

Investigation of Dyestuff Recycled from Wastewater Containing Indigo/Sulfur Dyes

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ABSTRACT

Turkey is one of the important centers of denim fabric production in the world. Warp yarn is usually dyed using indigo and/or sulfur dyes according to the impregnation method. The common feature of these two dyes is that they are insoluble in water and dye temporarily with a reduction reaction. The recovery of dyes in wastewater is targeted. Wastewater containing indigo and sulfur dyes taken from İskur Denim was sedimented using the chemical flocculation technique and solid material was obtained after drying. The sedimentation process was affected by the pH of the environment, the mixing speed and the concentration of sedimentation chemicals. The best sedimentation was achieved by adding flocculators supplied by AKKİM to the wastewater sample in the pH range of 8-8.5. The obtained sludge was subjected to condensation reaction with the developed binding agent. The energy levels of the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the dyes obtained from indigo and sulfur wastewater were determined as -4.78 eV and -4.04 eV, respectively, by cyclic voltammetry. These values are very close to the original dyes and give hope for dyeing performance.

İndigo/Kükürt Boyaları İçeren Atık Sulardan Geri Dönüştürülen Boyar Maddelerin Araştırılması

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Anahtar Kelimeler

İndigo boyar madde

Kükürt boyar madde

Atık su

Karbon ayak izi

Denim

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ÖZ

Türkiye denim kumaş üretiminde Dünya'nın önemli merkezlerinden biridir. Çözümlü ipliği genellikle emdirme yöntem ile indigo ve/veya kükürt boyarmaddeler kullanılarak boyanmaktadır. Bu iki boyar maddenin ortak özelliği, suda çözünmemesi ve indirgenme reaksiyonu ile geçici çözünür özellikte boyama yapmasıdır. Atık sularda bulunan boyar maddelerin geri kazanımı hedeflenmiştir. İskur Denim'den alınan indigo ve kükürt boyarmaddeleri içeren atık sular, kimyasal flokülasyon tekniği kullanılarak çökertilmiş ve kurutma sonrası katı madde elde edilmiştir. Çöktürme işleminin ortamın pH'sı, karıştırma hızı ve çöktürme kimyasallarının konsantrasyonu etkin olmuştur. En iyi çökelme; pH 8-8.5 aralığında atık su numunesine AKKİM'den temin edilen floklaştırıcıların eklenmesiyle sağlanmıştır. Geliştirilen bağlayıcı ajanla birlikte, elde edilen çamur kondenzasyon reaksiyonuna tabi tutulmuştur. Atıktan sudan elde edilen indigo ve sülfür boyalardan en yüksek dolu moleküler yörünge ve en düşük boş moleküler yörünge enerji seviyeleri sırasıyla -4,78 eV ve -4,04 eV olarak dönüşümlü voltametri ile belirlenmiştir. Bu değerler orijinal boyar maddelere oldukça yakın değerler olup, boyama performansı için umut vermektedir.

1. INTRODUCTION

In today's textile industry, with the acceleration of the concept of fashion and fast consumption, the need to explore different alternative materials is increasing day by day. For this purpose, new approaches to the production of yarns, fibers, fabrics and dyestuffs are emerging. Here, the perception of difference comes to the fore for customer satisfaction. Environmental factors and sustainability concepts have gained awareness in recent years thanks to the mandatory environmental policies of countries and the work of non-governmental organizations. The textile industry, which is a very large and important sector, employs approximately 35 million people worldwide and contributes 7% to total exports [1]. Today, denim is widely used in daily life for its ease of use and accessibility. Color is a very important concept in denim fabrics. Different color tones desired in the final products offer advantages in terms of wear and effect processes that give the feeling of being worn and tailor-made. It is often presented as a fabric made of many-colored cotton yarns, especially in different shades of blue and black [2]. Color is an important physicochemical property in denim fabric [3]. It is one of the most important factors determining the quality of the final product. For this purpose, denim dyeing, washing and effecting processes involve an important and multiple series of chemical processing steps. The large number of chemicals and dyes used in today's denim production facilities, as well as the high-water consumption, draws attention in terms of environmental sustainability.

The textile industry is a significant source of wastewater due to the discharge of pollutants such as dyes, which, like plastics, are not naturally degradable [4]. Intensive studies have been carried out on synthetic dyes to obtain more vivid and bright colors or more pastel colors in the variety of color charts. The use of transition metals to chemically transform color pigments into more complex structures is common [5]. This causes some difficulties in the denim industry in the recovery or removal of the excess of indigo derivatives that go to waste after the dyeing process. It makes it difficult to remove it from wastewater by photocatalytic or chemical processes in the literature [6]. Failure to recover or treat synthetic dyes from wastewater has the potential to pose serious environmental and health hazards. Studies on living life in locations where wastewater is concentrated provide evidence that long-term contact can cause skin and eye irritation, corneal lesions, and skin cancer in humans [7]. With a more specific approach, water consumption is quite high in processes used only for textile dyeing. The wastewater discharged to the environment shows numerical values directly proportional to this [8]. Here, we cannot only talk about waste dye in the dyeing process. Many chemicals used in the dyeing process are also included in this suspension mixture. For example, the excess of indigo blue and sodium hypochlorite reacts in the wastewater to form xylene and releases a very dangerous molecule for the environment [9]. Biological, physicochemical and advanced oxidation processes are the methods used to remove all kinds of dyes and other chemical pollutants in wastewater [10]. It is observed that the removal efficiencies of dyes containing natural color pigments are quite high in biological treatment processes, while the removal efficiency of dyes containing synthetic color pigments is quite low [11]. In some studies, it is reported that almost complete color removal is achieved by nanofiltration and reverse osmosis processes in textile wastewater [12]. In addition, Photo electrocatalytic processes provide 100% color removal of synthetic dyes in water [13] and Photo-Fenton process provides over 98% color removal in wastewater [14].

With the development and progress of the industry, the increase in demand for color pigments and therefore dyes have led to the research and development of synthetic production methods. When we look at the synthesis conditions, large-scale dyestuff production methods have been established with the use of environmentally unfriendly chemicals [15]. In the extraction process, which is one of the production methods, indigo dye is initially synthesized in the form of indigotin. It is then subjected to fermentation to obtain the indoxyl and indigo form. In addition to electrochemical and chemical reduction, new methods such as electrocatalytic and catalytic hydrogenation are also used to produce indigo dye [16]. When we look at the origin of indigo dyes used in denim dyeing, they are blue colored organic compounds obtained by biosynthesis of secondary metabolites of plants and marine mollusks [17]. In the electromagnetic spectrum, indigo dyes, which absorb the wavelength between 415-445 nm in the visible region, exhibit all notes of blue. When we look at its structure, there are carbonyl (RCO) and ketone groups (RCOR). In this respect, we can say that it dissolves more easily and more in polar solvents [18]. Approximately 57% of this dyestuff (indigo), which is widely used in the denim industry, is used in the textile industry, 21% in the construction dye industry, 10% in the pulp and paper industry, 8% in the leather tanning industry and 8%

in the dye industry [19]. Looking at the literature, limited research has been conducted on dye recycle except for chemical pollutants in wastewater. Recycle of the excess material that does not dye the fibers during and after the dyeing process without reacting with other chemicals in wastewater will offer serious advantages

In this study, it was aimed to develop a method to recover indigo and sulfur dyestuffs used in denim clothing from wastewater. The recycled dyestuffs will be examined in terms of reuse possibilities.

2. MATERIAL AND METHODS

2.1. Material

For this study, the wastewater samples generated because of the processes in which dyeing with sulfur and indigo dyestuff were obtained from İskur Denim R&D Center company. For this process, wastewater samples were taken regularly at certain time intervals (every 5 minutes) and collected in a 50-liter container. The water chemicals used for the precipitation process in dyed wastewater were Akua End 3210 (Decolorizing solution), Akua End 2110 (Poly Aluminum Chloride Solution), Akua End 5220 (Anionic Polyelectrolyte Solution), Akua End 6133 (Decolorizing solution) and Akua End 5450 (Cationic Polyelectrolyte Solution) were obtained from AKKİM. Sulfuric acid used for pH adjustment during the studies was obtained from Merck company. For chemical flocculation of wastewater, AZ Instrument AZ-86031 Water Quality Meter branded pH meter, Velp Scientifica branded FP4 Portable Flocculation tester model jar test devices and Nucleon NST 30 branded oven for drying process were used. ISOTEX branded magnetic stirrer with heater was used for mixing and RADWAG AS 220 R.2 PLUS model Analytical Balance was used for weighing. For the evaluation and analysis of the results, services were obtained from Kahramanmaraş Sütçü İmam University, USKİM R&D laboratory and Gaziantep University, Uluğ Bey Advanced Technology Application and Research Center (ULUTEM) Laboratories. For this purpose, IRTracer-100 Fourier Transform Infrared Spectroscopy (FTIR) was used.

2.2. Methods

2.2.1. Chemical Floccification of Sulfur Dyed Wastewater Sample

The pH of the wastewater sample, which was dyed with sulfur dye obtained from Iskur Denim Company, was checked for preliminary preparation before the chemical floccification process. The chemical precipitation process was carried out according to the in-house method. The pH value of the sample was measured with a pH meter and determined as 13.28. Since the pH value required for the effective use of the decolorizing water chemicals provided by AKKİM Chemical Industry and Trade Inc., is in the range of 8.00-8.50, sulfuric acid was added to the water to keep the pH value in the range of 8.00-8.50. Accordingly, the amount of sulfuric acid added to 1 liter wastewater sample with a micropipette and the pH values obtained accordingly are presented in Table 1. While the pH value of 1 liter wastewater sample was 13.28, the pH value was reduced to 8.47 by adding 3030 µL (3.03 mL) sulfuric acid.

Table 1. pH values changing with the amount of sulfuric acid added

| | Sulfuric acid (µL) | pH values |
|--|--------------------|-------------|
| Wastewater sample dyed with sulfur dye | 50 -1000 µL | 13.27-12.99 |
| | 1000-2000 µL | 12.99-12.31 |
| | 2000-3000 µL | 12.31-8.84 |
| | 3000-3030 µL | 8.84-8.47 |
| Wastewater sample dyed with indigo dye | 50- 250 µL | 10.58-9.96 |
| | 250-500µL | 9.96-8.94 |
| | 500-520 µL | 8.94-8.43 |

A preliminary study was carried out manually to determine the appropriate water chemistry and amount of the pH-adjusted wastewater sample. As a result of the preliminary study, Akua End 3210, Akua End 2110 and Akua End 5220 chemicals were used. Then, quantity work was done manually. In Figure 1, 100

ml of the pH-adjusted wastewater sample was taken into a beaker and placed in the magnetic stirrer. 100 μL Akua End 3210 and 100 μL Akua End 2110 were added to the magnetic stirrer and floc formation was observed by rapid mixing for 5 minutes. Then, 200 μL Akua End 5220 was added and the flocs obtained were precipitated by fast mixing for 2 minutes and slow mixing for 3 minutes. In Figure 1, it is observed that dye and foreign matter residues settle to the bottom because of chemical flocculation applied to the wastewater sample.

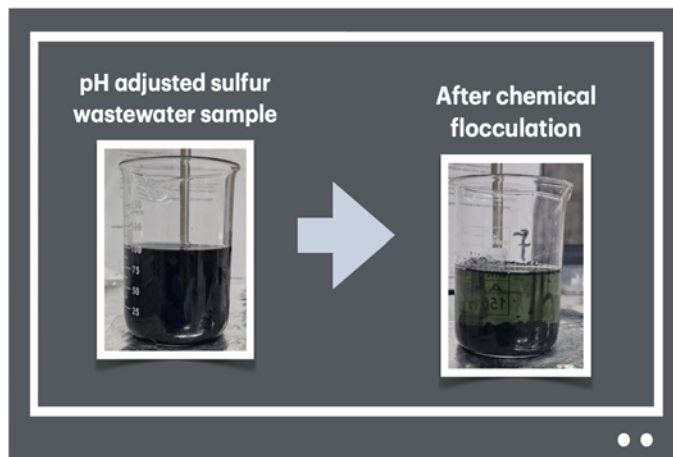


Figure 1. Chemical flocculation process

The same study was carried out on the jar test device. The pH-adjusted wastewater sample was taken into a 500 ml glass beaker. In Figure 2, 500 ml of wastewater sample was placed in the jar test device and rapid mixing was applied at 200 rpm for 2 minutes. In Figure 2, 500 μL Akua End 3210 and 500 μL Akua End 2110 were added to the wastewater sample, respectively, and rapid mixing was done at 200 rpm for 5 minutes, and it was observed that flocs were formed as a result. In Figure 2, 1000 μL Akua End 5220 was added and rapid mixing was done at 200 rpm for 2 minutes and the reaction took place. Then, the flocs formed by slow mixing at 50 rpm for 3 minutes are shown in Figure 2.

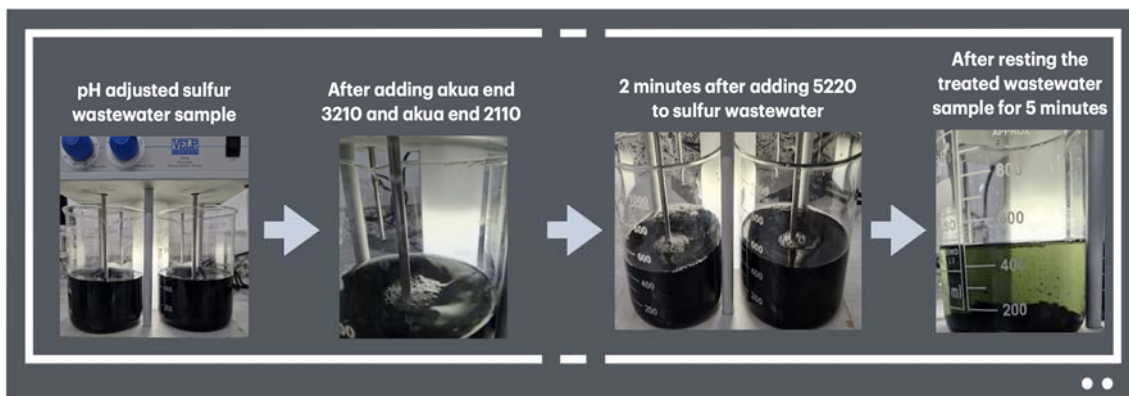


Figure 2. Chemical flocculation with jar test device

As a result of chemical flocculation, the materials that settled to the bottom and the filtrate were separated from each other. The obtained materials were taken into a beaker, and the sludge was subjected to the dewatering process. During this process, Akua End 5450 was added and first rapid mixing was performed at 200 rpm for 3 minutes, followed by slow mixing at 50 rpm for 2 minutes. Complete separation of the precipitated solid and liquid was achieved (Figure 3).

The solid that settled at the bottom was placed in a petri dish and dried in an oven at 110 degrees for 5 hours (Figure 3). In this way, an attempt was made to obtain dyed material by removing the moisture in the solid. The dye residue obtained because of the drying process was ground into smaller particles with the help of a grinder.

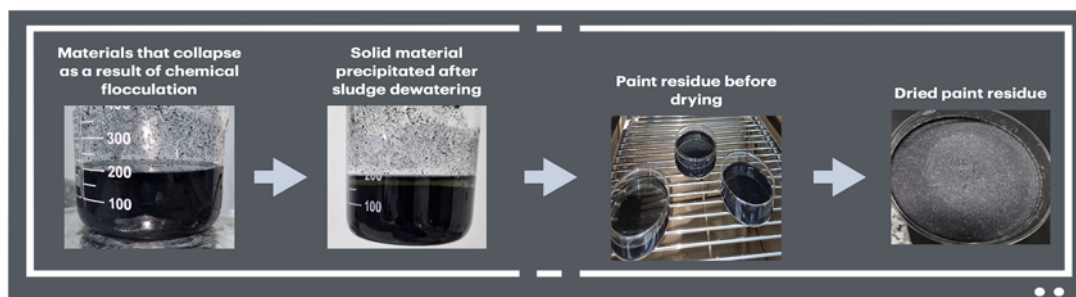


Figure 3. Solid material precipitated because of chemical flocculation

2.2.2. Chemical Flocculation Process of Wastewater Sample Dyed with Sulfur Dye

The pH values of the wastewater sample dyed with indigo dye were determined and recorded before the chemical flocculation process. The pH value of the sample was determined as 10.58. For the effective use of decolorizing water chemicals, the pH value is adjusted between 8.00-8.50 with sulfuric acid. In this context, the amount of sulfuric acid added to 1 liter of wastewater sample with a micro pipette and the pH values obtained accordingly are presented in Table 1. While the pH value of the 1-liter wastewater sample was 10.58, the pH value was reduced to 8.43 by adding 570 μL (0.570 mL) of sulfuric acid. Preliminary studies were carried out manually to determine the appropriate water chemistry and amount of the pH-adjusted wastewater sample. As a result of the preliminary study, it was decided to use the chemicals Akua End 6133 and Akua End 5220. Then, quantity work was done manually. In Figure 4, 100 ml of the pH-adjusted wastewater sample was taken into a beaker and placed in the magnetic stirrer. Floc formation was observed by adding 100 μL of Akua End 6133 to the magnetic stirrer and mixing rapidly at 200 rpm for 5 minutes. Then, 100 μL of Akua End 5220 was added and the flocs obtained were precipitated by rapid mixing at 200 rpm for 1 minute and slow mixing at 50 rpm for 3 minutes. In Figure 4, it was observed that dye and foreign matter residues settled to the bottom because of chemical flocculation applied to the wastewater sample.

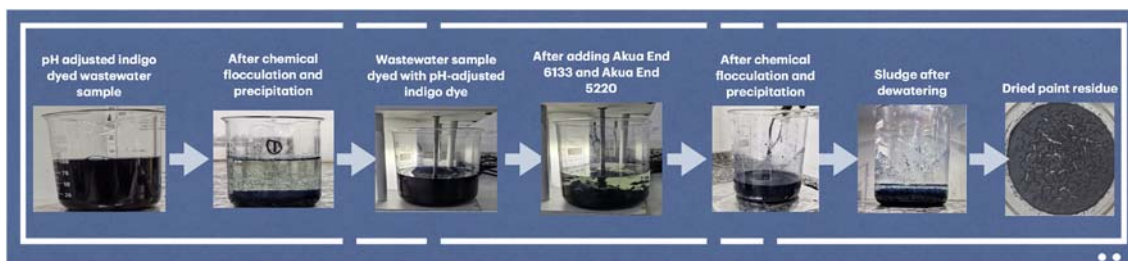


Figure 4. Chemical flocculation of wastewater dyed with indigo dye

The same study was carried out on the jar test device. The pH-adjusted wastewater sample was taken into a 500 ml glass beaker. In Figure 2.3, 500 ml of wastewater sample was placed in the jar test device and mixing was applied at 200 rpm. 100 μL of Akua End 6133 was added to the wastewater sample and rapid mixing was done at 200 rpm for 5 minutes and as a result, flocs were formed. 100 μL Akua End 5220 was added and rapid mixing was done for 2 minutes at 200 rpm and the reaction was completed. Then, by slow mixing at 50 rpm for 3 minutes, the flocs formed were precipitated as shown in Figure 4. The materials that settled to the bottom because of chemical flocculation and the filtrate were separated from each other and the obtained materials were taken into a beaker and subjected to the sludge dewatering process. During this process, Akua End 5450 was added and first rapid mixing was performed at 200 rpm for 3 minutes, followed by slow mixing at 50 rpm for 2 minutes. Complete separation of the precipitated solid and liquid was achieved. The solid that settled to the bottom was placed in a petri dish and dried in an oven at 110 degrees for 5 hours. In this way, an attempt was made to obtain dyed material by removing the moisture in the solid.

2.2.3. Purification of Residual Dyestuff

For this process, firstly, the dye residues were pulverized in a Resh II brand disc grinder until they became free flowing. Then, it was passed through sequential sieves (Brabender) to ensure that the particle sizes

were close to each other. With the new generation binding agent that our group had previously synthesized, the dye molecules in the residue were combined and their functional groups were activated. The obtained pure compound was characterized by analytical and spectroscopic methods. Single crystals of these compounds were obtained from the CHCl₃-EtOH solution by slow evaporation technique. Structural characterizations were made using FTIR and Raman techniques. The synthesis reactions of these compounds are given in Figure 5.

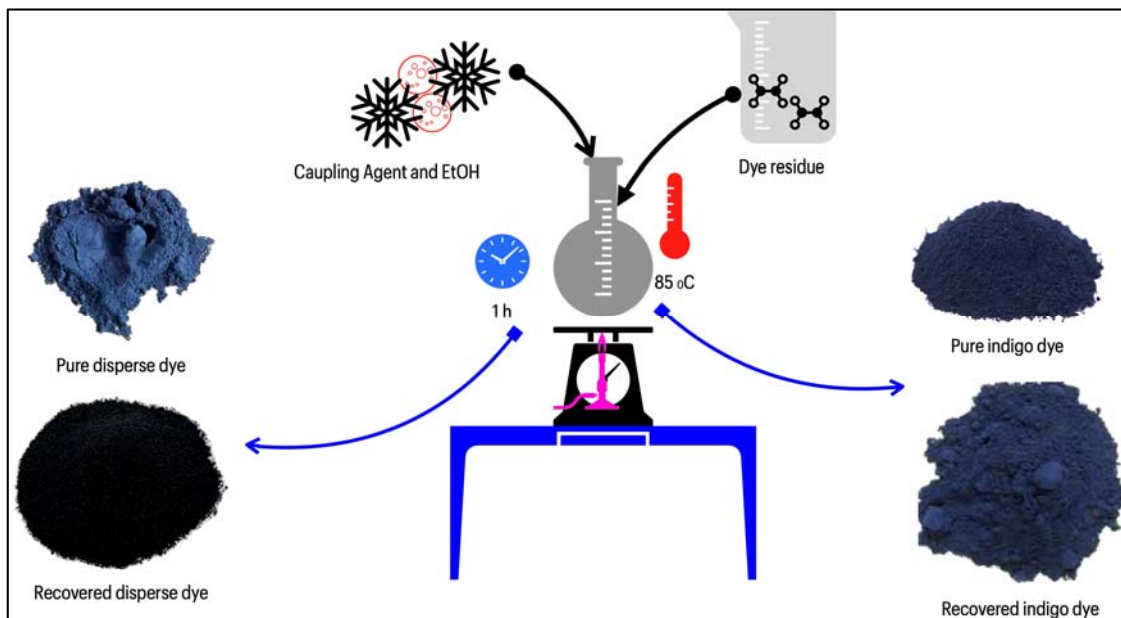


Figure 5. Synthesis step

3. RESULT AND DISCUSSION

This study is based on the recycle of the dyes used in the wastewater of denim factories in the textile industry, their recycling and inclusion in the dyeing process. The reason for choosing the denim industry as a target was the intense use of sulfur, indigo, cationic and reactive dyes [20]. The wastewater was supplied from Iskur Denim, one of the denim companies operating intensively in our region. For this purpose, samples were collected at regular intervals from the output of the dispatch and indigo dyeing lines. Again, precipitation agents were procured from AKKİM, which has an important product portfolio in textile treatment chemicals, and their effects on the chemical flocculation process were examined. For this purpose, certain amounts of samples were taken from the wastewater and the residues described in the previous section were obtained. The behavior of the obtained pure compound in organic and inorganic solvents was examined and is presented in Table 2.

Table 2. Resolution data

| | Pure indigo/sulfur dye | Residue dye | Recovered indigo/sulfur dye |
|---------------|------------------------|-------------|-----------------------------|
| Water | +++ / +++ | + | +++ / +++ |
| EtOH | +++ / +++ | ++ | +++ / +++ |
| MeOH | ++ / + | ++ | ++ / ++ |
| Acetone | + / + | + | + / + |
| Diethyl ether | + / + | + | + / + |
| Chloroform | ++ / + | + | ++ / ++ |
| DMF | +++ / +++ | +++ | +++ / +++ |

+: bad, ++: medium, +++: good

As can be seen from the infrared spectral data of the compound, the functional groups observed in the FTIR spectrum of the dye obtained after purification are shown in Figure 6. The peak aromatic $\nu(\text{C-H})$ stretch observed at 3022.45 cm^{-1} , the $\nu(\text{O-H})$ stretch of carboxylic acids observed at 2361 cm^{-1} , the $\nu(\text{N-H})$ bending at 1549.43 cm^{-1} , the peak at 1436.87 cm^{-1} . $\nu(\text{C-H})$ in-plane bending indicates the presence of carboxylic acid (C-O) at 1227.45 cm^{-1} , bends at 789.45 cm^{-1} indicate the presence of aromatic $\nu(\text{C-H})$, and at 670.76

cm^{-1} the presence of acid chlorine $\nu(\text{C-Cl})$. This peak corresponds to the chloroform $\nu(\text{CHCl}_3)$ peak used in purification and obtaining single crystals [21-25].

A similar situation is the case in the FTIR results of the recovered sulfur dye obtained as a result of the purification and condensation process after the residue obtained from the wastewater sample containing sulfur dye.

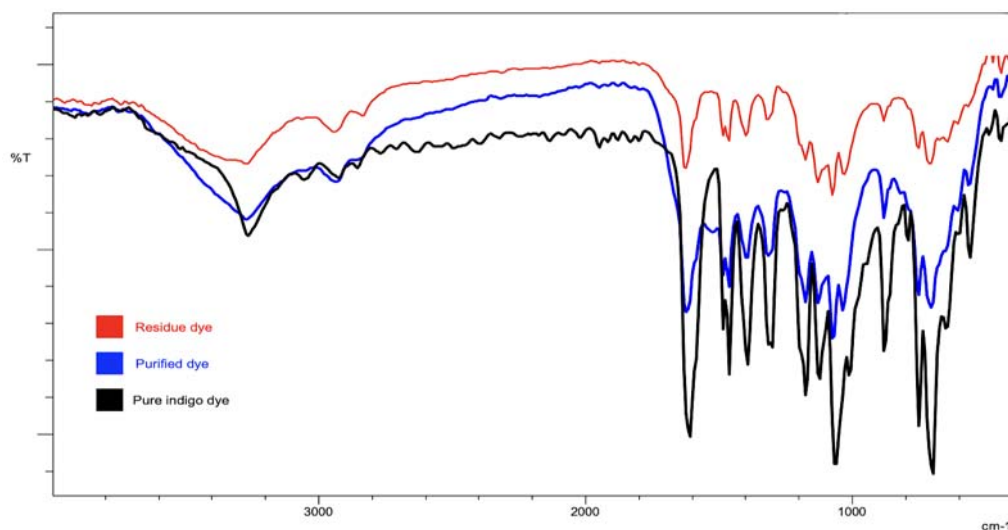


Figure 6. FTIR spectra of indigo dye

A similar situation is the case in the FTIR results of the recovered sulfur dye obtained as a result of the purification and condensation process after the residue obtained from the wastewater sample containing sulfur dye. The presence of azo and sulfonic groups is seen in the spectra of the residue and purified sulfur dye. However, the spectra of the dye recovered by purification are more intense. When examined, the spectrum peak belonging to the sulfonic group can be attributed to the $\nu(\text{S-S})$ stretching at 554 cm^{-1} , the $\nu(\text{C-H})$ stretching at 2932 cm^{-1} and the $\nu(\text{N-H})$ stretching at 3446 cm^{-1} . In the dye obtained as a result of purification and condensation, the aliphatic $\nu(\text{C-H})$ stretching gives an intense peak at 1458 cm^{-1} as a result of the combination of the degraded end groups with the binding agent. It is seen that the degraded disulfide group and azo group of the residual dye appear after the purification process. When we look at the spectra of the purified dye, $\nu(\text{N-H})$ bending is seen at 1545 cm^{-1} , $\nu(\text{C=O})$ stretching at 1735 cm^{-1} , $\nu(\text{C-H})$ stretching at 2971 cm^{-1} . In the sample of the residue, $\nu(\text{O-H})$ stretching showed irregular peaks in the range of $3500\text{-}300 \text{ cm}^{-1}$ (Figure 7).

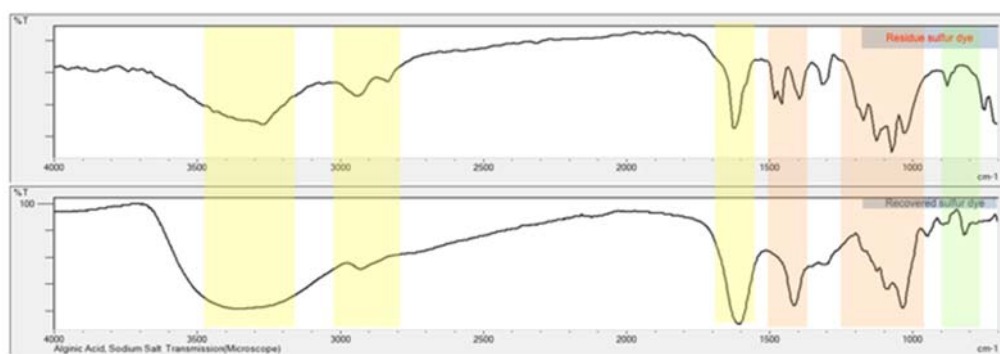


Figure 7. FTIR spectra of sulfur dye

The level energies of the highest occupied molecular orbital and the lowest empty molecular orbital of the dyes obtained from the original indigo wastewater were measured by cyclic voltammetry technique as -4.78 eV and -4.04 eV , respectively. These values are very close to the original dyestuff and give hope for dyeing performance. Alternating voltammetry technique was used for the original dye and the purified dye.

The electrochemical properties of the compounds were investigated at 293 °K with DMF-0.1 M Bu_4NBF_4 as the supporting electrolyte. All potentials mentioned were performed at scan rates in the range of 100–1000 mVs^{-1} . For calibration, it was checked using an internal ferrocene-ferrocenium standard. Electrochemical studies were carried out in a solution of 1×10^{-4} M concentration. Voltammograms of the original indigo dye and the dye purified from the residue are shown in Figure 7. Voltammograms were recorded in the range of -2.0 to 2.0 V against the Ag^+/AgCl reference electrode. In 1×10^{-4} M DMF solution, pure indigo dye has two anodic peak potentials in the range of -0.87-0.45 V at scan rates of 100-1000 mV/s . Additionally, two cathodic peaks are observed in the -0.36-0.91 V range. On the other hand, in 1×10^{-4} M DMF solution, there are anodic peak potentials in the range of -0.90-0.93 V and cathodic peak potentials in the range of 0.62-0.93 V at all scan rates of the ligand, respectively. For pure indigo dye at these concentrations, all redox processes are reversible.

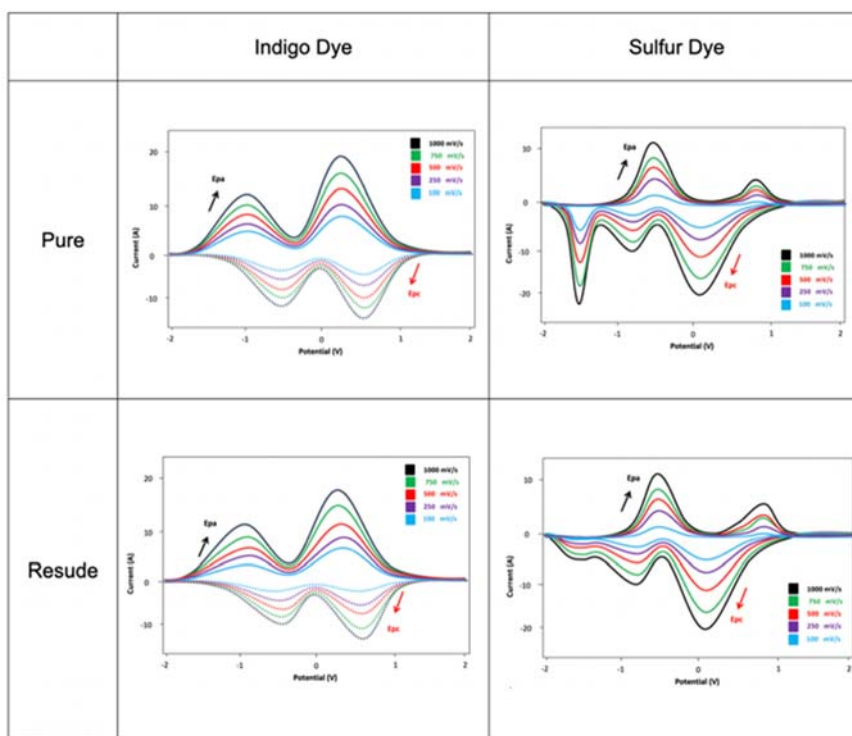


Figure 8. Cyclic voltammogram

This indicates to us that this material will have the potential to be reused after use. The dye residue purified in 1×10^{-4} M DMF solution shows reversible redox processes at all scan rates (Figure 8a-b). It has two anodic peak potentials in the range of -1.03-1.09 V at scan rates of 100-1000 mV/s . Additionally, the complex has two cathodic peaks in the -0.30-0.82 V range. In the electrochemical measurements of both indigo and sulfur dyes obtained by purification from the residues recovered from wastewater and indigo and sulfur dyes, reversible redox potentials were observed. When the voltammograms were examined, it was seen that they were approaching their pure states. There are two anodic and cathodic peak potentials. Anodic peak potentials are between -0.98mV and 0.47mV, and cathodic peak potentials are between 0.57mV and -0.48mV. All dye samples show reversible redox processes with two-electron reduction.

4. CONCLUSIONS

In the dye recovery study, the performance of commercially available flocculation chemicals was examined. Here, the flocculation capacities of Akua End 3210, Akua End 2110 and Akua End 5220 chemicals in wastewater were examined. Instead of water purification, which has been extensively studied in the literature, some studies have been carried out on the recovery and reuse of used dye. For this purpose, content analysis of the remains is important. In general, the presence of unprocessed chemicals depending on the processes puts the structure in a complex situation. For this reason, dissolution conditions in different solvents were examined and it was physically observed that it dissolves well in polar solvents and worse in

non-polar solvents. For this purpose, a water release reaction was carried out in combination with ethyl alcohol and binding agent to remove the contaminations in the structure. The resulting synthesis compound was purified by recrystallization from ethyl alcohol and analytical and spectroscopic characterizations were made. Among the parameters examined here, the values found in the FTIR spectroscopy of the original indigo dye, and the purified residual dye are almost the same, only there are decreases in the (C-H) bond strengths. In reversible voltammetry studies of the material, it is seen that the purified dye residue shows a lower redox potential than the original.

In the light of this information, it has been shown that dyestuffs close to the original one can be obtained by using basic purification processes that are not commercially costly. Thus, this developed method paved the way for the reuse of indigo and sulfur dyestuffs. In the continuation of the study, the ability of the recovered and characterized dyestuff to re-dye cotton materials will be investigated.

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