Desalination and Water Treatment
www.deswater.com

33 (2011) 147–155
September

doi: 10.5004/dwt.2011.2623

Colour and TOC reduction using biofilter packed with natural zeolite for the treatment of textile wastewaters

Alenka Ojstrsek*, Darinka Fakin

University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia
Tel. +386 (2) 220 7935; Fax +386 (2) 220 7990; email: alenka.ojstrsek@uni-mb.si, darinka.fakin@ui-mb.si

Received 22 January 2010; Accepted in revised form 15 November 2010

ABSTRACT

The main contribution of the presented research is to examine the potential of natural zeolite for colour and TOC reduction when packed in a fixed-bed system, considering various parameters such as wastewater characteristics, properties of natural zeolite, loading rate and hydraulic retention time. Firstly, the diverse chemical aspects of tuff were determined using scanning electron microscopy and infrared spectroscopy with the intention of establishing the impact of tuff surface and chemical composition on its adsorption properties and decolouration possibilities. Secondly, a series of dynamic experiments were conducted on laboratory-prepared wastewaters combining chemically differ reactive dyestuffs, auxiliaries and chemicals in order to investigate biofilter's treatment efficiency. Assessment of the biofilter's performance was verified by monitoring absorbance and total organic carbon in initial and treated wastewaters. The results showed that when increasing the load from 22 to 37 mg/m^{3}d (dyes) and from 84 to 154 mg/m^{3}d (organic), colour removal efficiency decreased from 57 to 20% (RB5), from 80 to 46% (RB19) and from 72 to 55% (RR22), and TOC removal efficiency from 75 to 31%. And, when increasing the hydraulic retention time from 11 up to 17 h, the decolouration increased from 20 to 57% (RB5), from 46 to 80% (RB19) and from 16 to 57% (RR22), and TOC removal efficiency from 30 to 75%.

Keywords: Biofilter; Zeolitic tuff; Synthetic textile wastewaters; Colour reduction; TOC reduction

1. Introduction

Textile dyeing processes are among the most polluting industrial processes because they produce enormous amounts of coloured wastewaters. This is a consequence of incomplete dye exhaustion on to the fibre and dyeing procedures, which are heavily polluted with various dyestuffs, auxiliaries, and chemicals [1]. The reactive dyeing of cotton fabrics takes place under highly alkaline conditions at pH 11–12, therefore, two types of reactions are possible, i.e. covalent dye-fibres bonding and alkaline hydrolysis of the dye, originating the non-reactive oxi-dye form that cannot be used further, and passes into the wastewater [2]. A literature review regarding dye-bath wastewater treatments reveals the consideration of different approaches to handling such effluents, which include adsorption, advanced oxidation processes, membrane separation and biological treatment [1,3–8].

The major pollution of water and waterside sources on the one hand, and the constructional and high cost of improving of wastewaters' sanitary conditions on the other hand, have stimulated research into the development of innovative, cheaper, and environmentally-friendly solutions such as bioremediation. Bioengineering

* Corresponding author.

Presented at the 2nd International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE), Mykonos, Greece, June 21–26, 2009.

treatment methods include ex-situ effluent treatment in constructionally-different biofilters, rotating biological contactors, reactors with fluidized beds, membrane bioreactors, activate sludge systems, etc. [9].

Systems with fixed biomass have been successfully used in numerous wastewater treatment processes, mainly as supplementary treatment for removal of organic pollutants [9], nitrification and denitrification [10,11], reduction of heavy metals [12], phosphates [13], and rarely for industrial wastewaters treatment [14]. Biofilters are divided according to the water inflow on biofilters with inflow at the top or at the bottom. Fluidized-bed biofilters comprise biomass with an exceedingly high degree of activity; therefore, biofilter treatment efficiency per its volume is a very high [15]. During the early stages of treatment when the biofilm is thin, larger insoluble pollutants particles may be filtered, and absorbed on the surface of the packing material. After long-term function and suitable conditions, microorganisms could grow on the surface producing a corresponding thickening of the biofilm required for biological conversion of pollutants in less harmful products (CO_2, H_2O, different inorganic substances, etc.).

In fixed-bed biofilters the microbial biomass is static — immobilized to the bedding (support) material, while the treated fluid is mobile — it flows through the biofilter. The selection of a bedding material depends on many factors including resistance to microbial degradation, mechanical strength, surface characteristics, the cost of the material, and the type of wastewater. Various bedding materials were used as biomass attached media, i.e. special biomass supports that are chemically-inert, (different plastic materials [16,11], ceramics, glass [17], stainless steel [18], etc.) or natural materials that are capable of chemically-bonding with diverse pollutants in wastewaters (soil and clay materials [12–14,19,20], waste agricultural products [21], etc.).

Natural tetrosilicate minerals are very effective adsorbents for organic contaminants such as dyestuffs and auxiliaries, due to their high surface area and molecule sieve structure [20]. The three-dimensional crystal structure of tuff with interior channels, which embody some cations and interlayer water, allows penetration of organic and inorganic ions together with solutes into the structure, thus inducing adsorptive properties and ion exchange capability. Moreover, numerous populations of microorganisms immobilized in a biofilm can colonize the material's surface that could significantly accelerate the organic pollutants' elimination during wastewater treatment by means of anaerobic/aerobic decomposition and transformation depending on molecules size and charge, toxicity, wastewater pH, salt content and also on system parameters (retention time, type and amount of support material, flow velocity, etc.). In the first stage of fixed-bed reactor performance the aerobic microorganisms in the upper layers are growing, and afterwards, only under appropriate conditions, i.e. temperature, oxygen lack, carbon and nitrogen content, the anaerobic populations of microorganisms are originating in the inferior layers [22]. The cell-wall of microorganisms essentially consisting of various organic compounds such as cistin, lipids, amino acids and other cellular components could provide a passive uptake of reactive dyes in a manner of surface adsorption, ion exchange, complex formation, and micro-precipitation [23].

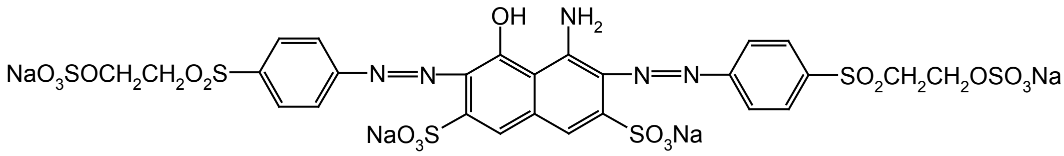
Hence, the aim of this study is to focus attention on the treatment efficiency of a fixed-bed system with zeolite tuff as a support media for the treatment of coloured textile wastewaters particularly from cotton dye-houses, regarding different loading rate and retention time. Emphasis was given to the impact of tuff chemical composition and surface structure on pollution parameters' reduction, without the addition of any microorganisms or enzymes in the system.

2. Materials and methods

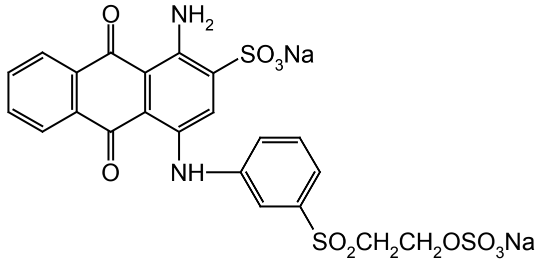
2.1. Wastewater composition

A series of dynamic trials were conducted on three synthetically-prepared wastewaters with different dyestuffs. Synthetic wastewaters were prepared on the basis of recipes for reactive cotton dyeing, diluted as much as a real effluent that came from collection reservoir of a textile dye-house. The initial dye-baths' wastewaters contained 0.03 g/L of reactive vinylsulphone dye (C.I. Reactive Black 5 or C.I. Reactive Blue 19 or C.I. Reactive Red 22), 0.3 g/L of Alvirol AGK (Textilcolor), 0.3 g/L of Cibaflow PAD (Ciba), 2 g/L of NaCl and NaOH for the regulation of the wastewater's salinity and alkalinity (pH 9–10). Commercial names of used dyes, their colour indexes and chemical constitutions are gathered in Fig. 1. Alvirol AGK is a sequestering agent for alkaline earth and heavy metal ions removal by complex formation during dyeing, and is a chemical mixture of polyacrylates and oxycarbonic acids. Cibaflow PAD is an anionic wetting and de-aerating agent, and is chemically based on an alkylphosphate and fatty alcohol etoxylate. All chemicals used for trials were of analytical grade: sodium hydroxide (NaOH) was purchased from Fluka and sodium chloride (NaCl) from Merck.

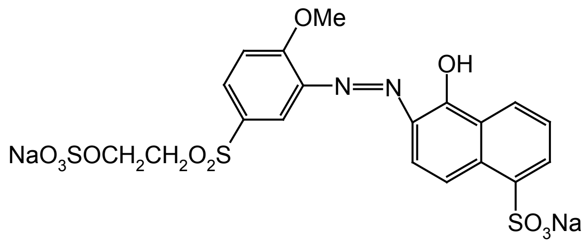
Fifteen litres of synthetic wastewater was prepared for each experimental study by dissolving individual dye, above mentioned chemicals and auxiliaries in a mixture of tap and distilled water in the ratio 2:3, with electrical conductivity of 374 μS/cm, thus simulating technologically water in a textile plant. The prepared wastewater was maintained in a plastic tank for 48 h at room temperature and without aeration to attain alkaline hydrolysis of the dye as in real textile effluents. Thereafter, it flowed with different velocity through the experimental set-up in



Bezaktiv Black V-B (C.I. Reactive Black 5 - RB5)



Bezaktiv Brilliant Blue V-R (C.I. Reactive Blue 19 - RB19)



Bezaktiv Red V-BN (C.I. Reactive Red 22 - RR22)

Fig. 1. Commercial names, C.I. generic names and chemical structures of applied dyestuffs.

order to establish the impact of loading rate and hydraulic retention time on colour and TOC reduction.

2.2. Experimental set-up

A continuous-flow laboratory-scale experimental set-up consists of a fixed-bed biofilter with an outlet pipe, a plastic reservoir for the wastewater and a settler for the excess biomass. Biofilter is a cylindrical polypropylene column with a diameter of 6 cm that provides an empty volume of 1 L (Fig. 2), and there was no gas collection system applied. The column was packed with rinsed natural zeolite, hereafter referred as a tuff, received from a quarry in Slovenia, with particle size of 4–12 mm and bed-porosity of 0.49. A bed height was 28.5 cm and filled weight 784 g.

Vertical wastewater flow (from 26 up to 37 mL/h, an average of 31.5 mL/h) from the wastewater reservoir downwards through the biofilter was achieved by a plastic pipe with a valve. Every experimental study was carried-out continuously for 19 days to reach stable conditions, and the samples for analyses were collected from the treated-water tank twice a day, at 8 a.m. and 4 p.m, with the exception of Saturdays and Sundays, and afterwards directly analysed. All experiments were performed at an ambient temperature of 22±2°C. Biofilter was operated at dye loading rates between 22 and 37 mg/m^{3}d and organic loading rates between 84 and 154 mg/m^{3}d, while the hydraulic retention time was between 11 and 17 h, to observe the effect of operational parameters on treatment efficiency.

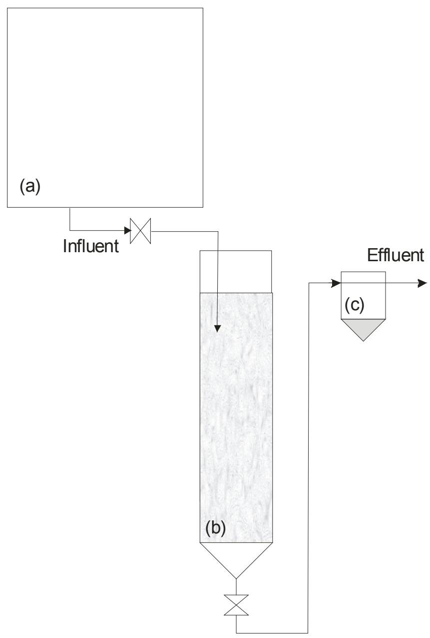


Fig. 2. A schematic flow sheet of column set-up: (a) reservoir for wastewater, (b) biofilter with tuff, (c) settler.

2.3. Analytical procedures

Diverse chemical aspects of natural zeolite were determined using infrared spectroscopy and scanning electron microscopy with the intention of ascertaining the impact of tuff chemical composition and surface structure, respectively, on its adsorption properties and decolouration possibilities. The chemical composition of the surface was examined by means of a spectrophotometer FT-IR System Spectrum GX (Perkin Elmer), in the mid-infrared region with wavenumbers ranging from 4000 to 650 cm^{-1}. The functional groups were determined regarding to the typical bond vibrations within atoms and molecules [24]. The SEM-image was taken on a scanning electron microscope Zeiss Gemini Supra 35 VP (Zeiss).

Assessment of the biofilter's performance was verified by means of measuring the absorbance (A) and total organic carbon (TOC) in the influent and effluent. Absorbance measurement of the initial and treated-samples was monitored at a wavelength of individual dye' absorption maximum, i.e. for RB5 at 600 nm, for RB19 at 595 nm and for RR22 at 517 nm, using a Cary 50 (Varian) UV-Vis spectrophotometer with a measuring probe of 10 mm optical length, according to the standard EN ISO 105-Z10. For the entireness information of colour changes, the completely spectrum (250–700 nm) of the initial and outflow water after the 19th day of dynamic experiment were scanned additionally. Before the absorbance measurement, the effluents were centrifuged for 10 min at 3000 rpm in polypropylene microcentrifuge tubes preventing the turbidity. The pH of synthetic wastewaters was measured regarding to the ISO 10523 standard using a MA 235 pH/ion Analyzer (Mettler Toledo). Total organic carbon (TOC) was measured by means of a DC-190 Analyzer (Dohrmann), with accordance to the ISO 8245 standard. The hydrodynamic conditions in the pipe-flow were constantly controlled, and the volume of flowed/treated wastewater was simultaneously measured.

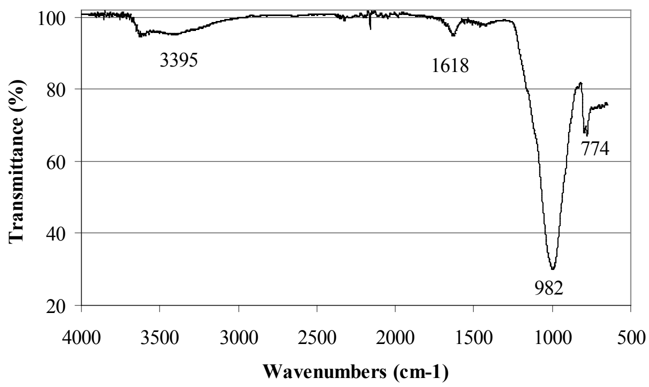


Fig. 3. IR transmittance spectrum of tuff.

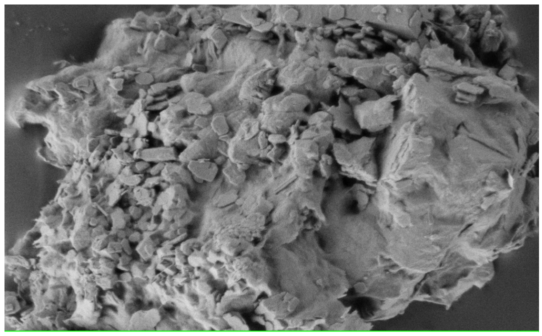


Fig. 4. Scanning electron micrographs of tuff surface, enlarged 35 000 times.

3. Results and discussion

3.1. Analysis of zeolitic tuff

The objective of this work was to assess the effectiveness of biofilter with attached biomass for the treatment of dye-rich textile wastewaters with special focus on colour and organic pollutants reduction. Tuff was selected as a support material because of its high porosity, easy accessibility and low-cost. Two analytical techniques were used in order to provide qualitative information about tuff chemical composition and its surface structure that could impact on adsorption, filtration, and microorganisms' growth and, consecutively, on biodegradation of the applied dyestuffs and auxiliaries in synthetically prepared wastewaters. The result of IR chemical analysis is shown in Fig. 3 and the magnification of tuff surface under the scanning electron microscopy in Fig. 4.

The natural zeolites have diverse capacity of ionic exchange and adsorption ability owing to their specific skeletal structure and chemical composition that are important information when various pollutant removals from effluent were carried-out. Within the IR spectrum, the assignment of characteristic band-positions can be a basis for the identification of materials and their structures [25] that could influence on the physical or even chemical attractions between dyes and biomass support media in a system.

From the analytical data of the tuff elemental composition curve (Fig. 3), it can be seen that the intensive bands occur in the area of low frequency at a wavenumber of 982 cm^{-1} correspond to the stretching vibrations of Si–O(Si) and Al–O(H) functional groups. Weak-bands within the range of 750–780 cm^{-1} can result from the vibrations of four-member rings. The bands at 3395 cm^{-1} and 1618 cm^{-1} are attributed to vibrations of O–H and H–O(H) of the water, due to absorbed moisture. In regard to the results obtained by examination of the vibrational spectra (IR and Raman) of 25 different natural zeolites scanned by Mozgawa [25], the selected tuff is a mixture of clay minerals such as Clinoptilolite, Heulandite and Mordenite.

The SEM image on Fig. 4 clearly shows a tuff-grained 3-D surface with large surface area to volume ratio that could be efficient medium for microorganisms' growth. From the results collected by spectrophotometry and TOC measurements (Figs. 5–7), it is also concluded that used dyestuffs, as well as auxiliaries, could be easily adsorbed on such a rough-structured surface; although, adsorption of negatively charged vinylsulphone reactive dyes can be hindered by the negatively charged tuff surface [19]. Nevertheless, extensive investigations carried out on adsorption of anionic dyes revealed that the extent of dye uptake was strongly influenced by the wastewater composition, predominantly, by the concentration and nature of the electrolyte ionic species added to the dye-bath [26]. Addition of salt in wastewaters lowers the surface strength on a boundary layer and, thus, improves dye sorption as dye solubility decreased [3]. Ultimately, on account of low velocity flow and long retention times applied in the presented research, various populations of microorganisms could colonize the tuff surface providing a passive uptake of reactive dyes and auxiliaries in a manner of surface adsorption, ion exchange, complex formation, and micro-precipitation.

3.2. Treatment efficiency

Biofilter filled with tuff as a biomass support media was operated continuously at different loading rates and hydraulic retention times. Its performance was established by monitoring the absorbance and TOC, and the obtained results are presented in Figs. 5–7. Experiments were conducted on three synthetic wastewaters combining an individual dye, two auxiliaries, NaCl and NaOH. In order to provide maximal treatment efficiency, the optimum conditions, i.e. velocity flow, retention time, and trial duration were examined before starting the experiments. It was found that superior dye-bath wastewaters' adsorption and decolouration/biodegradation took place when the velocity flow was approximately 30 mL/h, the retention time between 12 and 14 h and the trial duration 16 days minimum. The system was operated without backwashing; no clogging with excessive biomass was observed.

Fig. 5 displays the observed changes in absorbance after an acclimatization period of 11–14 days, attaining colour reduction of 57% (RB5), 51% (RR22) and 44% (RB19) on the last day of presented experimental study. Before the treatment processes started, the initial absorbances were determined in three synthetic wastewaters different in applied dyestuffs, i.e. 0.9985 (RB5), 0.7748 (RR22) and 0.4011 (RB19), respectively. During the first few days of the trials, absorbances were exceedingly low, owing to the rinse water remaining in the columns, but thereafter absorbances increased and stabilized at certain values, depending on the used dye. In spite of best filtration/adsorption of reactive antraquinone dye (RB19) on tuff between day 4th and 15th of the treatment process (reduction of colour was from 66 up to 80%) in comparison to the azo dyestuffs (RB5 and RR22), absorbance in treated-wastewater increased after 15th day and, hence, decolouration decreased (down to 44%). This could be due to the saturation of tuff surface and lower rate of dyestuff degradations under anaerobic conditions as compared to azo dyes that are also reported by Lee and Pavlostathis [27].

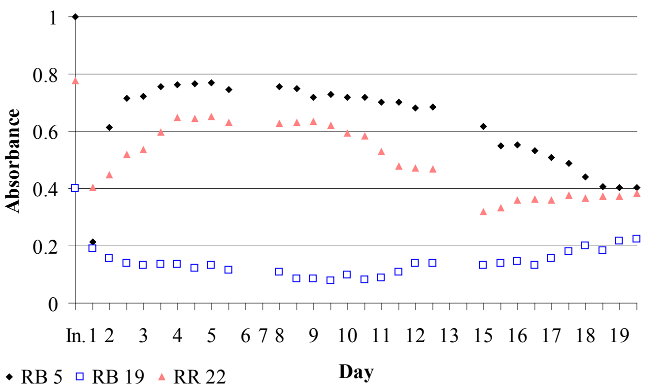


Fig. 5. Absorbance of initial and treated wastewaters at 600 nm (RB5), at 595 nm (RB19) and at 517 nm (RR22) during the biofiltration trials.

For better understanding the mechanisms that are responsible for colour reduction and for qualitative evaluation of tuff efficiency in the fixed-bed system, a complete UV/Vis spectra (from 270 nm to 700 nm) of the wastewaters' absorbances were scanned in both the initial and treated samples after 19th days of the dynamic trial period, and the results are presented in Fig. 6.

When wastewater with applied RB5 dye was treated, observable colour-change appeared between the 14th and 19th days, resulting in a hipsochromic shift of the RB5 characteristic absorption band within the visible spectrum from 600 nm to 564 nm (Fig. 6 – upper left) and, thereby, the colour of the treated-samples changed from dark blue, over reddish-blue to bright violet. Filtration and adsorption played a major part in colour reduction until the 14th day, but after that day absorbance discernibly decreased from 0.74 to 0.42, which entailed the biggest decolouration in comparison to the other dynamic experiments. RB5 have two peaks in UV region, i.e. an explicit absorbance maximum at a wavelength of 310 nm and a minor at 392 nm, which were shifted to lower wavelengths, 340 and 265 nm. It is generally believed that reactive dyes hardly decolourize under aerobic conditions concerning their high-solubility in aqueous medium whilst, just the opposite, systems without oxygen are more efficient in colour reduction. It is also well-documented that azo dyes readily reductive cleave via four-electron reduction at azo linkage under anaerobic conditions, thus produce colourless aromatic amines that are known to be toxic and potentially carcinogenic, and most of them can be aerobically biodegraded [1,4,5]. On account of the specific conditions employed in the present study (low velocity flow between 26 and 37 mL/h and long retention times of 11–15 h), we assume that anaerobic or anoxic conditions arose in the biofilter inferior layer, thus resulting in a decaying of the chromophore in the dye molecule and, consequently, in a colour change. This presumption was confirmed by complete decolourisation of treated-wastewater with RB5 when the retention time

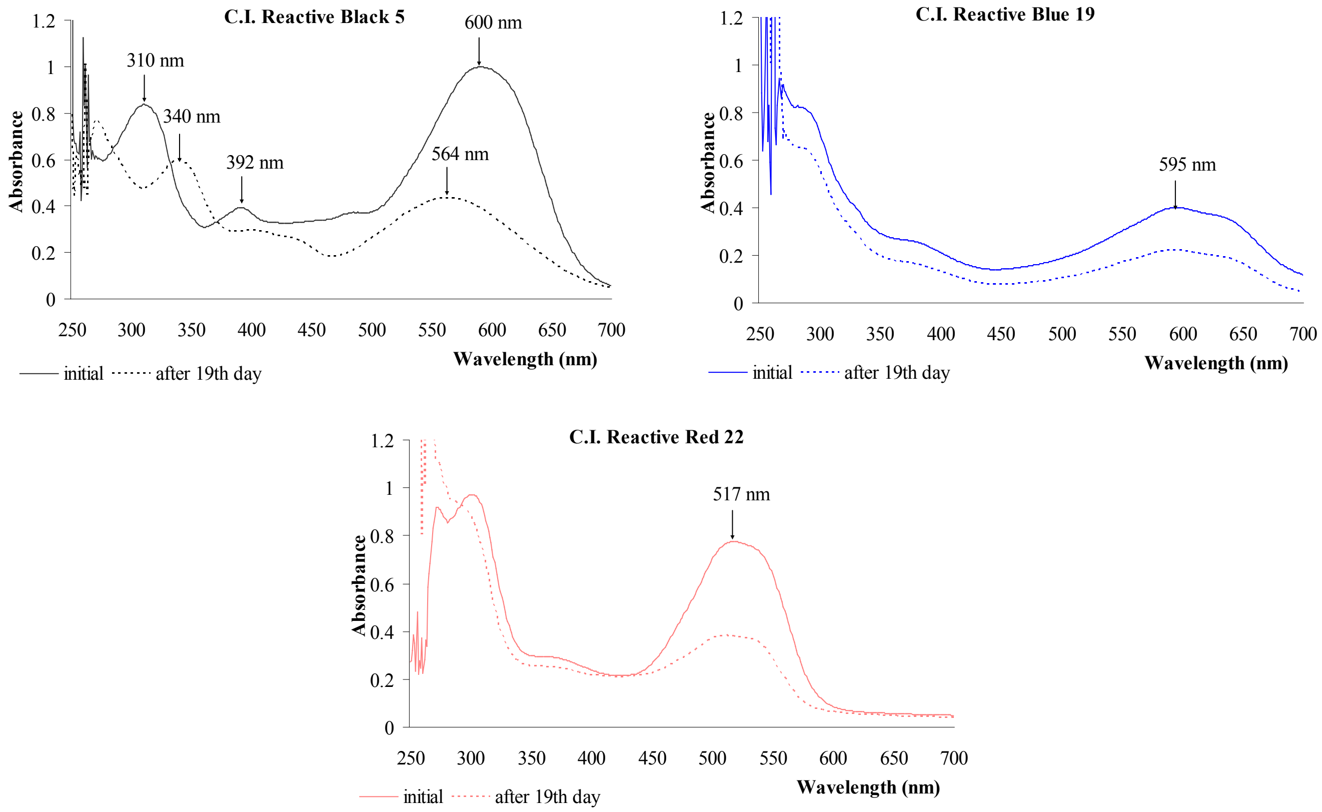


Fig. 6. UV/Vis spectra of initial and treated wastewater after 19th days included RB5 (upper left), RB19 (upper right) and RR22 (lower).

in biofilter was extended to by 5 days. Identification of the final products, intermediates and their toxicity are still in progress.

The same results as discussed above were noticed when a trial with wastewater containing RR22 was conducted (Fig. 6 – lower). During the 19-day experiment a change in colour was also manifested, even slightly earlier than the previous trial, i.e. between the 12th and 15th days, but it was not as obvious. Absorbance substantially decreased from 0.64 to 0.47, and the maximum absorption wavelength changed from 517 nm to 507 nm causing a reddish-yellow colour of final sample.

On the contrary, when we treated wastewater with blue anthraquinone dye (RB19) the absorbance was 0.223 after the 19th day (Fig. 6 – upper right), maximum absorption remained invariant at 595 nm, and colour change was not present.

It is obvious from Fig. 7 that the initial TOC values measured in synthetically wastewaters are very high, from 111 up to 139 mg/L. The lowest TOC values during the entire trial period and the best TOC reduction on the last day of the research (60%) were detected in wastewater containing azo RR22 dye, followed by TOC reduction in azo RB5 dye-bath wastewater (42%). In wastewater with applied anthraquinone RB19 dye, TOC values decreased

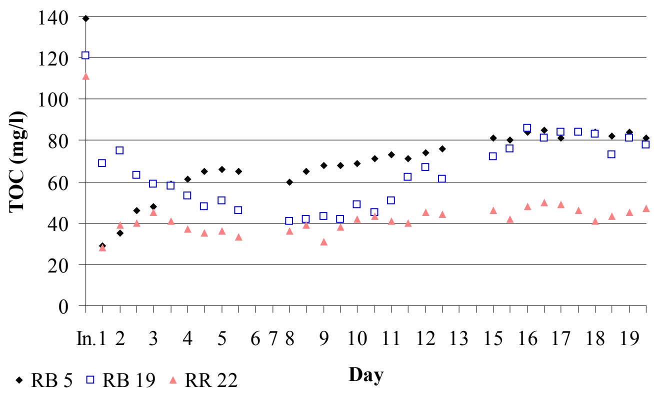


Fig. 7. TOC of initial and treated wastewaters during the biofiltration trials.

until the 9th day, and afterwards increased, as TOC in the dye-bath containing RB5. The main source of carbon in the synthetic dye-bath wastewaters was two auxiliaries contributing to the high TOC values (TOC of used dyes in concentration of 30 mg/L were between 6 and 11.6 mg/L). In the light of this fact, TOC reduction was verified as a result of preferable auxiliary molecules' filtration, adsorption, and biodegradation. Biodegradation of selected auxiliaries involved ultimate mineralization of both the parent auxiliary and its eventual originated intermediates, and was accomplished under aerobic conditions in preliminary experiments using the Zahn-Wellens test [28], by monitoring the reduction of total organic carbon (data not shown). The gained results varied from 40.2% up to 77.5%, depending on the auxiliaries' concentration, active mud dosage, and performance time [20].

The effects of dye loading rates and organic loading rates (left diagrams), and hydraulic retention times (right diagrams), respectively, on the colour and TOC removal efficiency are shown in Figs. 8–10.

In the loading rate ranged from 22 up to 37 mg/m^{3}d (dyes) and from 84 up to 154 mg/m^{3}d (organic), treatment efficiency decreased with increasing the load (Figs. 8–10) resulting in a decrease of colour removal efficiency from

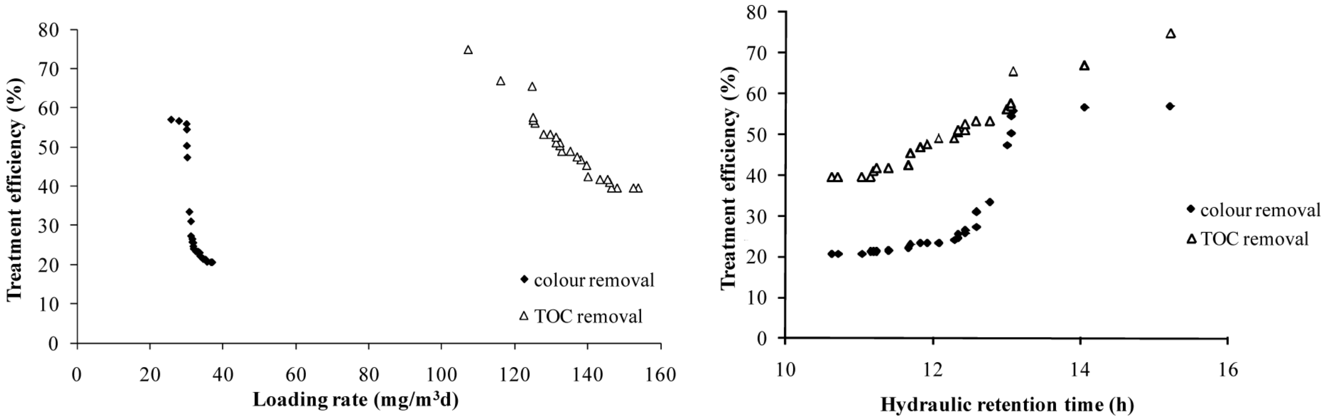


Fig. 8. Treatment efficiency of RB5 wastewater regarding loading rate and retention time.

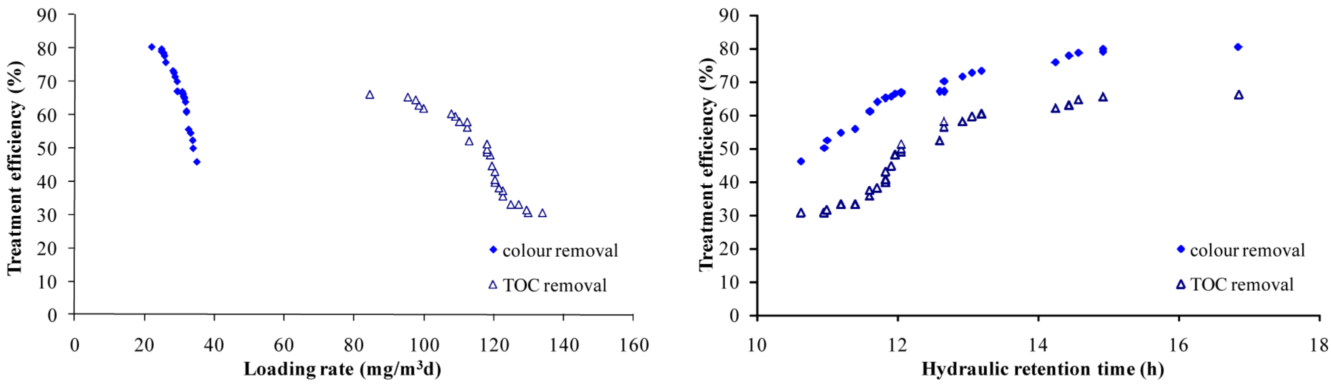


Fig. 9. Treatment efficiency of RB19 wastewater regarding loading rate and retention time.

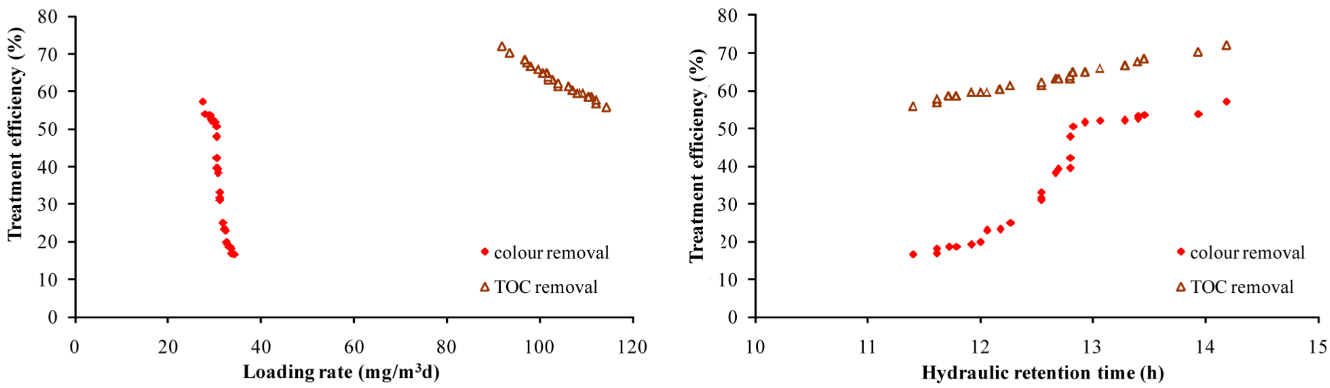


Fig. 10. Treatment efficiency of RR22 wastewater regarding loading rate and retention time.

57 to 20% (RB5), from 80 to 46% (RB19) and from 72 to 55% (RR22), and TOC removal efficiency from 75 to 31%. Low colour and TOC removal efficiency obtained at high loading rates can be explained by application of shock loading rates before the biofilter reached steady state conditions.

On the other hand, with increasing the hydraulic retention time from 11 up to 17 h, the decolouration increased from 20 up to 57% (RB5), from 46 up to 80% (RB19) and from 16 up to 57% (RR22). The main increase in efficiency was obtained when the hydraulic retention time increased from 12 to 13 h. The corresponding effluent dyes concentrations at these two hydraulic retention times were 26.2 mg/L and 14.9 mg/L (RB5), 11.6 mg/L and 9 mg/L (RB19) and 27.2 mg/L and 16.1 mg/L (RR22), respectively. High colour removal could be attributed to the cleavage of azo bond of RB5 and RR22 dyes under anaerobic conditions, and rather worse reductive transformation of the antraquinone nucleus of RB19. The effect of hydraulic retention time on TOC removal performance of the biofilter was also investigated and likewise mentioned above for colour removal, TOC removal efficiency increased equably from 30 up to 75% when prolonging the hydraulic retention time from 11 to 17 h. Increases in hydraulic retention time provide enough time for partial mineralization of auxiliaries and its eventual originated intermediates and, therefore, lowered TOC values in treated-wastewaters.

4. Conclusions

Textile dye-bath wastewater was treated utilizing a laboratory set-up biofilter filled with tuff as a biomass support media without the addition of any microorganisms or enzymes in the system. Treatment efficiency was verified by monitoring the pollution parameters, i.e. absorbance and TOC. Tuff analysis was performed for qualitative information, and the amount of flowed wastewater was measured. Overall, the laboratory trials and analyses demonstrate that the system with attached growth biomass had a significant effect on water quality parameters, i.e. reduce the colour by up to 80% and TOC by up to 75% after an acclimatization period of 11–14 days, depending on the chemical constitution of applied dyestuffs and operational parameters such as trial duration, the hydraulic retention time, loading rate, etc. Different retention times, which depend on velocity flow, have a significant influence on treatment efficiency. The longer the time, the greater the effects of wastewater treatment and the pollution parameters are lower. Particle size, porosity and surface texture of bedding material also played an important role in dye biodegradation because of solid adsorption capacity, ion exchange, and even microorganisms growth abilities.

The presented tuff fixed-bed system was confirmed as suitable for small volumes of textile wastewater, and also for tertiary treatment. Further work, combining the attached biomass biofilter with a properly-selected chemical treatment, is needed to improve wastewater treatment efficiency, and also to lower the retention time.

Symbols

A — Absorbance
C.I. — Colour index
FT — Fourier transform
in. — Initial
IR — Infra red
RB19 — Reactive Blue 19
RB5 — Reactive Black 5
RR22 — Reactive Red 22
SEM — Scanning electron microscopy
TOC — Total organic carbon (mg/L)
UV — Ultraviolet
Vis — Visible

References

[1] C.I. Pearce, J.R. Lloyd and J.T. Guthrie, The removal of colour from textile wastewater using whole bacterial cells, a review, Dyes Pigments, 58 (2003) 179–196.

[2] M. Gorenšek, Dye-bond stabilities of some reactive dyes on cotton, Dyes Pigments, 40 (1999) 225–233.

[3] S. Karcher, A. Kornmüller and M. Jekel, Screening of commercial sorbents for the removal of reactive dyes, Dyes Pigments, 5 (2001) 111–125.

[4] S. Şen and G.N. Demirer, Anaerobic treatment of real textile wastewater with a fluidized bedreactor, Wat. Res., 37 (2003) 1868–1878.

[5] J.A. Libra, M. Borchert, L. Vigelahn and T. Storm, Two stage biological treatment of a diazo reactive textile dye and the fate of the dye metabolites, Chemosphere, 56 (2004) 167–180.

[6] E. Khelifi, H. Bouallagui, Y. Tauhami, J.J. Gordon and M. Hamdi, Enhancement of textile wastewater decolourization and biodegradation by isolated bacterial and fungal, Desal. Wat. Treat., 2 (2009) 310–316.

[7] V. Golob and A. Ojstršek, Removal of vat and disperse dyes from residual pad liquors, Dyes Pigments, 64 (2005) 57–61.

[8] K. Turhan and Z. Turgut, Treatment and degradability of direct dyes in textile wastewater by ozonation: A laboratory investigation, Desal. Wat. Treat., 11 (2009) 184–191.

[9] V. L. Barbosa, R. Tandlich and J. E. Burgess, Bioremediation of trace organic compounds found in precious metals refineries' wastewaters: A review of potential options, Chemosphere, 68 (2007) 1195–1203.

[10] S. Villaverde, F. Fdz-Polanco and P. A. Garcia, Nitrifying biofilm acclimation to free ammonia in submerged biofilters. Start up influence, Wat. Res., 34 (2000) 602–610.

[11] J. Vrtovšek and M. Roš, Denitrification of groundwater in the biofilm reactor with a specific biomass support material, Acta Chim. Slovenica, 53 (2006) 396–400.

[12] L. Ringqvist, A. Holmgren and I. Öborn, Poorly humidified peat as an adsorbent for metals wastewater, Wat. Res., 36 (2002) 2394–2404.

[13] K. Sakadevan and H. J. Bavor, Phosphate adsorption characteristic of soils, slags and zeolite to be used as substrates in constructed wetland systems, Wat. Res., 32 (1998) 393–399.

[14] T. Robinson, G. McMullan, R. Marchant and P. Nigam, Remediation of dyes in textile effluent: a critical review on current

treatment technologies with a proposed alternative, Bioresource Technol., 77 (2001) 247–255.

[15] J.S. Devinny and J. Ramesh, A phenomenological review of biofilter models, Chem. Eng. J., 113 (2005) 187–196.

[16] F. Gebara, Activated sludge biofilm wastewater treatment system, Wat. Res., 33 (1999) 230–238.

[17] L. Gill, C. Doran, D. Misstear and B. Sheahan, The use of recycled glass as a filter media for on-site wastewater treatment, Desal. Wat. Treat., 4 (2009) 198–205.

[18] K. Kapdan, M. Tekol and F. Sengul, Decolorization of simulated textile wastewater in an anaerobic-aerobic system, Process Biochem., 38 (2003) 1031–1037.

[19] A. Bousher, X. Shen and R.G.J. Edyvean, Removal of coloured organic matter by adsorption onto low-cost waste materials, Wat. Res., 31 (1997) 2084–2092.

[20] A. Ojstršek, D. Fakin and D. Vrhovšek, Residual dyebath purification using a system of constructed wetland, Dyes Pigments, 74 (2007) 503–507.

[21] A. Ojstršek, Applications of different biomass supports for a dye-bath wastewater treatment, Doctoral rhesis, University of Maribor, Faculty of Mechanical Engineering, Maribor, 2007.

[22] S. Wijeyekoon, T. Mino, H. Satoh and T. Matsuo, Effects of substrate loading rate on biofilm structure, Wat. Res., 38 (2004) 2479–2488.

[23] Z. Aksu, Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modeling, Biochem. Eng. J., 7 (2001) 79–84.

[24] D.A. Skoog, F.J. Holler and T.A. Nieman, Principles of Instrumental Analysis, 5th ed., Harcourt Brace & Co, Orlando, 1998.

[25] W. Mozgawa, The relation between structure and vibrational spectra of natural zeolites, J. Molec. Struct., 596 (2001) 129–137.

[26] M. Alkan, S. Çelikçapa, Ö. Demirbaş and M. Doğan, Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite, Dyes Pigments, 65 (2005) 251–259.

[27] Y.H. Lee and S.G. Pavlostathis, Decolorization and toxicity of reactive anthraquinone textile dyes under methanogenic conditions, Wat. Res., 38 (2004) 1838–1852.

[28] EN 29888, Zahn-Wellens Method for Aerobic Biodegradation Determination.