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Adsorption Decolorization Technique of Textile/Leather – Dye Containing Effluents

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Abstract

The purpose of this study was to evaluate the potential of ion exchange resins to remove the color from industrial wastewaters. In textile-leather dyeing, paper, colour, printing, cosmetics, pharmaceutical and other industries the synthetic dyes are extensively used. Adsorption techniques are much used to remove certain classes of pollutants from waters, especially from industrial colored wastewaters. In recent years, functional polymers have been increasingly tested as a potentially alternative to traditional adsorbents due to their vast surface area, perfect mechanical rigidity, adjustable surface chemistry and feasible regeneration under mild conditions. The strongly basic anion exchanger resins were used as an adsorbent for the acid, direct and reactive dyes adsorption from the coloured wastewaters.

Keywords: Colored wastewater; Azo dyestuff; Adsorption; Ionic exchange (resin)

Introduction

Water-pollution control is now one of the major areas of scientific activity. Effluent discharge from leather, textile and dyestuff industries causing significant health concerns to environmental regulatory agencies. Color is the first contaminant to be recognized in wastewater and has to be removed before discharging into water bodies or on land. The economic removal of polluting dues is gaining great importance, particularly as new European Commission regulations on industrial effluent discharge are at present being enforced.

Synthetic azo dyes are used for a long time in textile-leather dyeing, paper, printing, color, photography, pharmaceutical, cosmetics and other industries. The textile and leather industry is one of the most complex and complicated manufacturing industry, is a large consumer of water and therefore produce large quantities of colored wastewater. During industrial processing up to 10-60% of the used dyestuffs are released in the effluent, being a major source for polluting the water resources.

The majority of synthetic dyes – bioresistant organic polluants - are considered as recalcitrant xenobiotic compounds due to the presence of an N = N bond and groups such as aromatic rings that are not easily degraded [1]. This wastewater that contains predominant dye substances is not only toxic to the biological world, its dark colour locks sunlight but leads to severe problems to the ecosystem. The discharge of these colored compounds into the effluents causes considerable environmental pollution by eutrophication of aquatic ecosystem and serious health-risks factors by bioaccumulation [2].

Therefore, decolorization of dyes is another important aspect of wastewater treatment before discharge into environment. There are several methods for dye removal: coagulation-flocculation, oxidation-ozonation, biological treatment, membrane technologies and adsorption techniques [3].

Adsorption is one of the most promising techniques applied for the decontamination of wastewater from dyes and it is considered superior compared to other available techniques for wastewater treatment in terms of initial cost, simplicity of design, and ease of operation [4]. Adsorption is a method that is preferred over other options because it is rapid, convenient and unaffected by the toxic contaminants [4].

The Purpose of this Applicative Research

This research proposed a method for decontamination/ decolorization of the industrial wastewater from ICPI microproduction leather dyeing and FROTTIEREX textile factory, using adsorbents macroporous ion exchange resin-IER. The removal of anions and cations from dye industry effluents can be carried out by ion exchange method, by passing the colored wastewater through the column of beds of IER [1].

Materials and Methods

In the research we used the following IER-PUROLITE type : strongly basic anion exchanger resins PUROLITE A 500, A500 Plus and PFA 500 MB, purchased from Purolite factory, Victoria, Brasov, Romania.

The studied industrial wastewaters contain Acid black 210, Direct black 234 [acid black NBH] [Sella Fast Black HM and HS-02- acid azo dyes], self-dispersible Pigment black 7 with modified surface from ICPI and contains Violet vinyl sulphone reactive dyes from FROTTIEREX.

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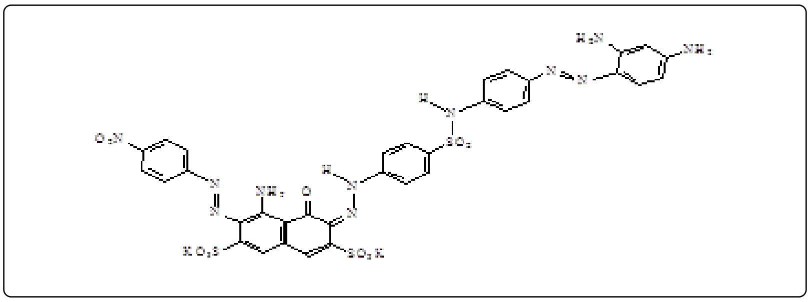
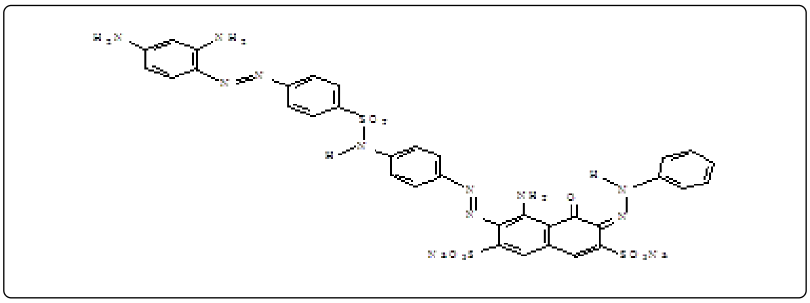
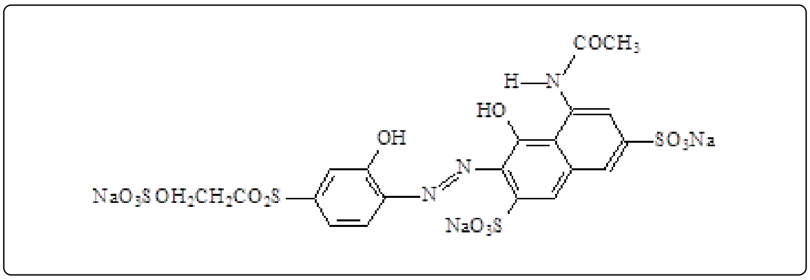
Wastewater origin	The chemical structure of the dye
ICPI - microproduction leather dyeing	 Acid black 210
ICPI - microproduction leather dyeing	 Direct Black 234 [acid black NBH]
ICPI - microproduction leather dyeing	Self-dispersible Pigment black 7 with surface-modified
FROTTIEREX textile factory	 Bezaktiv Violet V 5R

Table 1: Chemical structure of dyes – bioresistant organic polluants - contained in the wastewaters discolored with IER.

Origin, Compozition and Quantity of Studied Wastewater

The wastewater used in laboratory experiments in the treatment - discoloration through macroporous ion exchange resins proceeds from (Table 2):

Wastewater source	Working technique
Leather and Footwear Research Institute- ICPI, branch of National R&D Institute for Textiles and Leather (INCDTP), Bucharest	Research leather – footwear and dyeing leather and furs
FROTTIEREX textile factory, Bucharest	Manufacturer of textile garments from dyed cotton for towels / bathrobes, bed linen, tablecloths, upholstery fabrics

Table 2: Wastewater source.

Source	The quantity of wastewater (ml)
ICPI	10000
FROTTIEREX textile factory	20000

Table 3: Quantity of treated wastewaters.

The studied industrial wastewaters contain besides the azo-dyes and other auxiliary chemicals necessary in the dyeing process (Table 4):

Polluants	Trade name
I.C.P.I	
Trisazo acid black dye Acid Black 210	Sella Fast Black HM Sella Fast Black HS-02
Trisazo direct black dye Direct Black 234 [Acid Black NBH]	Sella Fast Black HM Sella Fast Black HS-02
Self-dispersible pigment with surface-modified	Pigment black 7
Acid for broaching and fixing	Formic acid
Fatliquoring agent semi-synthetic [anionic] –emulsion of natural and synthetic oils and fats	Coripol GF + SLG
FROTTIEREX	
Monofunctional vinyl sulphone reactive dye	Bezaktiv Violet V 5R
Exhaustion agent	NaCl
Fixing agent	NaOH, Na2CO3

Table 4: Dyes and chemical pollutants existing in treated wastewater with IER.

Adsorption

The process of adsorption involves the ions, atoms or molecules of the adsorbate to transfer and adhere to the surface of the adsorbent creating a thin film. Adsorption technique can be divided into physical and chemical adsorption. Another term of the physical adsorption process is physisorption and it is controlled by physical forces such as Van der Waals forces, hydrophobicity, hydrogen bond, polarity, static interaction, dipole –dipole interaction, Π-Π interaction etc. In the physical adsorption, pollutants get accumulated on adsorbent surface by the above mentions interactions while chemical adsorption is defined when the adsorbate is chemically bound to the adsorbent's surface due to the exchange of electrons [5].

The extent of adsorption depends on the nature of adsorbate such as molecular weight, molecular structure, molecular size, polarity and solution concentration. It also depends on the surface properties of adsorbent such as particle size, surface area, surface charge etc [5]. The efficiency of adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate.

Adsorption capacity, surface area, availability and total cost, influence the adsorbent's selectivity. However due to the high cost associated with adsorbents production and regenerating, researchers are developing alternative cost effective and nonconventional potential adsorbents in the removal of dye from its aqueous solution [5].

In the laboratory as well as in industrial plants, ion exchange resins are used in columns. The water or solution to be treated flows through the resin. The fresh resin gets progressively loaded with the ions from the feed solution. Ions from the resin are released into the treated solution. At the end some of the ions from the feed escape into the pure solution, and operation is stopped [6-9].

For discoloration the industrial wastewaters were used the next types of polymeric ion exchange resins (Table 5):

Name	Type	Ionic form	Total volum capacity	Remarks & Applications
PuroliteA 500	Strongly basic Type I, macroporous polystyrenic	Cl-	1.15 eq/L	High capacity for extraction of minerals dissolved and suspended matter.

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				Optimum performance in deionization and as an organic trap.
PuroliteA 500Plus	Strongly basic Type I, macroporous polystyrenic	Cl-	1.15 eq/L	For removal of the more strong-held colour bodies. Ensures good retention of organic compounds and color levels.
Purolite [Purofine] PFA 500 MB	Strongly basic Type I, macroporous polystyrenic	Cl-	1.19 eq/L	High efficiency and excellent kinetics. High sorption capacity of complex organic substances. Resisting to osmotic and thermal shock.

Table 5: The types of IER studied.

The treatment columns were filled with different amounts of three types of resins, it passes through different amounts of wastewater, depending on the final result of discoloration, as illustrated in Table 6.

Source	Column of IER	Type of IER used	Amount of IER from column, g	Amount of wastewater passed through the bed of IER, mL
ICPI	1	Purolite A 500	400	2500
	2	Purolite PFA 500MB	150	800
	3	Purolite A 500	400	1500
FROTTIEREX	4	Purolite A 500	400	4000
	5	Purolite A 500Plus	400	4500

Table 6: The amount of wastewater treated in different columns with IER.

Note: In column 3 was passed the neutralized wastewater.

The wastewaters were passed through the column containing beds of ion exchange resins and Figures 1 and 2 illustrate the decolored wastewaters taken in working.

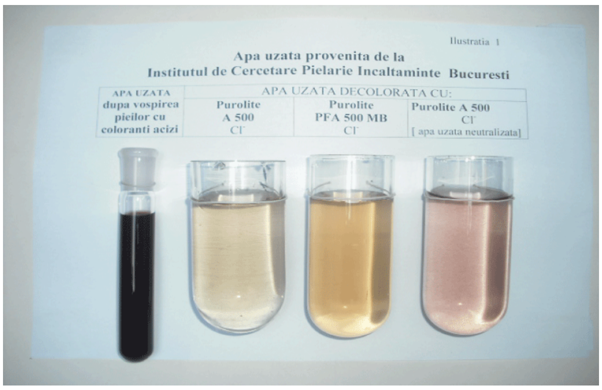

Figure 1: Discoloration of ICPI wastewater.

Figure 2: Discoloration of FROTTIEREX wastewater.

Analytical methods for evaluating the decontamination/ discoloration process of wastewater with IER

To determine the physical and chemical indicators of wastewater discolored following methods were used for analysis and instrumental analysis listed in Table 7.

No. crt.	Analytical test	Standard	Analytical device
1	pH	SR EN ISO10523/2012	691 pH Meter Metrohm
2	Conductivity	SR EN 27888/1997	Portable K912 Conductivity meters, Consort
3	Total Solids	STAS 9187-84	Drying stove, electric water bath
4	Turbidity	SR EN ISO 7027-2001	Portable Turbidity Meter HI 93703, Hanna Instruments
5	Chlorides	SR ISO 9297/2001	Potentiometer titrator
6	Sulphates	STAS 8601-70	Laboratory furnace, sand bath

7	DOC-Cr	SR ISO 6060/1996	Boiling installation with refluxing
8	Total nitrogen	SR EN 12260-2008	Analyser N/C 2100 S
9	Spectrophotometry	-	SPECORD UV-VIS M42 Karl- Zeiss Jena

Table 7: Physical and chemical indicators monitored and analytical methods.

Results and Discussion

The research study presented above describes the experiments on the application of sequestrant macroporous polymer like ion exchange resins in order to discoloration/purify industrial wastewaters that containing dyestuffs.

The experimental study involved the purchase of wastewater [10000 or 20000 mL] resulting from processes for dyeing cellulose materials and leathers from the technological platforms of ICPI and FROTTIEREX Factory in Bucharest.

Wastewater includes acid and direct trisazo dyes (Acid Black 210, Direct Black 234) and pigment with modified surface (Pigment Black 7) was not exhausted on the leather material, respectively vinyl sulphone reactive dye (Bezaktiv Violet V 5R) chemically unfixed on cellulose material, cotton.

We used three types of strongly basic anion exchange resins with macroporous structure: Purolite A 500, A 500 Plus and PFA 500 MB.

The colored studied wastewaters were passed through a laboratory plant that consists of column resin beds containing between 150-400 g IER.

The last stage of the research study was both to determine the parameters to characterize the quality of wastewater treated with the studied resins and the obtained discolored waters.

Experimental study also involves the identification and characterization of analytical methods to establish the various quality parameters of wastewater and discolored wastewater: pH, solids-total, conductivity, chlorides, sulphates, total nitrogen, COD, turbidity and colour.

Analysis of the results of discoloration experiments of wastewater that containing dyes by using strongly basic anion ion exchange resins, as intermediate stage in the general flow of sewage highlights the following:

For wastewater containing acid and direct dyes and pigment with modified surface proceeds from ICPI.

Spectrophotocolorimetric as well as visual analysis shows those coloring matters in wastewaters that have not been exhausted on leather, are almost entirely retained by the resins used. Discoloration is not complete because, during the process of passage of wastewater through the bed of resin, the fatliquoring agent saturates the resin and hinders the adsorption of coloring materials. The UV - Visible absorption spectra indicate a decoloration of ~ 96% (Figure 3).

At the same time it was shown that the resins used are helpful for wastewater treatment, this fact was demonstrated by reducing chemically of indicator DOC-Cr with ~ 80-90%, reduction of a sulphate indicator with ~ 95%, the turbidity parameter showing a reduction with ~ 80-90% of suspensions which decrease the water transparency (Tables 8 and 9), depending on the type of resin used.

For an industrial waste water containing vinylsulphonic reactive dye chemically unfixed and hydrolyzed, which was removed at the washing process of dyed cellulose material, from FROTTIEREX factory.

Spectrophotocolorimetric as well as the visual analysis show an incomplete discoloration of ~ 92%, because of the dye structure and its low molecular weight (Figure 4).

Physico - chemical parameters of treated water are relatively improved, thus the turbidity is reduced by ~ 85%, DOC-Cr with ~ 50-60% and total nitrogen by ~ 50-60% depending on the type of resin used and the residual dye (Tables 8 and 10).

The UV-visible spectrum of the colored and the decolored waters is illustrated by Figures 3 and 4.

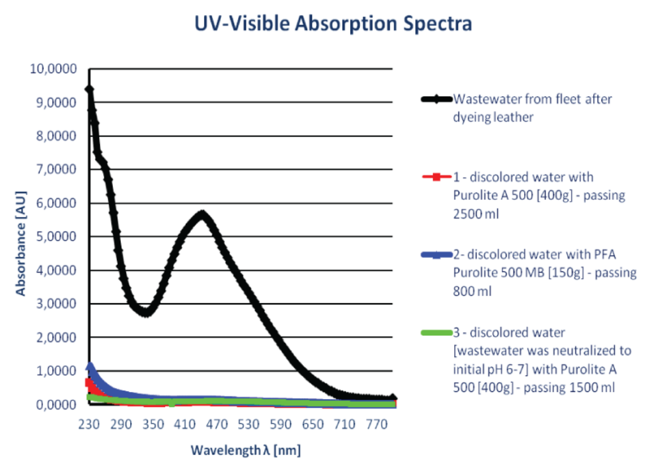

Figure 3: UV-visible spectrophotometric analysis of the colored and the decolored waters of ICPI.

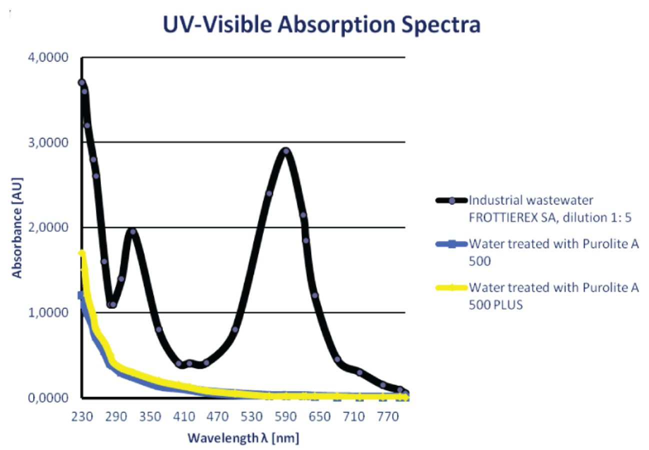

Figure 4: UV-visible spectrophotometric analysis of the colored and the decolored waters of FROTTIEREX.

The parameters of physico-chemical indicators are presented in Table 8.

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Physico-chemical indicators	Waste water ICPI Black acid dyes	Purolite A 500	Purolite PFA 500 MB	Purolite A 500 - neutralized waste water	Waste water FROTTIEREX Violet reactive dye	Purolite A 500	Purolite A 500 PLUS
pH	3.11	2.7	2.4	5.5	11.40	11.20	11.30
Solids total, mg/L	3118	2711	2344	5128	81070	64200	63600
Sulphates, mg/L	1.553	109	5.1	88.4	1768	1708	1746
Total nitrogen, mg/L	38.4	23.9	19.4	20.6	14.10	5.10	6.90
DOC-Cr, mgO/L	1643	338	214	111	2023	988	706
Turbidity, FTU	95.6	8.67	10.7	16.8	149	28	18
Colour, note	5 Dark brown	1-2 Light greenish brown	1-2 Lightyellowish brown	2 Light reddish brown	5 Dark violet	2	2

Table 8: Physico-chemical indicators of colored wastewater and of decolored water.

The efficiency of decontamination/discoloration process

Based on the obtained results from physico-chemical analysis for determining the indicators characteristics of wastewater and treated water, to demonstrate the efficiency of treatment method using ion exchange resins, the discoloration process efficiency was calculated (Tables 9 and 10).

Physico chemical indicators	A 500	PFA 500 MB	A 500 neutralized wastewater
Solids total	13	25	-
Sulphates	93	97	94
Total nitrogen	38	49	48
DOC-Cr	80	87	93
Turbidity	91	89	82
Colour	96	96	96

Table 9: The efficiency of decontamination/ discoloration process, wastewater from IPCI.

Physico-chemical indicators	A500	A500 Plus
Solids total	21	22
Total nitrogen	64	51
DOC-Cr	51	65
Turbidity	81	88
Colour	92	92

Table 10: The efficiency of decontamination/discoloration process, wastewater from Frottierex.

Conclusions

The main objective of wastewater treatment is the removal therefrom of, the substances found in suspension, colloidal substances or those dissolved into solution, toxic substances, microorganism, the ultimate goal representing environmental protection [emissaries, soil and air] in general and a health of humans and living beings particularly.

The problem of wastewater treatment has now become more complex due to residual substances existing in waste water which, very little removed or practical unmodified through the steps of conventional mechanical-biological treatment (detergents, phosphates, nitrogen based compounds, dyestuffs, salts inorganic, persistent organic compounds, pesticides, other various chemicals) create extremely serious problems for the environmental and living matters.

This study shows that the strongly basic anion exchanger with macroporous structure containing tertiary amine functionalized on the polystyrene cross linked with divinylbenzene matrix can be practically used for color removal from the wastewaters containing the bio resistant organic pollutants for environment: anionic azo acid dyes, reactive dyes and self-dispersible pigments.

The decolorization performance of IER was evaluated by the yield of quality parameters of treated wastewater: remove of 95% for sulphates, 38-64% for total nitrogen, 50-85% for DOC-Cr, 80-90% for turbidity and ~ 95% for colour, depending on the type of wastewater: leather or textile dyeing.

The research conducted within the Romanian Nucleu Project "The utilization of macroporous resin by developing active and passive nanostructures for wastewater treatment" demonstrated that the unconventional discoloration-treatment process for industrial wastewater containing dyestuffs is a viable intermediate step, usefulness and effectiveness of their retention from wastewater.

The dyes adsorption technology - bioresisting pollutants - through polymeric ion exchange resins from wastewater represent an important step in the advanced treatment technology of wastewater system, thus treated waters finally can be discharged into sewers or receiving waters

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in accordance to the Standards on pollutant loading limits of industrial wastewater and wastewater discharge conditions in sewers networks or directly into sewage treatment plants.

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