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Residual dyebath purification using a system of constructed wetland

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Abstract

A constructed wetland model, comprising two different substrate mixtures, was used to purify textile dyebath wastewater. Three laboratory prepared wastewaters containing three commercial dyes of different classes and chemical constitution (one vat and two reactive dyes), different chemicals (NaOH, NaCl) and auxiliaries (migration inhibitor, sequestering, defoaming and wetting agents) were employed. Purifying efficiency was verified by measuring pollution parameters, such as absorbance, pH, total organic carbon (TOC), chemical oxygen demand (COD) and electrical conductivity (EC).

It was found that the constructed wetland model reduced dye concentration by up to 70%, lowered the TOC and COD values up to 88%, electrical conductivity up to 60% and pH from 12 to 7.6.

Keywords: Constructed wetland model; Reactive dye; Vat dye; Dyebath wastewater; Purifying

1. Introduction

The textile industry consumes large volumes of pure water and produces large amounts of wastewater that contains, typically, a variety of dyes and associated chemicals. Coloured wastewater is a consequence of incomplete dye exhaustion; the presence of unnatural colours is aesthetically unpleasant and tends to be associated with contamination [1]. Textile dyes are resistant to fading upon exposure to heat, water, light and oxidizing agents, making them stable and resistant to biodegradation [2]. Government environmental legislation forces the textile industry to treat its effluent to a high standard. Currently, the common methods for textile wastewater treatment are coagulation and flocculation, oxidation, membrane separation and adsorption on activated carbon [3]. However, these methods suffer from significant disadvantages that include incomplete ion removal, high-energy requirements and generation of toxic sludge or other waste products. Hence, there is a need to find an alternative treatment method, which is efficient, simple to use, inexpensive and environmentally friendly. Constructed wetland (CW) is a treatment system (relatively new for textile wastewater treatment) that fulfils these requirements by establishing optimal physical, chemical and biological conditions that occur in natural wetland ecosystems [4].

Constructed wetlands were initially developed about 40 years ago in Europe and North America to treat domestic wastewater for small communities [5]. Today, they are also applied to treat industrial wastewater and to diffuse pollutants such as mine wastewater and highway runoff [6,7].

Constructed wetland designs include horizontal surface or subsurface flow, vertical flow and floating raft systems [7]. In subsurface flow systems, wastewater flows horizontally or vertically through the substrate, which is composed of river sand, gravel, soil, clay, peat, rock and zeolite, planted with macrophytes. The purification processes occur during contact with the surface of the substrate and the plant rhizospheres. Therefore, the most important thing in CW planning is the selection of suitable substrates, viz type and size, hydraulic

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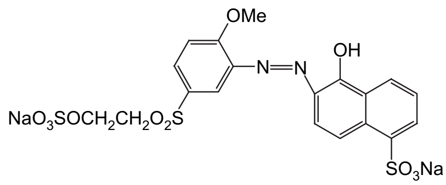
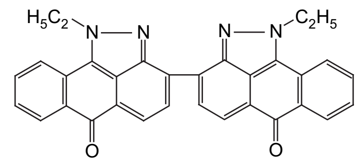
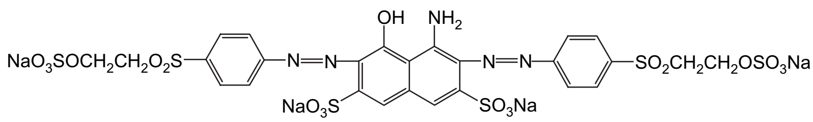


C.I. Reactive Red 22 (RR 22)



C.I. Vat Red 13 (VR 13)



C.I. Reactive Black 5 (RB 5)

Fig. 1. The chemical structure of the used dyes.

conductivity, porosity, filtration ability, sorption, ion exchange and complex formation [8]. A suitable substrate has to satisfy the following criteria:

- high affinity and capacity for target compounds;
- regeneration must be possible;
- safe and economically viable treatment/disposal of regenerate;
- tolerance for a wide range of wastewater parameters;
- usable for most dyes [9].

Constructed wetland reportedly removes a variety of pollutants from textile wastewaters, including metals (copper, zinc), suspended solids, colour, organic compounds and some toxic substances [10]. The mechanisms by which pollutants are removed from wastewater include adsorption on soil, ion exchange, filtration, chemical precipitation, uptake by plants, and aerobic/anaerobic microbiological activity. Compared to conventional treatment systems, CW has low construction and operating costs and offers an easily operated and maintained biological and physical environment [11]. A disadvantage is its relatively slow operation rate.

The aim of the work reported herein was to select an appropriate substrate combination from a range of various commercially available substrates, which are most often used in constructed wetland systems for potential use in textile dyebath wastewater purification. The efficiency of treatment was verified by measuring pollution parameters such as absorbance, pH, COD, TOC and electrical conductivity.

2. Materials and methods

2.1. Residual dyebaths

Experiments were conducted on three laboratory prepared residual dyebaths, referred to as A, B and C, containing three commercial dyes of different classes and chemical constitution, namely C.I. Reactive Red 22, C.I. Reactive Black 5 and C.I. Vat Red 13 – Fig. 1, different chemicals: NaOH, NaCl, and auxiliaries: migration inhibitor (Irgapadol MP – Ciba), sequestering agent (Alvirol AGK – Textilcolor), defoaming agent (Cibaflow PAD – Ciba) and wetting agent (Alviron VKSB – Textilcolor). Fifteen-litre dyebaths were prepared by dissolving the dyes and other additions (Table 1) in a mixture of tap and distilled water (as a means of simulating typical water, with a conductivity of 485 μS/cm). The prepared "waste" dyebath solution was kept for 24 h, and thereafter passed through the constructed wetland model. Each experiment was conducted in duplicate.

2.2. Experimental equipment and design

The trials were performed in a vertical-flow constructed wetland model (Fig. 2), made from polyethylene plates and Plexiglas, measuring 0.8 m in length, 0.3 m in width and 0.6 m in height. The constructed wetland model was placed in the atrium of the Faculty of Mechanical Engineering, Maribor, Slovenia, and, as such was exposed to all weather conditions.

The model employed PTFE-liners and was filled with two different substrate combinations, the first with three different substrates (CW without peat) up to 29 cm, and the second with four different substrates (CW with peat) up to 34 cm. The following substrates were used (from the bottom to up):

- washed gravel (particle size 8–12 mm), from a local quarry, 0.36 porosity;

Table 1
Three laboratory prepared dyebath wastewaters (15 l)

Dyebath A	Dyebath B	Dyebath C
0.5 g C.I. Reactive Red 22	0.5 g C.I. Reactive Black 5	0.5 g C.I. Vat Red 13
7.5 g Alvirol AGK	5 g Alvirol AGK	5 g Alvirol AGK
10 g Alviron VKSB	6 g Alviron VKSB	25 g Irgapadol MP
30 g NaCl	30 g NaCl	5 g Cibaflow PAD
30 ml NaOH (32.5%)	30 ml NaOH (32.5%)	

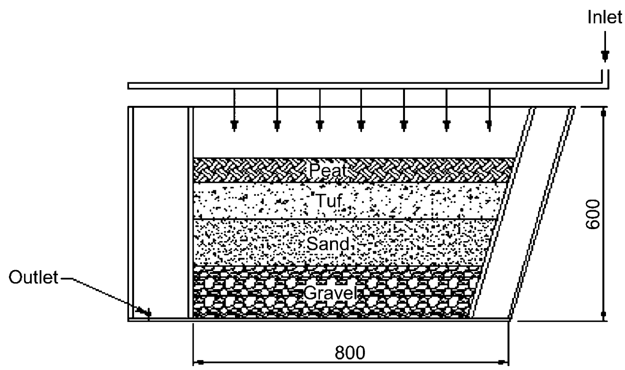


Fig. 2. A schematic representation of the constructed wetland model containing various substrates.

- washed sand (particle size 0–4 mm), from a local quarry, 0.34 porosity;
- washed natural zeolite (Tuf, particle size 9–12 mm), from a local quarry, with composition of 62.95% SiO_2, 15.92% Al_2O_3, 3.10% Fe_2O_3, 3.81% CaO, 1.31% MgO, 4.67% Na_2O, 4.67% K_2O, 0.03% SO_3, and 0.49 porosity;
- peat (pH 4.5–5).

The empty model volume was 144 l, and the filled model volume was 69.6 l (without peat) or 81.6 l (with peat).

A constant flow of residual dyebath from the vessel to the model (across its entire width) of 0.2–0.24 l/min was achieved using a perforated plastic pipe, located at the top of the model. Treatment (contact) time was 1, 2, 3, 4, 5 and 24 h. The outlet for the treated effluent was located at the bottom of the model.

2.3. Analytical methods

Six treated samples, each of 250 ml, were taken from the inflow after 1, 2, 3, 4, 5 and 24 h and were directly analysed. Parameters, standards and devices for the dyebath wastewater analyses are presented in Table 2. The hydrodynamic conditions in the pipe flow were controlled and, also, the air temperature was measured.

The absorbance of the dyebath wastewater before and after treatment was measured at the wavelength of maximum absorption for each dye. Prior to absorbance measurement, the effluents are centrifuged for 10 min at 3000 rpm to prevent turbidity.

Table 2
Parameters, standards and devices for analyses

Parameter	Standard	Device
Absorbance	SIST EN ISO 105-Z10	Carry 50 (Varian)
pH value	SIST ISO 10523	MA 235 (Mettler Toledo)
COD – chemical oxygen demand	SIST ISO 6060	
TOC – total organic carbon	SIST ISO 8245	DC-190 Analyzer (Dohrmann)
Electrical conductivity	SIST EN 27888	Multilab P5 (WTW)

The amount (percentage) of colour reduction, CR was calculated according to the following equation:

$$CR\ (\%) = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where:

A_0 – initial absorbance;
A – absorbance after treatment.

3. Results and discussion

The trials were conducted from September to November 2004 with the day temperature above 20 °C and the night temperature below 10 °C.

Table 3 summarizes only those results of absorbance measurement in the CW model which contained the substrate combination without peat, because of the colour change when peat was present (different wavelength of absorption maximum). Best results were achieved when treating dyebath B, for which the percentage colour reduction was between 53% (after 1 h) and 70% (after 24 h). Generally, minimum decolouration was achieved for dyebath A (only 2% after 1 h and up to 40% after 24 h).

Figs. 3 and 4 show the changes in COD and TOC values of three "waste" dyebaths (including reactive red, reactive black or vat red dye) before and after passage through the mixture of substrates over different contact times (1, 2, 3, 4, 5 and 24 h), separately, in both the presence and absence of peat in the CW model. It is obvious from that the initial COD and TOC values were very high; especially for dyebath C which included the

Table 3
Absorbance of three "waste" dyebaths before and after treatment (in CW without peat), and reduction of colour

Dyebath	Treatment time/h	λ/nm	A before treatment	A after treatment	Colour reduction/%
A		514	0.6378		
(C.I. Reactive Red 22)	1	512		0.6257	2
	2	512		0.5568	13
	3	512		0.4916	23
	4	512		0.4186	34
	5	510		0.3779	41
	24	510		0.3809	40
B		621	0.8044		
(C.I. Reactive Black 5)	1	617		0.3756	53
	2	610		0.3453	57
	3	606		0.3053	62
	4	600		0.2883	64
	5	600		0.2912	64
	24	591		0.2404	70
C		540	0.8805		
(C.I. Vat Red 13)	1	540		0.6234	29
	2	540		0.5828	34
	3	540		0.5699	35
	4	540		0.5201	41
	5	540		0.4941	44
	24	540		0.5057	43

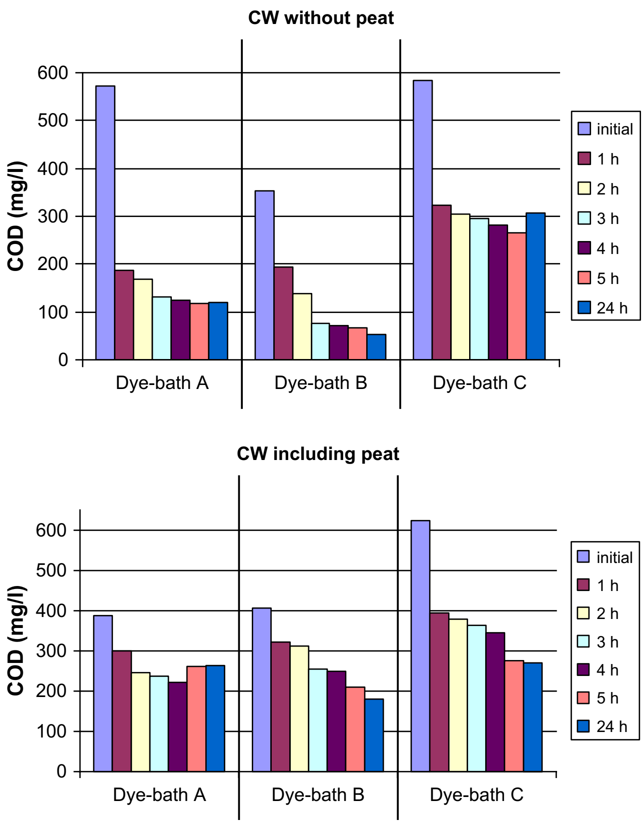


Fig. 3. COD values before and after treatment.

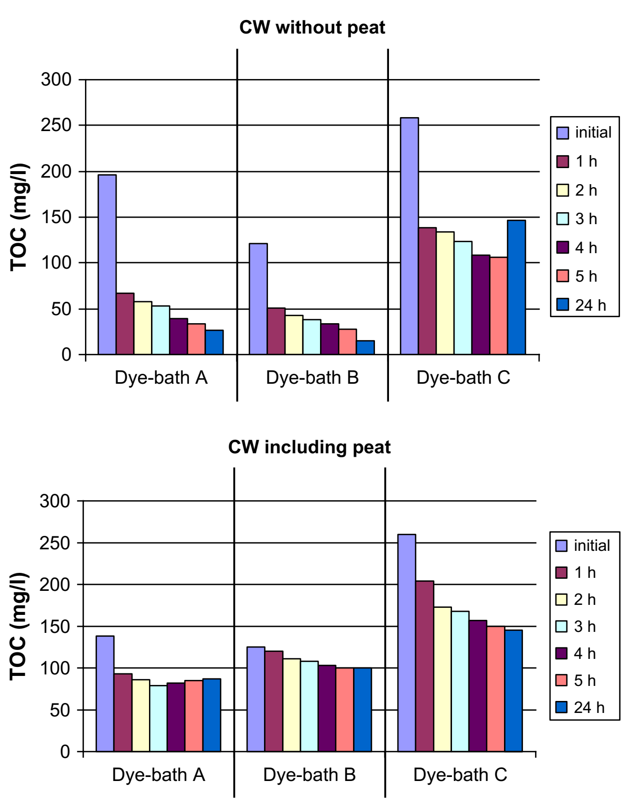


Fig. 4. TOC values before and after treatment.

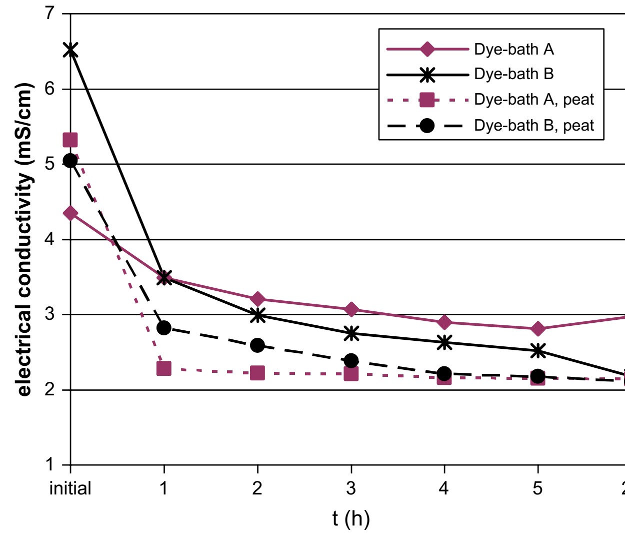


Fig. 5. Electrical conductivity before and after treatment.

red vat dye. The decrease of COD and TOC after treatment was confirmed as a result of the dye molecules' filtration and/or adsorption. The lowest COD values (maximum COD reduction – up to 88% for dyebaths A and B for an adsorption time of 24 h) were reached using the CW without peat, depending on the composition of the dyebath wastewater and treatment time. Similar results were obtained by measuring TOC values; in the CW in which peat is included, the decreases in COD and TOC values are minor, because of the organic character of the peat.

Fig. 5 shows the change in electrical conductivity of two dyebath wastewaters, A and B (which included the red reactive dye or black dye), and Fig. 6, the changes in pH of all three dyebath wastewaters before and after treatment. It is evident that both the electrical conductivity and pH decreased for all dyebaths, especially when peat was present.

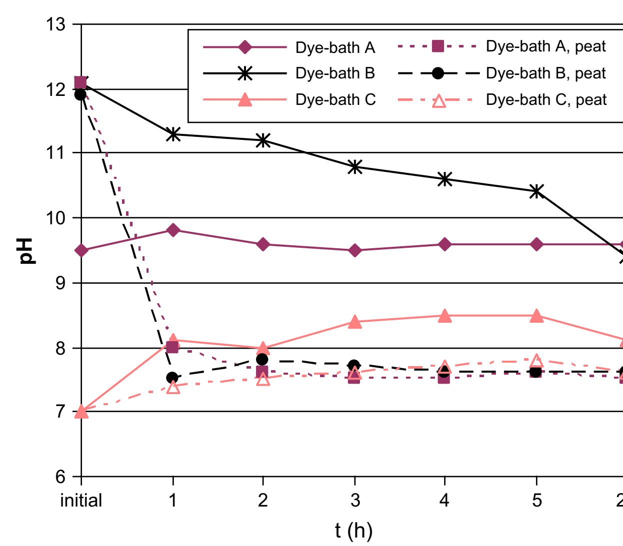


Fig. 6. pH values before and after treatment.

Electrical conductivity fell by some 60% and pH dropped from 12 to 7.6 depending on treatment time. In dyebath C, in which a red vat dye was present, the pH increased slightly (from 7 to 7.8). As peat has a pH of around 4–4.5, this probably reduced the pH values of highly alkaline dyebath wastewaters.

4. Conclusions

The results indicate that the constructed wetland model used in this study, which contains two different mixtures of substrates (CW with and without peat), had significant effects on water quality parameters. Specifically, treatment using a system of constructed wetland reduced the extent of the colour (up to 70%) present in the dyebath wastewater and appreciably lowered the electrical conductivity; it also lowered the COD, TOC and pH of all three dyebaths. The results showed that the extent of purification depends on the combination of substrate, treatment time, composition of the dyebaths and the chemical constitution of the dyestuffs. It was found that peat reduced both pH and electrical conductivity, but increased both COD and TOC; in addition, all parameters measured decreased with increasing time of treatment.

Further studies are focused on the dyebath wastewater purifying efficiency of various macrophytes (which is also an integral part of COD and TOC reduction) planted in a constructed wetland model, containing these two substrates mixtures.

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