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RECOVERING OF INDIGO DYE FROM DENIM WASTEWATER WITH H_2O_2 IN THE PRESENCE OF KI CATALYST

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Abstract

Today, the textile industry, which is rapidly developing and growing in proportion to the human population, poses serious environmental and health problems in terms of waste. In the world, indigo dyes are widely used in the manufacturing of jeans fabrics especially in textile factories producing cotton fabrics. The overall objective of the present study is to recover indigo dye which is referred to as the pollutant released into the wastewater and to assess the removal of color via oxidation. For this purpose, denim wastewater containing solid particles and small size cotton fibers was filtered by the physical holding-separation process. Indigo dye which is dissolved in wastewater was then oxidized with H_2O_2 in the presence of KI catalyst at room temperature, and precipitated with ethanol and filtered. While the maximum recovered indigo dye was obtained as 0.0234 g (coded IN-20) in 0.5 g KI and 100 ml ethanol medium. The reaction efficiency was recorded as 78.00% by recovering 0.024 grams of 0.030 g indigo dye in 250 mL wastewater. Whilst the color value of the denim wastewater was 3500 (Pt-Co), this value was recorded as 600 (Pt-Co) as a result of the oxidation method. The structure of the recovered indigo dyes has been characterized by ^{1}H-NMR, FT-IR and UV-Vis spectroscopic methods and compared with commercial indigo and literature. In the FTIR spectrum of recovered indigo dye, the vibration bands formed at 3264-3252 cm^{-1} can be originated from the N-H group. In the proton NMR spectrum of Indigo, since the resonance of the N-H group in the indole ring was observed at a chemical shift of 10.44 ppm in the literature, these chemical shift values were observed in the same region, namely between 10.44 and 10.45 ppm in the recovered indigo dyes. The recovered indigo dyes showed maximum absorbance values at wavelengths of 300-335, 320-335 nm and 615-620 nm in the UV-Vis spectrums.

*Key words:*denim wastewater, indigo dye, NMR, recovery

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1. Introduction

Indigo obtained from plant sources (Indigoferatinctoria) is one of the oldest dyes used by humanity. A number of archaeological finds in the Indus valley in India have shown that indigo has been used since ancient times (Kerry and David, 2001; Chavan, 2015). Synthetic indigo dye was first introduced in Germany and commercially released in 1897 (Amutha, 2017; Buscio and Gutierrez-Bouzan, 2017). It is known to dissolve in dimethyl sülfoksit (DMSO), nitrobenzene, chloroform, or concentrated sulfuric acid. Leuco is a reduced form of indigo and is water-soluble. It is mainly applied for dyeing cellulosic fiber, polyamide, and wool (Paul, 2015).

Denim fabric was made entirely of cotton and is the most widely used fabric type, especially because it shows durability even after many types of washing

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(Paul, 2015). Denim of which is a subsector of the textile industry has an important significant role in the world's clothing and home textile products. Considering that the production of jeans is over 3.5 billion units in the world, the environmental damage caused by this industry is quite large (Kalesh et al., 2020). An average pair of jeans weighs 600 g and the total textile consumption of jeans is over 2.1 million metric tons per year. In denim processes, high water consumption and water pollution are the most important problems during the sizing, bleaching, mercerized dyeing, printing, and finishing processes (Chen et al., 2017; Kahraman and Simsek, 2020b). Colored textile wastewater accumulating in water prevents light from penetrating the water, which causes eutrophication. This causes the death of the aquatic ecosystem by reducing the amount of dissolved oxygen in the water (Namal, 2017; Kahraman and Simsek, 2020a; Pal et al., 2017). Further, the textile industry wastewaters have non-biodegradable organic and inorganic solid materials, coloring agents, organic and inorganic solids, salts, acids and bases, and toxic substances (Kahraman and Simsek, 2020a; Zazou et al., 2019).

Worldwide, nearly 800,000 tons of dyes are the production per year. Depending on the dyeing processes, about 10% and 50% of residual dyes are discarded into the environment. Thus, these textile dyes which are readily soluble in water have resulted in negative effects on the ecosystems and represent serious environmental problems (Bhatia et al., 2017). As result of these disadvantages, especially the recovery and reuse of indigo dyes have been the focus of many research studies. This approach will include both environmental and economic benefits (Buscio and Gutierrez-Bouzan, 2017).

Effective and economical studies were carried out for the treatment of wastewater from textile industries to protect the environment and human health, especially in recent years. For this purpose, processes that are physicochemical, biochemical, or a combination of both methods are used to remove water-soluble or insoluble dyes and pollutants. However, the high cost (electrical energy and chemicals requirements), low treatment efficiency in terms of color removal, causes volatile emissions, susceptible to toxins or antibiotics, and production of a large volume of sludge limits the use of some of these methods (Cuerda-Correa et al., 2020; Singh and Arora, 2011). In addition, the main objective of physical and chemical treatment is to remove undissolved chemicals and particulate matter present in wastewater. Biological treatment systems are known to be capable of removing color through conventional anaerobic, aerobic, and combined anaerobic-aerobic biodegradation techniques (Bhatia et al., 2017). However, integrated systems work at full capacity, and equipment requirements at any stage affect all stages. Also, due to the large amounts of toxic, non-biodegradable organic compounds, salts and heavy metals, traditional biological treatment is not efficient (Blanco et al., 2014).

Some membrane technologies can effectively remove indigo dye from the wastewater but are prohibitively expensive. The wider application of these techniques is therefore inhibited owing to toxicity or cost considerations (Wambuguh and Chianelli, 2008). For these reasons, we have determined an easy to apply and effective method for the removal and recovery of indigo dye in denim wastewater. The method, which is determined for the recovery of indigo dye in the denim wastewater, is developed by us and it was improved with our experimental study. Hydrogen peroxide was chosen due to it is environmentally safe, non-toxic, easy to use and it is not generating additional waste. It acts in a non-selective manner to organic and organometallic contaminants in the aqueous medium (Cuerda-Correa et al., 2020). It is a key reactive oxygen species, has a strong oxidizing property, and is widely used in various fields, including organic synthesis, food production, paper bleaching, as well as pharmaceutical, clinical and environmental analysis (Juan et al., 2018; Yoko et al., 2003). Nevertheless, H_2O_2 does not show good oxidizing properties, it can become more effective when combined with catalysts (Cuerda-Correa et al., 2020).

Here we reported the catalytic reaction system in which iodide could catalyze the oxidation reaction of a peroxidase substrate indigo dye product by H_2O_2. Noteworthy, indigo, in the wastewater of the denim industry, was precipitated until distinguished by the naked eye. Thus, the structure of recovered indigo dye was characterized by ^{1}H-NMR, FT-IR, and UV-Vis spectroscopic methods and compared with commercial indigo and literature. Thus, it has been understood that this method can be applied effectively in the denim industry to recover indigo dye from wastewater because it is simple without spending much time and efficient results were obtained.

2. Materials and methods

2.1. Materials

Denim dyeing wastewater was kindly supplied by ISKUR Denim Factory in Kahramanmaras, Turkey. Hydrogen peroxide (H_2O_2), ethyl alcohol (C_2H_5OH), potassium iodide (KI) was purchased from Merck. All the chemicals were reagent pure grade and were used without further purification. Following each recovered indigo dye from the wastewater of a denim industry were characterized by spectroscopic and analytic methods. Agilent 400 MHz NMR Magnet spectrometer was used to characterization by the required amount of the recovered indigo in $CDCl_3$ at 25°C for ^{1}H-NMR. For the Fourier Transform Infrared Spectroscopy (FT-IR) analyses, a Perkin Elmer Spectrum 400 spectrophotometer was employed. The ultraviolet absorption spectrum of all indigo dyes in chloroform was examined in the range of 200-400 nm using a Perkin Elmer Lambda 45 spectrophotometer, UV–Vis recording Spectrometer. Elemental analyses (C, H, N) were performed using a LECO CHNS 932.

2.2. Methods

The wastewater used in this study was taken from the factory before it got into the wastewater network. The denim dyeing wastewater characterization used in the experimental study is given in Table 1. The supplied dyeing wastewater was stored at +4 °C in a dark environment. In this wastewater sample, solid substances insoluble in wastewater, such as fiber, and dust, were separated by filtering from ordinary filter paper. The initial pH of wastewater was usually around 12. It was observed that the pH values did not change much after the addition of other chemicals, namely hydrogen peroxide, potassium iodide and ethanol. However, after the addition of distilled water, which is the finishing step and pH control after heating, it was varied between 8.50 and 8.75.

100 mL sample was taken from the wastewater and mixed with 250 ml flasks for 15 minutes at room temperature in magnetic stirrers. By adding 0.15, 0.20, 0.25, 0.30, 0.50, 0.75 and 1.00 mL H_2O_2 to this mixture, optimum amount of hydrogen peroxide was found as 0.25 mL at room temperature. Then, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50 and 0.60 g KI were added separately to each sample as a catalyst and stirring was continued to increase the efficiency of hydrogen peroxide. Finally, Indigo dye was precipitated by adding 25, 50, 75, and 100 mL of ethyl alcohol to each sample, and the time spent in this precipitation was given in Table 2. These wastewater samples, which were observed sedimentation in certain proportions, were filtered through a porous (2-3 µm) filter paper. The filtered samples were taken into 75 mL of distilled water and mixed for 15 minutes at 50 °C and allowed to reach room temperature. It was filtered through 2-3 µm porous filter papers (see Fig. 1), which was previously fixed and dried in the oven at 50 °C. The filter papers kept in the desiccator were weighed on a sensitive scale and the amounts were calculated.

Table 1. The characteristics of wastewater used for experimental studies

Parameters	***Value***
COD (mg/L)	4000
BOD_5 (mg/L)	800
Ammonium NH_4-N	38
Chloride (mg/L)	0.5
Total Chromium (mg/L)	9
Sulfide $^{2-}$ (mg/L)	0.9
Suspended solids (mg/L)	550
Turbidity (NTU)	34
pH	12
Color (Pt-Co)	3500

Table 2. Experimental condition and yield of the recovered indigo dyes

Sample	***KI (g)***	***Ethanol (mL)***	***Time (h)***	***Indigo (g)***	***Yield (%)***
IN-1	0.1	25	24	0.0197*	65.67
IN-2	0.1	50	22.5	0.0172	57.33
IN-3	0.1	75	15	0.0139	46.33
IN-4	0.1	100	13	0.0188	62.67
IN-5	0.2	25	21	0.0203*	67.67
IN-6	0.2	50	17	0.0183	61.00
IN-7	0.2	75	13	0.0166	55.33
IN-8	0.2	100	10	0.0181	60.33
IN-9	0.3	25	19	0.0155	51.67
IN-10	0.3	50	16	0.0197	65.67
IN-11	0.3	75	11	0.0179	59.67
IN-12	0.3	100	7.5	0.0203*	67.67
IN-13	0.4	25	15	0.0185	61.67
IN-14	0.4	50	11	0.0132	44.00
IN-15	0.4	75	8	0.0210*	70.00
IN-16	0.4	100	6	0.0197	65.67
IN-17	0.5	25	15	0.0168	56.00
IN-18	0.5	50	8.5	0.0156	52.00
IN-19	0.5	75	5.5	0.0198	66.00
IN-20	0.5	100	4	0.0234*	78.00
IN-21	0.6	25	12	0.0147	49.00
IN-22	0.6	50	6	0.0136	45.33
IN-23	0.6	75	4.5	0.0157	52.33
IN-24	0.6	100	3	0.0196*	65.33

**the most recovered indigo dye in its group*

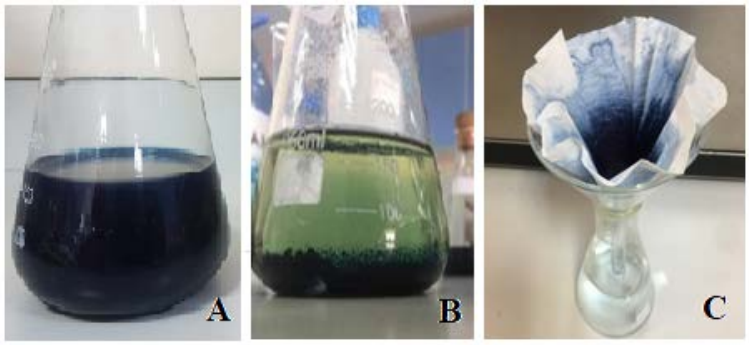

Fig. 1. Denim wastewater (A), precipitation (B) and filtration (C)

3. Results and discussion

Physical, chemical, and mostly biological technologies are widely used to remove color in the textile industry wastewater (Türgay et al., 2011), but some of these commonly use chemicals. These chemicals can potentially cause even more toxic chemicals in the wastewater through disruption or replacement of the conjugated dye system. We investigated the feasibility of recovery indigo dye in denim wastewater using hydrogen peroxide and reported on a simple and potentially effective method. It has been understood that this method can be applied effectively in the denim industry to recover indigo dye from wastewater because it is simple without spending much time and efficient results were obtained.

The recovery of indigo dye involved two steps: Precipitation step; the partially dissolved and dispersed indigo dye in the wastewater of the denim textile industry, which performs indigo dyeing, was precipitated with hydrogen peroxide, potassium iodide and ethyl alcohol. The iodide-catalyzed disproportionation of H_2O_2 to H_2O and O_2 in aqueous solution (Eqs. 1-3) at neutral pH has been extensively studied for a long time (Dalmazio et al., 2008).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (1)$$

In the mechanism accepted, the following pathways have been suggested:

$$H_2O_2 + I + H^+ \rightarrow HOI + H_2O \quad (2)$$

$$HOI + H_2O_2 \rightarrow H_2O + O_2 + I^- + H^+ \quad (3)$$

Purification step; in the first stage, the indigo dye, which was precipitated together with the other substances solubilized in water, was purified by dissolving in distilled water (Scheme 1). In this way, the structure of the recovered indigo dye was characterized by FT-IR, UV-Vis, and ^{1}H-NMR spectroscopy and compared to the indigo dye used commercially. It was understood that the results of the proton NMR spectra of the indigo dyestuff recovered from textile wastewater are in agreement with the results of the commercial indigo and indigo dye given in the literature. The oxidation reaction of the indigo dye is given in Fig. 2.

The amount of KI catalyst used for precipitation, the amount of ethanol, and the recovered indigo were given in Table 2 and grouped in Fig.3 according to the KI amounts. As seen in Fig. 3, the amount of added ethyl alcohol was only changed the precipitation time of indigo dye in wastewater that is, shortening the precipitation time. It did not affect the amount of recovered indigo much, but it showed an irregular increase or decrease. As can be understood from the graphic that was seen collectively in (Fig. 3), the most recovered indigo dye was 0.0234 g and it has been realized in 0.5 g KI and 100 ml ethanol medium. The least amount of the recovered indigo dye was obtained as 0.0132 g from the medium of 0.4 g KI and 50 mL ethanol.

The reaction efficiency was recorded as 78.00% (see Table 2) by recovering 0.024 g of 0.030 g indigo dye in 250 mL wastewater. Whilst the color value of the denim wastewater was 3500 (Pt-Co), this value was recorded as 600 (Pt-Co) as a result of the oxidation method.

3.1. Elemental analysis

The theoretical amounts of the C, H and N atoms of the indigo molecule, the elemental analysis percentage amounts of commercial indigo and the recovered indigo dye (IN-20) were given in Table 2. It is clear that commercially used indigo dye was not a pure indigo molecule. Therefore, it can be considered that as a mixture of certain chemicals in certain proportions. Thus, it was seen that IN-20 was obtained purer tha commercial Indigo.

3.2. Characterization by FT-IR Spectroscopy

The vibration bands of the FT-IR spectra of the recovered indigo dyes and commercial indigo dye were given in Table 3. As can be seen in (Fig. 4), when the FT-IR spectrum of the commercial indigo is examined, the band at 3263 cm^{-1} can be attributed to the stretching vibrations of the N-H group and adsorbed H_2O molecule.The vibration bands formed at 3264-3252 cm^{-1} can be originated from the N-H group of the recovered indigo dye. The stretching vibration band observed at 1623 cm^{-1} in commercial indigo can be attributed to vibration of C = O coinciding with C = C.

Table 3. Elemental analysis results of Indigo

Sample	*Element (%)*		
	C	*H*	*N*
Theoretical calculation	73.27	3.84	10.68
Commercial indigo	40.37	2.76	5.18
IN-20	56.27	3.86	7.41

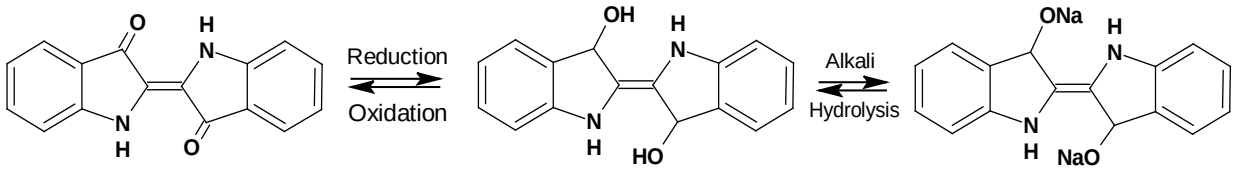

Fig. 2. Reaction of indigo dye to leucoform (soluble form) (Sala, 2012)

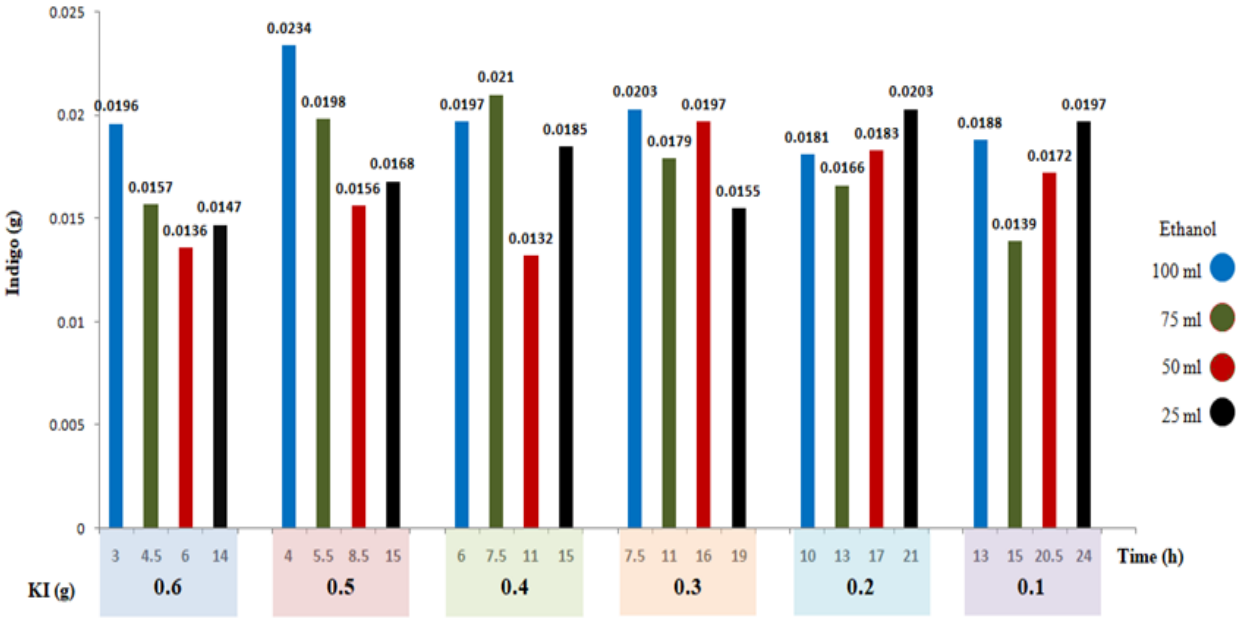

Fig. 3. The quantities of the recovered indigo dye

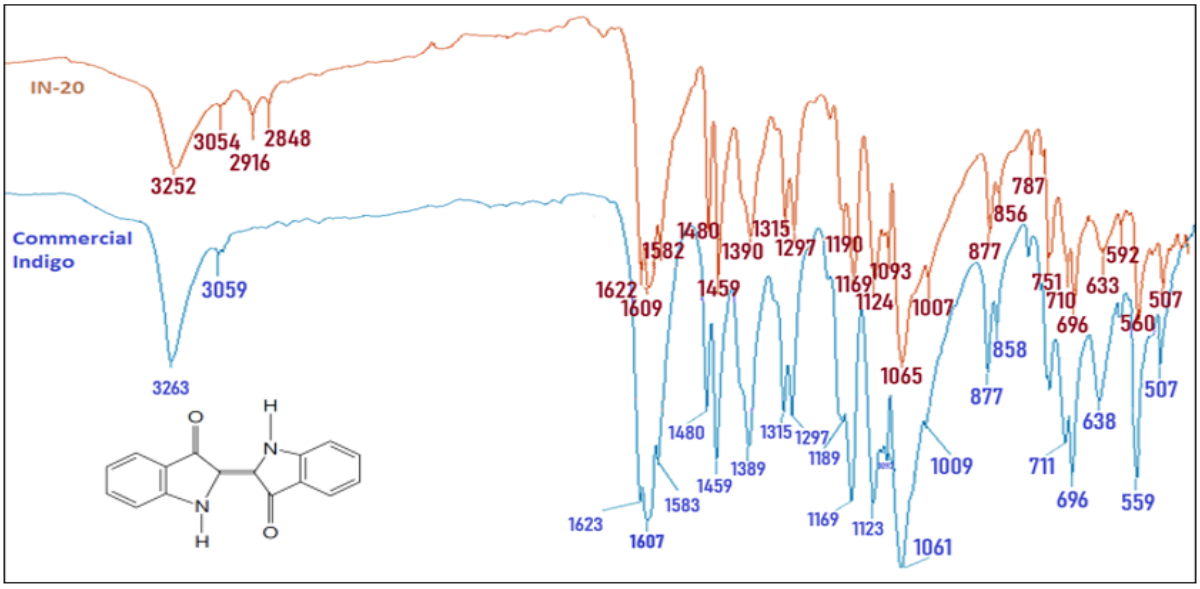

Fig. 4. FTIR spectra of IN-20 and commercial indigo

In the recovered indigo, it can be said that the bands between at 1625-1622 cm^{-1}belong to these two groups. C-N vibration bands of the imine group of the recovered indigo dyes between 1392 and 1007 cm^{-1}were observed in the commercial indigo ranging from 1389 to 1009 cm^{-1}. In addition, due to the vibration of the C-H molecule of the bending plane in the aromatic ring, the bands are observed at 877 cm^{-1} to 696 cm^{-1} both of commercial indigo and the recovered indigo dyes (Baran et al., 2010; Hilor and Datta, 2010; Sri et al., 2017).

3.3.Characterization by ^{1}H-NMR Spectroscopy

In Figs. 5 and 6, a comparison of the ^{1}H-NMR spectra of some recovered indigo dyes and commercial indigo was given, while Table 4 showed chemical shift values. In the proton NMR spectrum of commercial indigo, it is attributed to the resonance of the N-H group in the indole ring, observed at a chemical shift of 10.44 ppm in (Fig. 4). The chemical shift is observed between 10.44 and 10.45 ppm in the recovered indigo dyes. While the peaks seen in the region between 6.91 and 7.57 ppm originates from the H atoms of the aromatic ring, they were observed between 6.91 and 7.57 ppm in the recovered indigo dye (Hee et al., 2017). The peaks formed at 4.05 ppm correspond to the resonance of the C(H)-N group in the commercial indigo, while the chemical shift of this imine group in the recovered indigo dyes are observed between at 3.8 and 4.3 ppm (Priti and Ravindra, 2014).

For a better understanding of the structure of the indigo dye recovered from denim wastewater, the proton NMR spectrum of the recovered indigo dye from each experimental condition was taken and compared to commercial indigo. In this comparison, it was observed that the purity of the recovered indigo dye changed according to the amount of added KI catalyst and the amount of ethanol used for precipitation. As can be seen from the spectra in (Figs. 6 and 7), it has been understood that some of the recovered indigo dyes cannot be fully purified. However, when compared to proton NMR spectrums of the commercial indigo dye and the recovered indigo dye by precipitation with the addition of 0.3 and 0.2 g of KI and 25 mL ethanol, it was seen that the peaks and chemical shift were very close to each other (Table 5). Unexpectedly, when looking at the ^{1}H-NMR spectra of the indigo dyes recovered by adding 25 and 100 ml of ethanol, accompanied by 0.6 g KI catalyst and without depending on the amount of used ethanol for precipitation, it was seen that those have a purer form than obtained by adding 50 and 75 ml of ethanol (Fig. 6). Thus, the results of the proton NMR spectra demonstrate that commercial and recovered indigo dyes are in harmony.

3.4. Characterization by UV Spectroscopy

UV-Vis spectrums of the recovered indigo and commercial indigo dyes were taken between 200 and 800 nm wavelengths and maximum absorbance values were observed in three different wavelengths (Figs. 6 and 7). The commercial indigo showed maximum absorbance values at wavelengths of 300, 330 and 615 nm. Similarly, it was observed in the recovered indigo dyes at 300-335, 320-335 nm, and 615-620 nm. These electronic transitions can be attributed to the n→π* or π→π* transitions of the indigo dye molecule (Dennis and Russell, 2008).

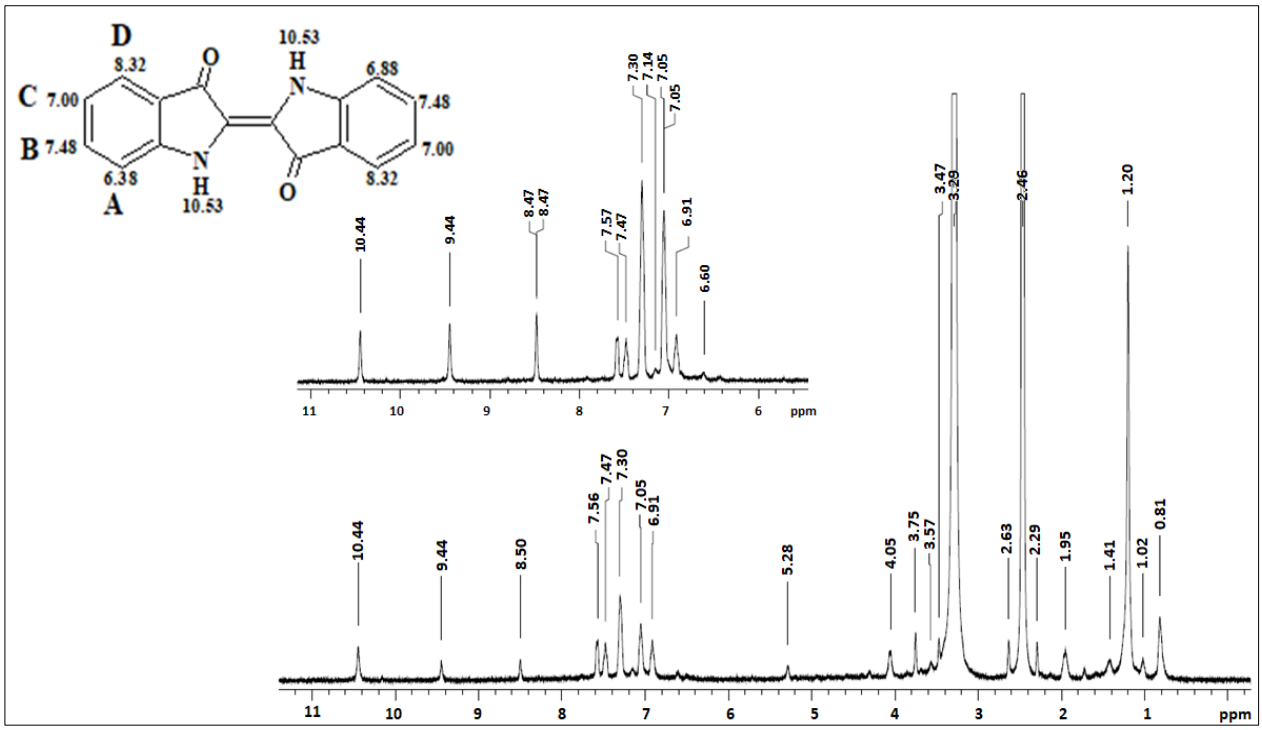

Fig. 5.^{1}H-NMR spectra of the IN-20 (upper) and commercial indigo (bottom)

Table 4. The characteristic vibration bands of indigo dyes

Samples	*N-H*	*C=O, C=C*	*C-N*	*C-H*
Literature*	3266	1626	1391-1010	878-699
Commercial Indigo	3263	1623	1389-1009	877-696
IN-1	3253	1625	1390-1007	877-696
IN-5	3252	-	1391-1010	877-696
IN-12	3252	1622	1392-1007	877-696
IN-15	3264	1623	1390-1007	877-697
IN-20	3252	1622	1390-1007	877-696
IN-24	3263	-	1390-1007	877-696

Baran et al. (2010)

Table 5. The chemical shift of indigo dyes

Samples	*N-H(ppm)*	*A(ppm)*	*B(ppm)*	*C(ppm)*	*D(ppm)*
Literature*	10.53	6.88	7.48	7.00	8.32
Commercial Indigo	10.44	6.92	7.48	7.31	7.56
IN-1	10.45	6.91	7.48	7.31	7.57
IN-5	10.44	6.92	7.47	7.31	7.57
IN-12	10.44	6.92	7.47	7.29	7.56
IN-15	10.44	6.92	7.48	7.30	7.59
IN-20	10.44	6.92	7.48	7.30	7.58
IN-24	10.44	6.91	7.48	7.30	7.59

Hee et al.(2017)

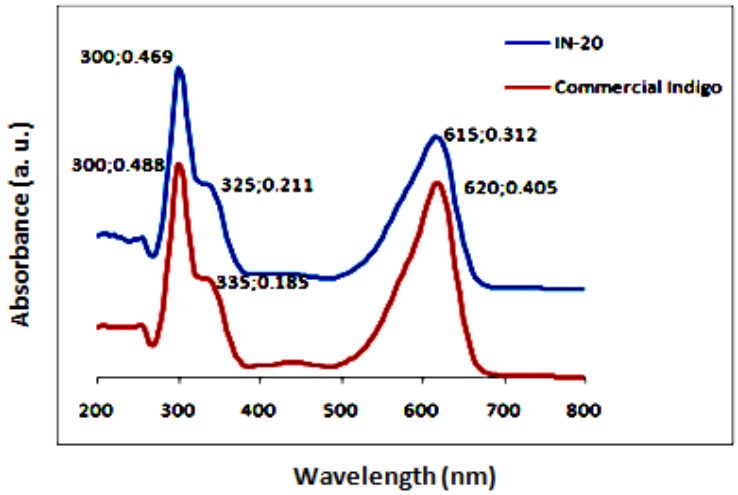

Fig. 6. UV spectra of IN-20 and commercial indigo

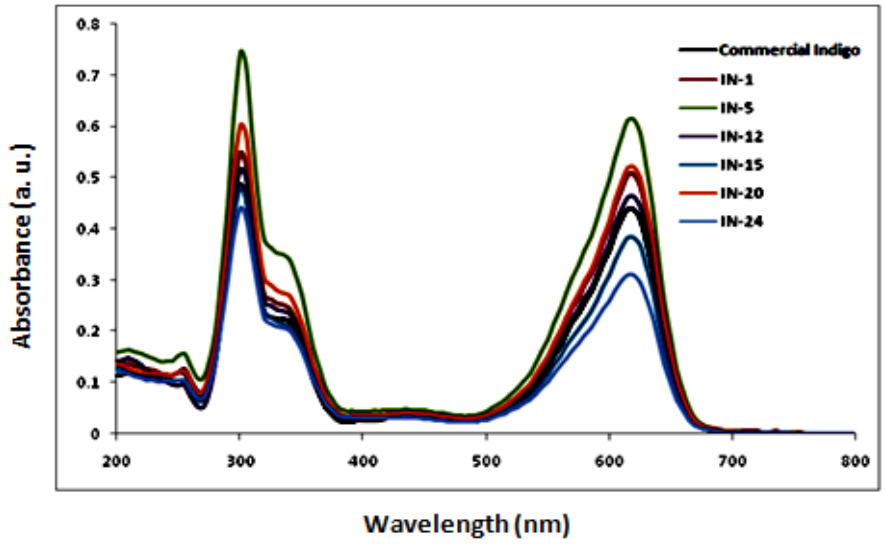

Fig. 7. UV spectra of the recovered indigo dyes and commercial indigo

4. Conclusions

The environmental pollution problems due to the textile industry's wastewater effluents have increased in recent years. The discharge of untreated textile industry wastewater especially containing the indigo dye has aroused the concerns of many environmentalists. Therefore the recovery and reduction of these indigo dyes have become necessary. The method for the recovery of indigo, described in this study, is quite simple and efficient. This approach has shown that it can be applied effectively in the denim industry to recover indigo dye from wastewater.

The results of our study showed that using the iodide-mediated catalytic reaction strategy, the quantitative and selectively indigo dye in the wastewater of the denim industry was successfully achieved by H_2O_2 at room temperature for 4-24 hours in the presence of ethanol. With the addition of 0.5 g KI and 100 mL ethanol in the presence of constant hydrogen peroxide, the most recovered indigo dye amount was found to be 0.0234 g in IN-20 coded sample in 4 hours. The structure of the recovered indigo dyes was characterized by spectroscopic methods, and it was found to be in harmony by comparison with commercial indigo and literature.

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