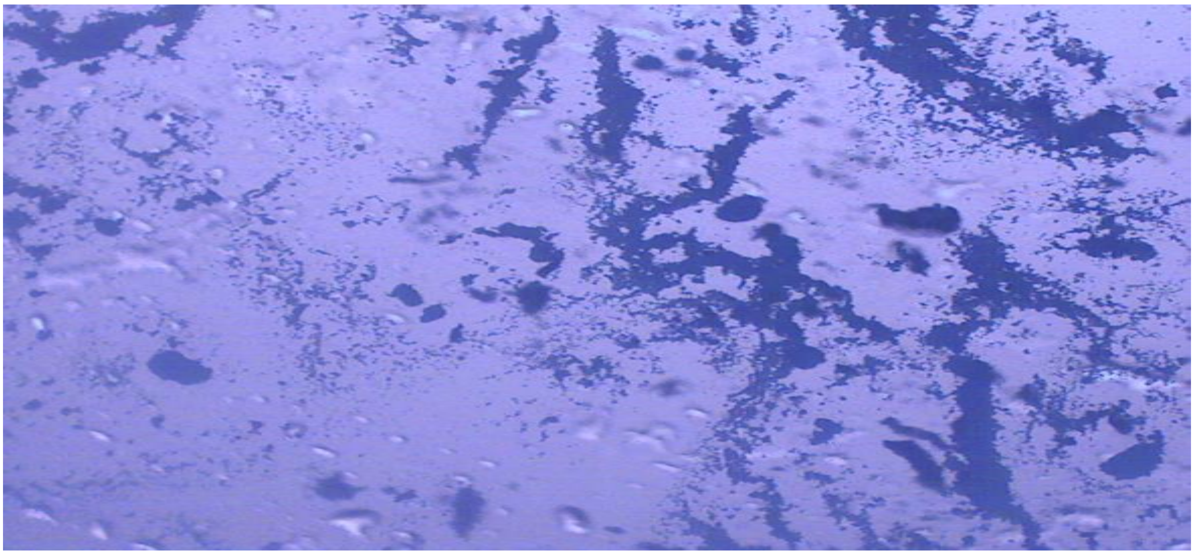


Plate 2: Image of ITO Electrode after Embedment of AgNPs Using Motic Light Microscope



The modified ITO electrodes were identified to be relatively insensitive to the interference with the electro-active species suspended in the textile azo dyes effluent. Similar results were also obtained by Aswatul et al. (Azwatul et al., 2023). The electrodes represented in Plates 1 and 2 above also revealed that they were stable even after a long period of time. They were also selective, reproducible with greater resistivity to conducting material foulings, which were consistent with the prior findings (Ameen et al., 2023), which are the fundamental amperometry of nanoparticle biosensors that can be utilised in complex in nature matrices (Alduraihem et al., 2023). The resultant versions of such electrochemical biosensor electrodes, as a product of the silver nanoparticles usage, turned out to accommodate the required chemical and physical attributes in the form of a larger surface area, mass transportation and catalysis in the process of azo dye degradation.

Efficiency of Degradation on Spectral Analysis UV-Vis.

The azo dye concentration in the textile effluents discharged at the Rivatex Textile Industry in Uasin Gishu County in Kenya and at the Mombasa Textile Industry in Mombasa County in Kenya was determined using ultraviolet visible (UV- Vis) spectroscopy before and after the treatment. Figures 1-5 below indicate that the spectral signals depict the efficiency of the degradation process in monitoring the variation that occurred in terms of absorbance of azo dyes dissolved in textile waste waters dyes using different electrodes. In Figure 1, the UV-Vis spectrum involved the degradation of the azo dyes in the effluent using an ITO electrode, whereas Figures 2 and 3 involved the degradation of the azo dyes using an ITO electrode together with silver nanoparticles, and Figures 4 and 5 involved electrocoagulation. When a nanocomposite electrode was used, the degradation performance was greatly enhanced. The values below, therefore, showed the wavelengths and the highest absorption (lmax) of the Azo dyes of Rivatex and Mombasa textile industries effluents respectively. The percent of azo dyes degradation at electrocoagulation, ITO and ITO-AgNPs coupled electrode, based on the formula discussed above, were as respectively: 68.4, 72.5 and 93.1 and comparable to (Zhou et al., 2021). The usefulness of this analytical instrument was determined in the context of the decolourisation property of these coloured Azo dyes of textile (Laouini et al., 2021). The alteration in the look of the colours in the spectrum of visible gave a hint of its strength in relation to curves and colour lines. Generally speaking, in all the values quoted, it was found that the strength of the coloured chromophores decreased in relation to the quantity of dye degradation time (Masarbo & Karegoudar, 2022). In this regard, where such measurements were involved, there was no compulsion to be calibrated for the purpose of using absolute values in irradiation, because relative values on spectral signals generated a satisfactory result, and therefore was in consideration (Alsamhary et al., 2022). During the measurement of the normalisation of the absorption maximum of the samples, a gradual decrease in absorbance was observed in the samples as the attaching chromophores were being removed during the process of treatment (Khaled et al., 2022). This thus determined that ITO-AgNPs coupling electrode-based scattering was successfully operating in the degradation of the colour of these Azo dyes dissolved in the textile effluents, and that these results agreed with the earlier investigations on the same field (Esmaeili et al., 2020).

Figure 1: Textile Azo Dye Effluent Degradation Using ITO Electrodes without Embedding Silver Nanoparticles Electrocatalyst at 24 V for 50 Minutes.

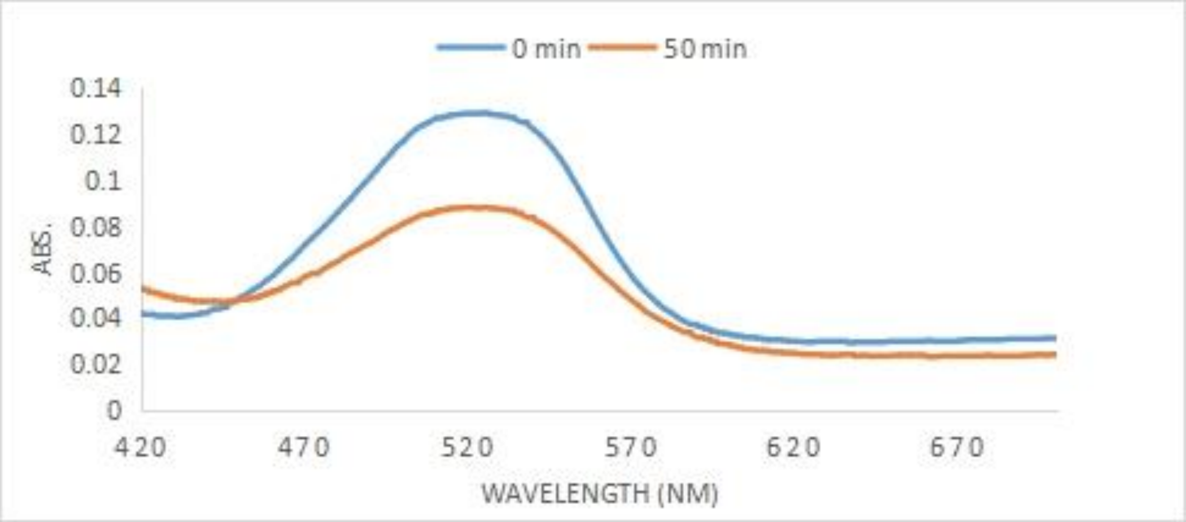


Figure 2: Textile Azo Dye Degradation Using Silver Nanoparticles (AgNPs) Embedded on ITO Electrodes at 24 V for 50 Minutes.

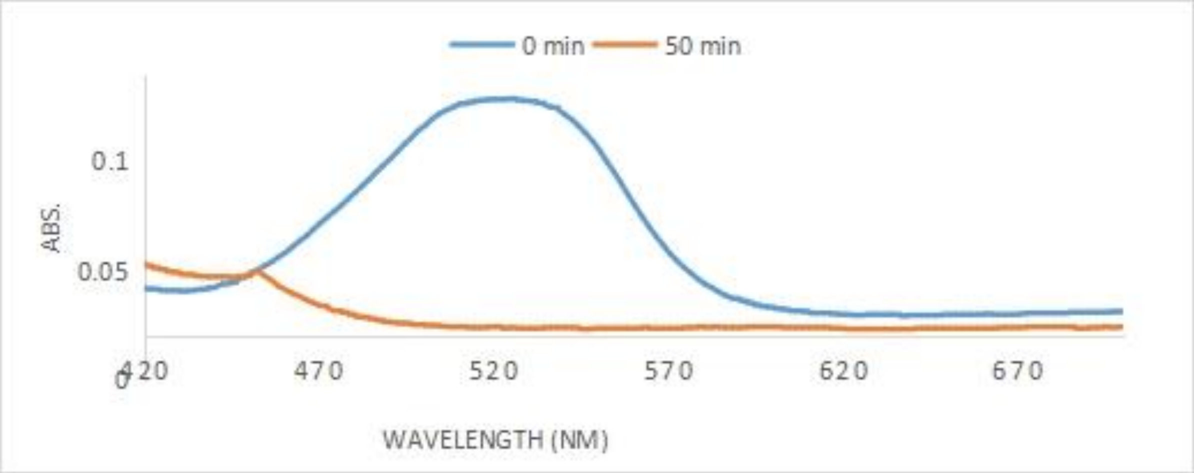


Figure 3: Rivatex Azo Dye Effluent Degradation Using ITO Electrodes Embedded with Silver Nanoparticle Electrocatalyst at 24 V for 40 Minutes

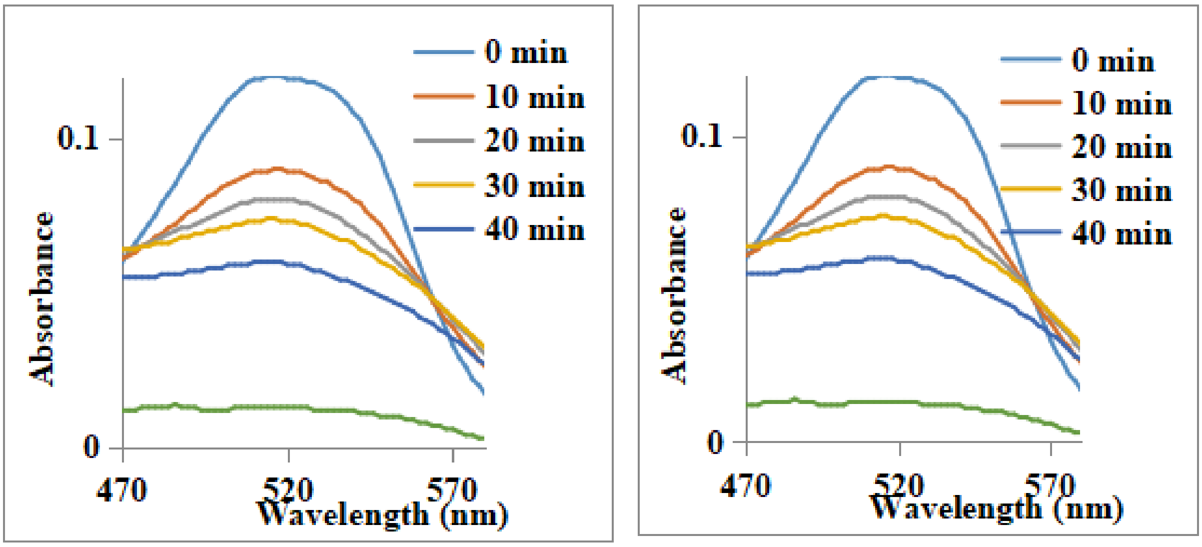


Figure 4: Rivatex Textiles' Azo Dye Effluent Electrocoagulation Using Stainless Steel Electrodes at 24 V for 40 Minutes.

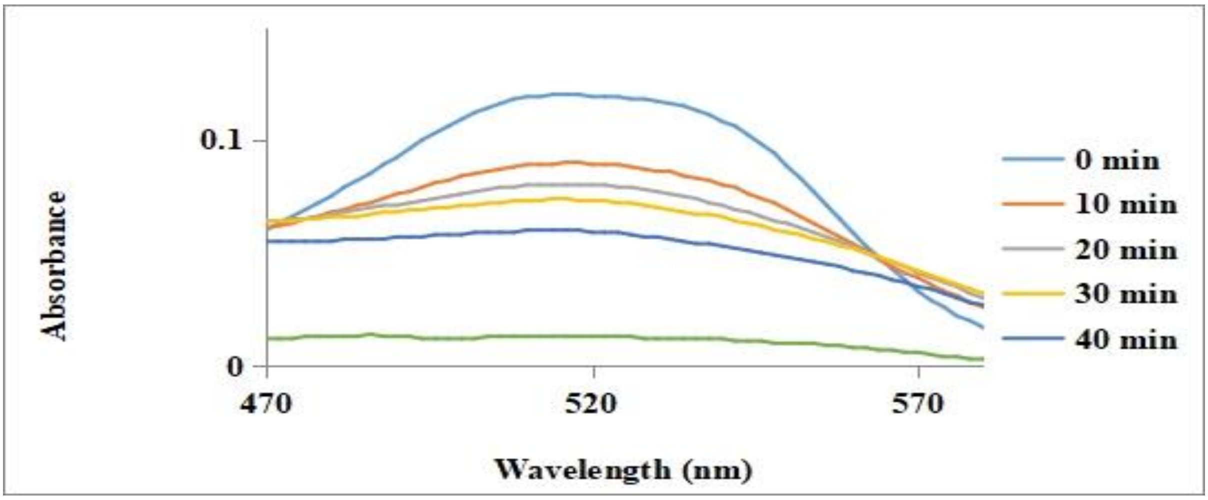
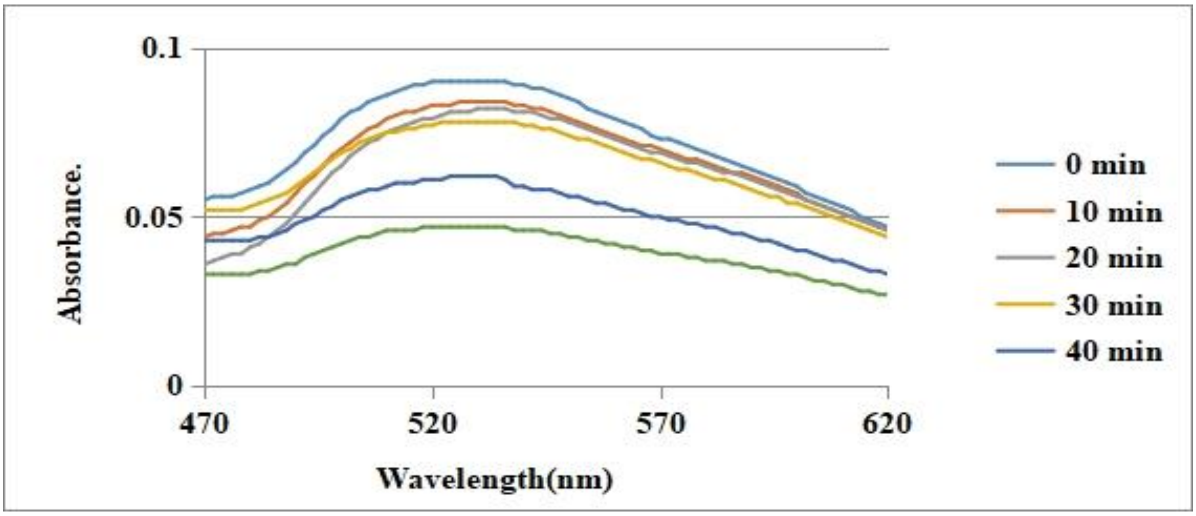


Figure 5: Mombasa Textiles' Azo Dye Effluent Electrocoagulation Using Stainless Steel Electrodes at 24 V for 40 Minutes



Results of Colour Removal Level during Azo Dye Electrochemical Degradation

The conventional methods of colour units using platinum-cobalt (Pt-Co) by APHA were used to measure azo dye colour of the textile effluent samples ER 8, ER 9, EM 8 and EM 9. Table 1 provides the details about the determination of the degree of colour removal of the Azo dyes in the textile effluent before and after the treatment through the application of different electrodes. Standard equipment is a spectrophotometer (HACH DR 2000), which is used in the determination of the colour of various samples (Shindhal et al., 2021). The platinum-cobalt colour unit of 2004+-0.5 was registered in the ER 8 effluent sample as opposed to the EM 9, with the lowest units of 1003+-0.2 in platinum-cobalt colour unit in the electrochemical degradation process, as indicated in Table 1 below. These fall within the range of the results presented by Asfaha, who found the range of the azo dyes in the textile effluent in units of platinum-cobalt colour to be 950-2050 (Asfaha et al., 2022). The four samples of the effluents with ITO electrodes combined with AgNPs were ER 8, ER 9, EM 8 and EM 9, in which this technique was concluded to be a highly effective and efficient method used in destroying azo dyes in the textile wastewaters. Among the criteria, one of them is that a method employed should possess the ability to eliminate the coloured chromophores emitted by Azo dyes to concentrations that can no longer be detected (Bustos-Terrones et al., 2021).

The two-way ANOVA test conducted at 95 percent confidence, which was obtained in Appendix VI (e), demonstrated that there was actually a significant difference between the samples before the degradation and after the usage of the silver nanoparticles on the ITO electrodes (p=0.000441). These findings are in line with the findings when using DSA electrodes during the process of azo dye degradation (Ozturk et al., 2021). In addition, the latter results also agree with the earlier indication that the use of electrocoagulation as an exclusive treatment of textile effluent is ineffective in the breakdown of the azo dyes since it is typified by the flocs' regeneration (Okur et al., 2022).

Table 1: A Table Showing Determination of Colour Removal Level of the Azo Dyes in the Textile Effluent Before and After Treatment using Different Electrodes

Samples	Pt-Co colour units before treatment	Pt-Co colour units after treatment using: -	
		ITO electrodes coupled with AgNPs	SS electrodes
ER 8	2004±0.5	0.047	180.7
ER 9	1981±1.5	0.087	129.0
EM 8	2317±2.0	0.054	298.3
EM 9	1003±0.2	0.076	91.6

CONCLUSIONS

Silver nanoparticles (AgNPs) were the neo-nanoparticles used in this study and on indium tin oxide (ITO) to eliminate azo dyes. These dyes are especially applied in the textile factories, where they turn out to be very dangerous. AgNPs catalyse the ITO electrodes, and this enhances the catalytic qualities. This type of degradation demonstrated the high efficiency of azo dye degradation, which proved that the usage of coupled AgNPs on ITO electrodes is the fundamental procedure applied to eliminate dyes. In this paper, the deposit of silver nanoparticles on indium tin oxide (ITO) electrodes has been achieved to degrade azo dyes. The results revealed a potential application of the given nanocomposite substance in the environment, particularly in wastewater treatment.

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