Available online at www.sciencedirect.com
SCIENCE DIRECT
Dyes and Pigments 64 (2005) 57–61
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Removal of vat and disperse dyes from residual pad liquors

Vera Golob*, Alenka Ojstršek

University of Maribor, Faculty of Mechanical Engineering, Textile Department, Smetanova 17, 2000 Maribor, Slovenia

Received 13 February 2004; received in revised form 6 April 2004; accepted 13 April 2004
Available online 1 July 2004

Abstract

The efficiency of three wastewater treatment techniques, coagulation/flocculation, adsorption and ultrafiltration, has been studied for the removal of vat and disperse dyes from residual pad liquors. Three inorganic coagulants $Al_2(SO_4)_3 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$ and commercial cationic flocculant, as individuals and in combination, were tested for the coagulation/flocculation methods. Granular activated carbon was used as an adsorbent in the adsorption technique. Ultrafiltration was performed using a polyethersulfone membrane with a molecular weight cut-off of 10 kDa. Dye removal was evaluated as the difference between concentrations of dyes in pad liquors before and after a particular treatment using absorbance measurements. The obtained results indicated over 90% of dye removal using appropriate coagulants and only 40% using activated carbon. The best results, dye removal over 98%, were achieved using the ultrafiltration technique.

Keywords: Coagulation/flocculation; Adsorption; Ultrafiltration; Vat dyes; Disperse dyes; Decolouration

1. Introduction

Textile dye-house effluents represent severe environmental problems as they contain various chemicals, auxiliaries and dyestuffs. Dyestuffs are divided into classes according to their chemical constitutions and technological application, and give coloured wastewaters that have high COD and TOC values and low BOD values [1]. Dyes are difficult to biodegrade in the environment due to their resistance to light, heat, chemicals and water, but partial decomposition of dyes leads to an even more potentially harmful and toxic aromatic compound. This can lead to an acute and/or chronic effect on the exposed organisms. The risk, which dyes represent in wastewaters, depends on their chemical structure, physical properties, concentration and exposure time [2,3].

Several methods such as physical, physico-chemical, chemical and biological are available for the removal and/or decolouration of dyestuffs in dye-house effluents. Choosing the most appropriate treatment methods or their combinations depends on the dyestuffs and the dyeing methods used in the textile production. The continuous dyeing of cotton and polyester fabrics or their blends of various ratios in industrial production can be performed by pad steam and thermosol methods using vat and disperse dyes. Water insoluble vat dyes are based on derivatives of indigo or anthraquinone and related polycyclic systems, with two or more carbonyl groups linked by a conjugated system [4]. Disperse dyes are structurally classified as mainly an azo and anthraquinone chromophoric system with small molecular size and low aqueous solubility [5]. The residual pad liquors represent a low volume of highly concentrated insoluble vat and disperse dyes which should be sanitised before they are discharged into the effluents. This present paper describes a comparative study of removing three vat and three disperse dyes from pad liquors using coagulation/

* Corresponding author. Tel.: +386-2-220-7891; fax: +386-2-220-7990.
E-mail address: vera.golob@uni-mb.si (V. Golob).

0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2004.04.006

flocculation and adsorption methods and an ultrafiltration technique.

Coagulation is the process of destabilising colloidal and other matters to form small discrete particles, and flocculation is the process of agglomerating these small particles. Wastewaters from dye-houses are suspended particles with average diameters of 5–20 nm, and are negatively charged because of OH^- bounded ions that prevent aggregation and precipitation. The sedimentation process may only take place with destabilization, followed by agglomeration of the colloids in two different ways: with coagulation and/or flocculation [6,7].

Although several materials can be used as adsorbents, activated carbon is the most widely employed adsorbent for the waste treatment of dyes [2] because it has a large internal surface, and is able to remove a broad range of adsorbates [8]. Activated carbon is suitable for removing organic contaminants, which are nonpolar with a large molecular mass. It is most often used for the tertiary treatment of bio-undegradable sewage as well as for wastewater decolouration from dye-houses. Activated carbon is prepared in granular (GAC) or powdered (PAC) forms. Eventually, the carbon medium becomes saturated and the carbon must be regenerated, which adds to the cost of the process. Therefore, the treatment efficiency and operational costs for large textile wastewater volumes become disproportionate [7].

Ultrafiltration is a low-pressure physical removal process in which solids smaller than about 0.001–0.02 μm are separated from the water as it is forced through a membrane. Typical materials used for membranes are: cellulose acetate, polyamide, polysulfone, nylon, polycarbonate, polypropylene, polytetrafluoroethylene, etc. [9]. Polyethersulfone membranes are widely used for UF applications, which have wide temperature limits, wide pH tolerances, fairly good chlorine resistance, wide range of pore sizes, etc. The main disadvantages of polyethersulfone are low-pressure limits and hydrophobicity: therefore, it interacts strongly with a variety of solutes.

2. Materials and methods

The three Cibanon vat dyes (Yellow G—C.I. Vat Yellow 46, Red 6B—C.I. Vat Red 13 and Navy DB-01—mixture) and three Terasil disperse dyes (Yellow W-6GS—C.I. Disperse Yellow 114, Red W-4BS—C.I. Disperse Red 376 and Navy W-RS—mixture) were used in this study, as supplied by Ciba Speciality Chemicals. The chemical structure of C.I. Vat Red 13 is shown in Fig. 1, while only the chromophores of the other dyes are known. The yellow vat dye based on flavanthrone, blue vat dye on benzanthrone, yellow disperse dye on pyridone, and the other two disperse dyes are nonsoluble monoazo dyes. All six dyes were used without purification.

The efficiency of the coagulation process and the adequate amount of coagulants for dye removal from pad liquors were evaluated using a jar test. Coagulants,

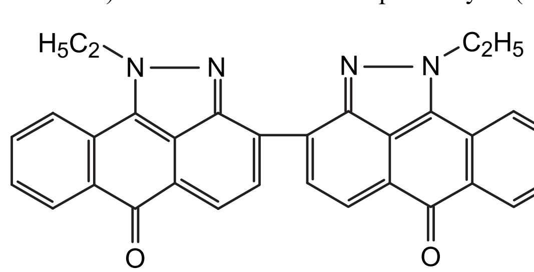

Fig. 1. The chemical structure of C.I. Vat Red 13.

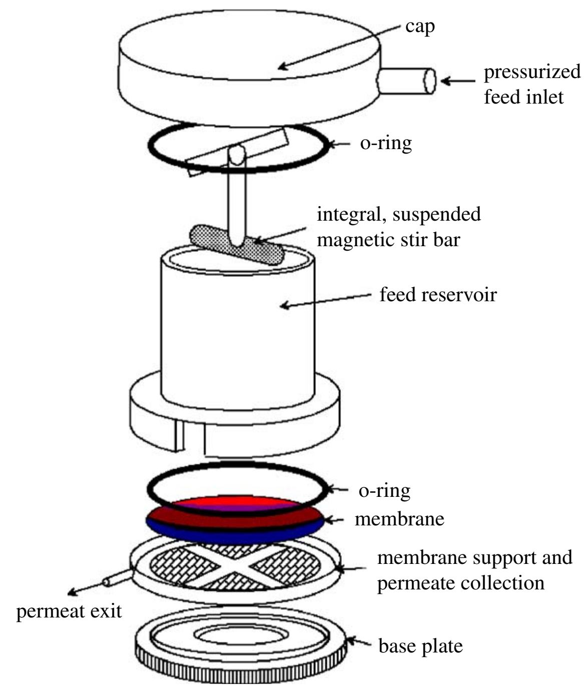

Fig. 2. Expanded schematic view of the ultrafiltration assembly.

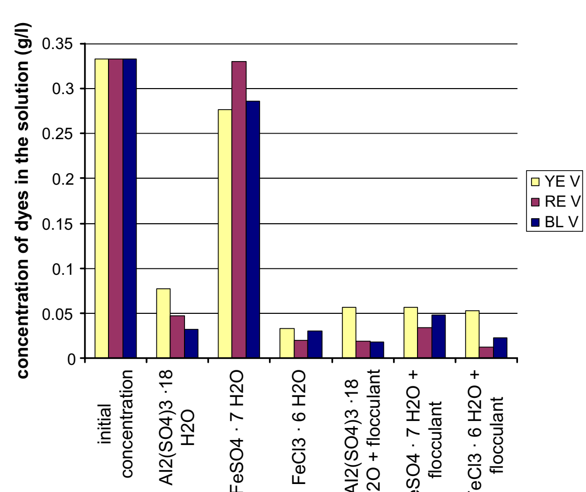

Fig. 3. Effect of the coagulants and flocculant on reducing the concentrations of vat dyes.

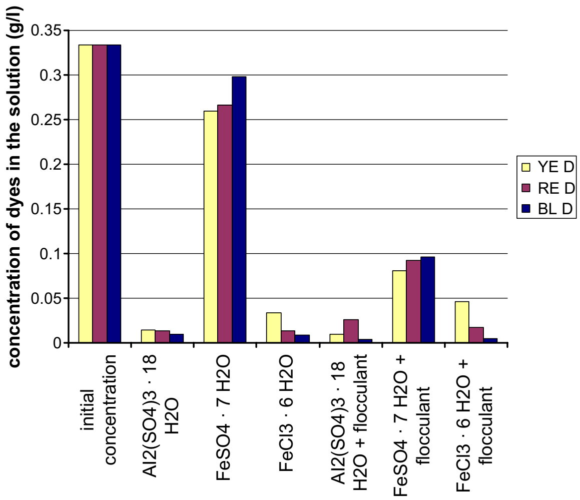

Fig. 4. Effect of the coagulants and flocculant on reducing the concentrations of disperse dyes.

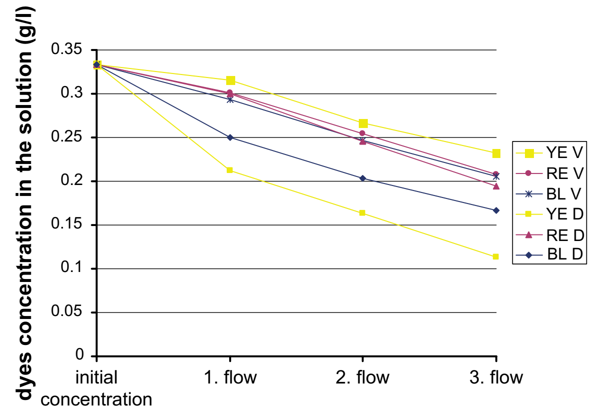

Fig. 5. Effect of activated carbon on reducing the concentrations of dyes.

$Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4{\cdot}7H_2O$, $FeCl_3{\cdot}6H_2O$ and the commercial flocculant (Colfloc RD—Ciba), were tested in this research. Samples (1000 ml; dispersion of 0.33 g/l vat or disperse dyes) were placed in six vessels and stirred at high speed (100 rpm) with various doses of inorganic coagulant. This rapid mixing phase (2 min) was followed by a 5-min period of gentle mixing (30 rpm) and then, the organic flocculant (5 mg/l) was added under rapid mixing (1 min). The speed was then reduced to 30 rpm and stirring continued for 5 min. After settling the suspension for 30 min, visual evaluation of the jar test was followed, and the absorbance of the supernatant was measured.

Three progressive columns with 600 ml volume of activated carbon were equipped for the adsorption process. Granular activated carbon was obtained from Sigma–Aldrich Laborchemikalien. Dye dispersion flow through the column was from 0.15 to 0.2 l/min.

The crossflow ultrafiltration system is schematically shown in Fig. 2. A polyethersulfone membrane with a pore size of approximately 10 nm and a molecular weight cut-off (MWCO) of 10 kDa was used for the performed experiments. The transmembrane pressure of the UF system was 250 kPa.

The absorbance of the pad liquors was measured at a wavelength of maximum absorption for each dye using a Carry 50 spectrophotometer (Varian), and dye concentrations were determined according to the Lambert–Beer law:

$$T = 10^{-klc}, \quad A = -\log T = klc \tag{1}$$

where T is the transmittance; A is the absorbance; k is the absorptivity coefficient (l/g cm); c is the concentration (g/l) and l is the optical length (cm).

Vat dyes were diluted in a solution of NaOH and $Na_2S_2O_4$ for measuring the absorbance before and after treatment, and the disperse dyes were diluted in a 75% solution of ethanol in the ratio of 1:4. The dye removal percentage DR was calculated according to the following equation:

$$\mathrm{DR}\ (\%) = \frac{c_0 - c}{c_0} 100 \tag{2}$$

where c_0 is the initial dye concentration (g/l); and c is the dye concentration after treatment (g/l).

Chemical oxygen demand (COD) was measured according to the ISO 6060 standard using a Termoproc TBGE. Total organic carbon (TOC) was measured using a DC-190 Analyzer (Dohrmann).

Table 1
The percentage of dye removal by coagulants and flocculant

Dye	Dye removal (%)					
	$Al_2(SO_4)_3$	Fe_2SO_4	$FeCl_3$	$Al_2(SO_4)_3$ + flocculant	Fe_2SO_4 + flocculant	$FeCl_3$ + flocculant
Cibanon Yellow G	76.7	16.9	90.2	93.2	83.2	94.1
Cibanon Red 6B	85.9	0.9	94.1	94.3	89.8	96.2
Cibanon Navy DB-01	90.5	14.2	90.9	94.7	85.6	93.1
Terasil Yellow W-6GS	95.6	22.1	89.8	97.2	75.9	86.0
Terasil Red W-4BS	96.0	20.1	95.9	92.2	72.2	94.7
Terasil Navy W-RS	97.2	10.4	97.3	98.8	71.2	98.5

Table 2
The percentage of dye removal after adsorption treatment

Dye	Dye removal (%)		
	After 1st flow	After 2nd flow	After 3rd flow
Cibanon Yellow G	5.2	19.9	30.3
Cibanon Red 6B	9.5	23.6	37.8
Cibanon Navy DB-01	12.0	26.0	38.5
Terasil Yellow W-6GS	36.2	51.0	65.9
Terasil Red W-4BS	10.0	26.1	41.7
Terasil Navy W-RS	24.9	38.8	49.9

Table 3
The influence of ultrafiltration on decreasing the concentrations of dyes

Dye	λ_{max} (nm)	c_0 (g/l)	c after UF (g/l)	Decolouration (%)
Cibanon Yellow G	440	0.33	0.0060	98.1
Cibanon Red 6B	540	0.33	0.0020	99.4
Cibanon Navy DB-01	580	0.33	0.0020	99.4
Terasil Yellow W-6GS	420	0.33	0.0015	99.5
Terasil Red W-4BS	514	0.33	0.0107	96.8
Terasil Navy W-RS	590	0.33	0.0013	99.6

c_0 = initial concentration of the dye.
c = concentration of the dye after ultrafiltration.

3. Results and discussion

The removal of six selected dyes from 0.33 g/l pad liquors using an equal amount of coagulants (30 mg/l) and/or flocculant (5 mg/l) is depicted in Fig. 3 for vat dyes and in Fig. 4 for disperse dyes.

It is obvious from Fig. 3 that some inorganic salts, which are used as coagulants, significantly reduced the concentrations of vat dyes in the pad liquors. Good results were obtained with $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3{\cdot}6H_2O$, where the dyes were removed by up to 97% (Table 1). The least efficient for vat dye removal was $FeSO_4{\cdot}7H_2O$. The coagulation process with this coagulant was poor and incomplete: flocks and precipitate were not rising, dye dispersion was only slightly thickened. The addition of the commercially prepared flocculant to the solution, where the coagulants were already present, improved results only when $FeSO_4{\cdot}7H_2O$ was used (percent of dye removal increased from 14% to 85%), whilst with the other two coagulants, dye removal was only slightly improved. This might be attributed to the fact that all selected dyes are colloidal particles of sizes around 1 μm, which are negatively charged, and the addition of cation coagulant destabilized the system that leads to the agglomeration.

Dispersion treatments of disperse dyes give similar results, as illustrated in Fig. 4, as previous vat dyes. Generally, minimum decolouration was reached using $FeSO_4{\cdot}7H_2O$ (22%). Yellow, red and blue disperse dyes are almost removable from the dispersion using aluminium sulphate and ferrous chlorate, which have a similar effect (the percent of dye removal is up to 97%, Table 1). The combination of flocculant and coagulant only has advantages before the coagulant in the case of ferrous sulphate.

Fig. 5 depicts the concentrations of vat and disperse dyes before and after treatment using granular activated carbon. This diagram shows the decrease in concentration of the vat and disperse dyes depending on the number of flows through the column using granular activated carbon. The higher the flows, the lower the concentration. The poor carbon adsorption of these dyes is a consequence of their colloidal nature and low solubility. The best results were reached by decolourizing the yellow disperse dye. The percentage of colour removal after the first flow through the column was 36.2% and after the third flow was 65.9% (Table 2). Just the opposite decolouration was achieved when treating the solution of yellow vat dye, where the concentration of dye in the pad liquors reduced from 0.33 g/l to 0.23 g/l (only 30.3%).

It is evident from Table 3 that the dye removal was either complete or almost complete (96.8 up to 99.6%) when the pad liquors flowed through the ultrafiltration membrane. The COD and TOC of the pad liquors were also determined (Table 4), because of the lowest absorbance values after ultrafiltration in comparison to the other two treatments. The COD values after ultrafiltration are below the limit value allowed by Slovenian environmental regulations (200 mg O_2/l), with the exception of vat red and disperse red dyes (337 mg/l and 571 mg/l, respectively). The TOC values after ultrafiltration decreased by up to 95%, on average

Table 4
The influence of ultrafiltration on decreasing the COD and TOC of the pad liquors

Dye	COD (mg O_2/l) before UF	COD (mg O_2/l) after UF	Decreasing of COD (%)	TOC (mg C/l) before UF	TOC (mg C/l) after UF	Decreasing of TOC (%)
Cibanon Yellow G	1822	169	90.7	172	8	95
Cibanon Red 6B	2065	337	83.7	177	16	91
Cibanon Navy DB-01	1741	109	93.7	175	9	95
Terasil Yellow W-6GS	1578	190	88.0	151	39	74
Terasil Red W-4BS	2230	571	74.4	151	54	64
Terasil Navy W-RS	1605	169	89.5	152	33	78

11 mg C/l for vat dyes and 42 mg C/l for disperse dyes, which are below the limit allowed by Slovenian regulations (60 mg C/l). Slovenian environmental regulations for COD, 120 mg O_2/l, and TOC, 30 mg C/l [10], used for all discharges of urban and industrial wastewaters from treatment plants, are comparable with EU regulations for COD, 125 mg O_2/l, and TOC, 35 mg C/l [11]. In addition, specific industrial sectors (textile, leather, metallurgy) in Slovenia use regulations which allow higher limit values (for the textile industry COD, 200 mg O_2/l, and TOC, 60 mg C/l) when discharging wastewaters into surface waters or sewage systems.

4. Conclusions

The obtained results indicate that coagulation/flocculation process and ultrafiltration technique are suitable for the efficient removal of water insoluble vat and disperse dyes from residual pad liquors. The adsorption process using granular activated carbon is less suitable for the purification of pad liquors containing these dye classes.

A comparison of the different coagulants and their combinations with flocculant used in this research shows the efficiency of two coagulants: $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$. The best results were achieved using a combination of aluminium sulphate and flocculant, where the percent of decolouration for different dyes was from 83.2% to 98.8%.

The removal of used dyes by adsorption is maximally 65.9% (dispersion of yellow disperse dye). Any increase in the number of flows through the column increases decolouration (up to 70%) thus extending the cost of the process.

Ultrafiltration was the most appropriate method for separating used vat and disperse dyes from pad liquors. Dye removal attained 99% for most dyes, the exception being the dispersions of red disperse dye (96.8%) and yellow vat dye (98.1%). COD and TOC values decreased in addition to reducing colour.

References

[1] Pearce CI, Lloyd JR, Guthrie JT. Dyes Pigments 2003;58:179–96.
[2] Reife A, Freeman HS. Environmental chemistry of dyes and pigments. John Wiley and Sons, Inc; 1996.
[3] Robinson T, McMullan G, Marchant R, Nigam P. Bioresour Technol 2001;77:247–55.
[4] Shore J, Colorants and auxiliaries: organic chemistry and application properties. Colorants, vol. 1. Society of Dyers and Colourists, BTTG—Shirley; 1990.
[5] Zollinger H. Color chemistry: syntheses, properties and application of organic dyes and pigments. VHC Verlagsgesellschaft mbH; 1991.
[6] Lee R. Water Wastewater 2000;141:29–32.
[7] Masschelein WJ. Unit processes in drinking water treatment. Marcel Dekker, Inc.; 1992.
[8] Kurnik J. Nekatalitska in katalitska oksidacija monoazo barvila Acid Orange. II. Doktorska disertacija. Ljubljana: Fakulteta za kemijo in kemijsko tehnologijo; 1998.
[9] Cheyran M. Ultrafiltration and microfiltration handbook. Technomic Publishing Company; 1998.
[10] Uradni list RS 35/96. Uredba o emisiji snovi pri odvajanju odpadnih vod iz objektov in naprav za proizvodnjo, predelavo in obdelavo tekstilnih vlaken. p. 2969–72.
[11] Directive 91/271/EEC on Urban Waste Water Treatment, 21.5.1991.