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ENVIRONMENTALLY FRIENDLY TECHNIQUES FOR WOOL DYEING PROCESS

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Abstract: The aim of this research was to evaluate the influence of dyeing process on the quality of surface waters contaminated with heavy metals and organic compounds, resulted after the wool dyeing process. In order to mark out this aspects an environment friendly method was proposed which involves dyeing wool fiber with new complex combinations derived from a new acid dyes which were complexed, using copper, iron, nickel and zinc salts at 2:1 combination ratio. In order to point out the environmental point of view of wastewaters an experimental protocol was tested by dyeing wool fiber at different pH. Evaluation of complexed combinations impact on the environment involve the following indicators: consumption degree of dyeing solution from the process bath, treatment degree related to the organic content expressed by COD indicator and treatment degree related to the heavy metal concentration respectively.

***Keywords**: environment, wastewaters, complex combinations, dyeing process.*

Introduction

Textile dyeing is a significant consumer of water and producer of contaminated aqueous waste streams. The textile industry has a global

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impact in many areas and in particular in relation to the effluent that is released, which is often complex, with intense color, chemical oxygen demanded (COD) and suspended solids.[1] Because of the complexity of the textile wastewater and the residual color associated with dyes, the color removal is a major priority for the textile industry.[2-4] Removal of dyes from industrial wastewaters is of global concern because dyes cause many problems in aqueous environments. Dyes may significantly affect photosynthetic activity in aquatic life because of reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, chloride etc. [5-9]

There are many dyes which are used for various textile applications. Acid dyes designed to have better wash fastness properties, usually contain solubilising and or additional hydrophobic groups, and, in addition could contain acid groups such as -OH, -NH_2 and -COOH which are capable to lead the formation of chelate complexes with cations of transition metals. The resulted complexed compounds are often used in dyeing wool processes. Since their introduction into textiles technologies, 1:2 metal-complex recorded good popularity which are attributable the superior all-round fastness properties on wool and the less damaging conditions required for their application to wool.[10]

The aim of this research was to determine the influence of dyeing process on the quality of surface waters contaminated with heavy metals and organic compounds, which result after the wool dyeing process.

Experimental

Materials

The complexed compounds presented in this paper have been synthesized by the coordination reaction between Fe(III),Cu(II), Ni(II) and Zn(II) ions and four organic ligands:

- sodium(E)-2-((1-hydroxy-4-sulfonatonaphtalen-2-yl)diazenyl) 6methoxybenzo[d]thiazole5 or 7-sulfonate, denominated as ligand HL^1;
- sodium(E)-2-((2-hydroxy-6-sulfonatonaphtalen-1-yl)diazenyl) 6methoxybenzo[d]thiazole5 or 7-sulfonate, denominated as ligand HL^2;
- sodium(E)-3-hydroxy-4-((6-methoxy-5 or 7 – sulfonatobenzo [d] thiazol - 2yl)diazenyl)naphthalene-2,7-disulfonate, denominated HL^3;
- sodium(E)-2–((1-amino-4-sulfonatonaphthalen-2-yl)diazenyl) 6methoxybenzo[d]thiazole5 or 7 -sulfonate denominated HL^4.[11-13]

The formation of the complexed compounds was conducted in order to obtain new complexed dyes for wool dyeing processes. The salts used as complexation reagents were $FeCl_3$, $CuCl_2$, $NiCl_2$ and $ZnCl_2$ which were purchased form Merck.

Formation of complexed combinations in liquid phase

In order to highlight their formation and stability the coordination compounds were synthesized in liquid phase. The Harvay-Manning method was applied to determine the stability constants for the new obtained compounds. The absorbance measurements were spectrophotometrically determined at the maximum wavelength for the formed complex compound between HL^1, HL^2, HL^3 and respectively HL^4 and each complexation reagent.

Formation of complexed dyes in solid phase

The synthesis in solid phase was done at room temperature by mixing 200 mL of 10^{-2} M ligand solution with 100 mL of 10^{-2} M metallic salts solution under continuous stirring, for 90 minutes. The reaction products were separated by repeated centrifugations and washings with an equimolecular mixture water: ethanol in order to remove the impurities and the un-reacted products, after which they were dried at 105 ºC until constant pound.[14-20] The yields were 98% for all the experiments.

Dyeing processes

The synthesized dyes were used for wool dyeing, at 100 °C for 30 min with the Polycolor tip P 4702 device (Mathis) as follows: 3% dye (owf), 1:100 MLR (material to liquor ratio), pH 2 and 5 adjusted by adding of 5M CH_3COOH solution.

Methods

In order to mark out the environmental impact on the resulted wastewaters, after the dyeing process, three indicators were taken into account:

1. The decolorization degree (D) of the final solutions from the dyeing bath was calculated with the following equation:

$$D = \frac{A_i - A_f}{Ai} \cdot 100 \qquad (1)$$

where Ai is the initial absorbance of the solution resulted after the dyeing process and Af is the final absorbance of solution after decolorization process. The absorbencies for each of the complexed dyes were measured at the maximum absorbance λ_{max} using an UV-VIS Perkin-Elmer Spectrum 100 spectrophotometer.

2. For determination of COD indicator, the spectrophotometric method based on dichromate potassium was used using the following equation:

$$COD = \frac{COD_i - COD_f}{CODi} \cdot 100 \qquad (2)$$

3. Concentrations of heavy metals were determined by atomic absorption spectrometry.

Results and discussions

The stability constants calculated for each resulted complexed combinations are summarized in Table 1.

Table 1. The stability constants for complexed dyes with each metallic salt.

Compound	Maximum wavelength λ_{max}[nm]	Stability constant $[L \cdot M^{-1}]$
L^1Fe	480	$\beta = 25.51 \cdot 10^{13}$
L^1Cu	530	$\beta = 22.82 \cdot 10^{13}$
L^1Ni	570	$\beta = 21.42 \cdot 10^{12}$
L^IZn	485	$\beta = 24.74 \cdot 10^{13}$
L^2Fe	535	$\beta = 19.76 \cdot 10^{13}$
L^2Cu	590	$\beta = 18.46 \cdot 10^{12}$
L^2Ni	470	$\beta = 13.51 \cdot 10^{12}$
L^2Zn	490	$\beta = 23.77 \cdot 10^{11}$
L^3Fe	485	$\beta = 12.38 \cdot 10^{19}$
L^3Cu	610	$\beta = 17.23 \cdot 10^{21}$
L^3Ni	460	$\beta = 9.54 \cdot 10^{19}$
L^3Zn	475	$\beta = 14.67 \cdot 10^{17}$
L^4Fe	530	$\beta = 7.83 \cdot 10^{22}$
L^4Cu	560	$\beta = 17.53 \cdot 10^{21}$
L^4Ni	550	$\beta = 23.21 \cdot 10^{20}$
L^4Zn	520	$\beta = 19.82 \cdot 10^{20}$

From Table 1 resulted that through interaction between HL^1, HL^2, HL^3 and respectively HL^4 and each complexation reagent resulted stable complexed and the highest stability constant had the L^4Fe complex.

The dyed wool fibers in acid pH cover a a wide range of shades and colors due to complexation process, the color being in a line with the changing used metallic salts. Also, the resulted complexed compounds obtained by complexation reaction between each ligand and metallic ions in 2:1 combination ratio showing a good affinity for wool fibers actually observed for the entire acid pH range used in dyeing processes.

In order to put into evidence the effects of dyes (free and complexed) on environment, the decolorization degree, COD and concentration of heavy metals were tested. The dyeing processes were carried out at pH 2 and 5, and the decolorization degrees for the waste solutions resulted after dyeing processes are shown in Figure 1 and Figure 2.

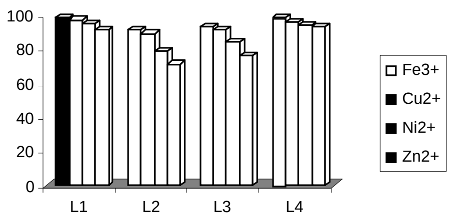

Figure 1. The variation of decolorization degree in function of the ligand and metall used at pH 2.

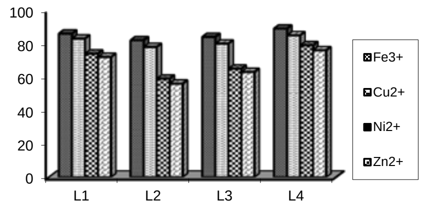

Figure 2. The variation of decolorization degree in function of the ligand and metall used at pH 5.

The experimental results show that the decolorization degree pronuncedly increased for the dyeings achieved at pH = 2, finally the dyeing at this pH could effectively modify the environmental impact by using of this synthetized complex compound. The best results of decolorization rate can be observed when were used the complexed dyes derived from HL^4 and respectively HL^1 as a result by complexation reaction with Fe(III). In conclusion the dyeing wool fibers from decolorization point of view it`s recomended to be achieved with HL^4 complexed with Fe(III).In the present study the decolorization rate follows the order $Fe^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$ from complexation reagent point of view and $HL^4 > HL^1 > HL^3 > HL^2$ from used ligand point of view.

The recorded COD values for each resulted wastewaters after dyeing process at different pH are shown in the Figure 3 and Figure 4. As how it`s showing in the graphical representation the results are in concordance with the obtained results for decolorization rate in the experimental errors limit. When the pH 5 for dyeing process was used COD values were more higher in comparison with obtained COD values for pH 2. Like in the decolorization case the COD values increasing with the increasing pH and the best values can be observed in the ligand HL^4 case wich was complexed with iron ion. As in all environmental indicators case the pH values plays an important role in decreasing environmental impact.

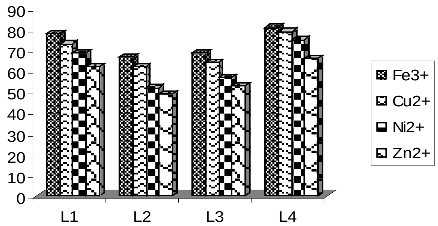

Figure 3. The COD variation in function of the ligand and metal used at pH 2.

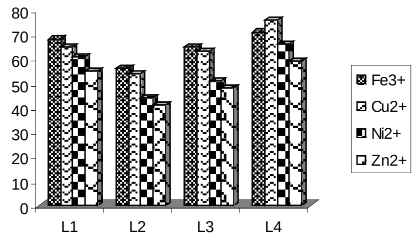

Figure 4. The COD variation in function of the ligand and metal used at pH 5.

The heavy metalls concentration in wastewaters can be explicated by the uncompleted complexed compounds diffussion into the fiber due to many external factors. The variation heavy metalls concentration as a function of the ligand and meallic used ion at pH 2 and pH 5 was recorded for resulted wastewaters after dyeing process with complexed compounds, with the results shown in the Figure 5 and Figure 6.

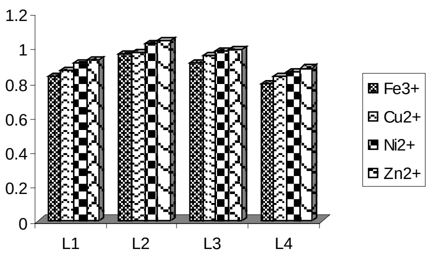

Figure 5. The heavy metalls concentration in function of the ligand and metall used at pH 2.

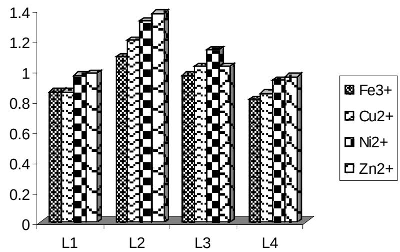

Figure 6. The heavy metalls concentration in function of the ligand and metall used at pH 5.

Heavy metalls concentration was much less at pH 2 and all the values are in 0,79-1,04 mg M/L range, beeing in the same time under admited limit. In the pH 5 case can be observed that the values are up of this limit and in conclusion this value at pH it` s not recomanded to be used in the technological process wool dyeing with this new complexed compounds from environmental point of view.

In order to carried out the played role of the complexation reaction for the aiming to decrease environmental impact the decolorization rate and COD indicator for each free dyes used in dyeing wool were registered. As in the casses mentioned above are dyeing was done at different two values at acid pH and the results are shown in the Figure 7 and Figure 8.

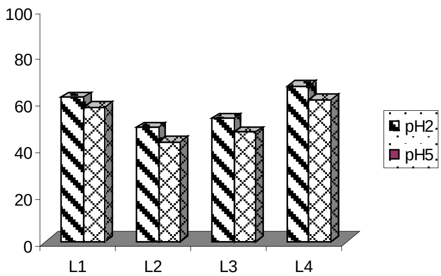

Figure 7. The decolorization degree in function of the uncomplexed dye at pH 2 and pH 5.

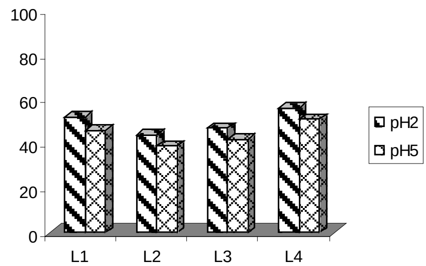

Figure 8. The COD values in function of the uncomplexed dye at pH 2 and pH 5.

The use of pH 2 in dyeing processes lead to obtain the highest values for decolorization degree, but smaller in comparring with the obtained values for decolorization degree for complexed dyes (Figure 7). This thing could be the same atributed to the complexation reaction wich lead to more stabil compounds, in addition to better fiber adhesion and uniformity of colour and in a conceques the dyeing with them can increase the colour removal from wastewaters.

Figure 8 showed the similar variation of the COD values at different pH and the values are more less in comparring with the obtained COD values for each new complexed dyes.

Conclusions

In the preliminary investigations was observed that the acid pH used at different values had significant removal complexed dyes efficiency in addition with the increasing the decolorization degree. The decolorization degree increase with the pH decreasing, the best results were obtained for the HL^4 at pH 2 in the both case, when was used uncomplexed and complexed with iron ion. The COD values are in according with the obtained values for the decolorization degree in all cases in experimental limit errors. A reverse trend was observed for the heavy metals concentration, with decreasing pH values the concentration heavy metals it`s decreased, was obtaining values under admitted limit for the complexed dyes at pH=2. There for pH 2 was considered to be a more effective and it can admited that the experimental conditions could obtimise this process both from environmental and technologycal point of view.

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