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Shallow pond systems planted with *Lemna minor* treating azo dyes

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ABSTRACT

A higher demand on textile materials has resulted in an increase of the number of textile factories particularly in the developing world, which consequently negatively effects the environment due to their contaminated effluents. Textile effluents are highly coloured and mixed with different chemicals and pollutants. Shallow pond systems are a promising, cheap and effective technique for the treatment of contaminated wastewater. The aim of this study is to assess the performance of pond systems vegetated by *Lemna minor* L. (duckweed) for textile dye removal under controlled laboratory conditions. The key objectives of this study are to assess the influence of design variables on water quality parameters, the dye and chemical oxygen demand (COD) removal of dyes, and the effect of dye accumulation as a function of the relative growth rate of *L. minor*. Findings indicate that the simulated shallow pond system (as a polishing step) is able to remove only Basic Red 46 (BR46) in low concentrations, and ponds containing *L. minor* significantly ($p < 0.05$) outperformed algae-dominated ponds and control ponds. The simple chemical structure, absence of sulpho-group and small molecular weight associated with neutral pH values enhanced the capacity of the uptake of BR46 molecules. Furthermore, the total dissolved solid concentrations were within the threshold set for discharge to the aquatic environment.

1. Introduction

1.1. Background

The industrial revolution and rapid population growth have increased the demand for textile materials, which has consequently increased the number of textile industries and their effluents (Khataee et al., 2012). Synthetic dyes are used to add colour to fibres (Sivakumar et al., 2013). However, in this process, a large volume of water is used, which as a result, discharges considerable amounts of dyeing effluent as waste into receiving waters.

In commercial terms, azo dyes are seen as the largest group of synthetic dyes (Pandey et al., 2007), and it is estimated that between 60% and 70% of the dyes applied in the textile industry are azo compounds. This group of dyes is distinguished by the presence of one or more double bonds between nitrogen atoms (Pandey et al., 2007; Cumnan and Yimrattanabovorn, 2012). In textile dyebaths, dyes cannot bind with fabrics completely, resulting in some of the dyes being lost (Pearce et al., 2003). The dye wastewater effluents are high in colour, pH, suspended solids (SS), COD (Verma et al., 2012), biochemical oxygen demand and metals (Sekomo et al., 2012). Typically, textile industry-processing effluents contain dyes in the range between 10 and 200 mg/l (Pandey et al., 2007).

Most textile dyes with a rather low concentration of below 1 mg/l can be detected by the human eye (Pandey et al., 2007). Therefore, this aesthetic problem is one of the major challenges for receiving watercourses. In addition, a high concentration of these dyes in the receiving water body will prevent light penetration and negatively affect the ecosystem by reducing respiration and photosynthesis of aquatic organisms (Reema et al., 2011; Saratale et al., 2011). Moreover, these effluents pass through soil layers and may contaminate nearby surface and ground waters (Sivakumar, 2014). Furthermore, some textile dyes and their intermediate products are deleterious due to their toxicity, mutagenicity and carcinogenicity to life (Khataee et al., 2012).

Biological treatment alternatives using constructed wetlands are sustainable and cost-effective (Means and Hinchee, 2000). This technology is well-accepted to be environmentally friendly, cheap, simple-to-use and effective to treat diverse municipal sewage, storm water, agricultural runoff and industrial wastewaters worldwide (Scholz, 2010; Sani et al., 2013). Literature indicates promising results for textile dye removal using vertical and/or horizontal up-flow or down-flow wetland systems (Davies et al., 2005; Mbuligwe, 2005; Bulc and Ojstrsek, 2008; Ong et al., 2009; Cumnan and

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Yimrattanabovorn, 2012). The high removal efficiency in terms of dye, COD and other contaminants was due to the complex interactions between plants, water, soil and micro-organisms. Recently, there has been attention towards using shallow pond systems to treat textile wastewater contaminated with dyes using aquatic plants as a cheap, effective and environmentally friendly method. However, the literature in this area is still limited, and there are only short-term studies treating wastewater contaminated with textile dyes in shallow pond and wetland systems in Turkey and India (Muthunarayanan et al., 2011; Sivakumar et al., 2013; Sivakumar, 2014; Uysal et al., 2014).

1.2. *Lemna minor*

Wetland plants can play a major role in dye wastewater treatment (Mbuligwe, 2005). For example, *Lemna minor* is a rather small free-floating macrophyte, which grows rapidly and adapts easily to diverse aquatic conditions in stagnant ponds or slow-flowing streams (Movafeghi et al., 2013; Khataee et al., 2012). This plant has the ability to accumulate and assimilate pollutants from wastewater (Bekcan et al., 2009). It is also used for the removal of heavy metals (Sekomo et al., 2012) from industrial and textile wastewaters. In addition, it is a good source of fodder, because it has high concentrations of protein and low fibre content (Bekcan et al., 2009).

1.3. Aim and objectives

The overall aim is to assess the performance of simulated shallow pond wetland systems vegetated by *L. minor* for the treatment of artificial textile dye wastewater under controlled conditions. The corresponding objectives are to (a) evaluate and compare the water quality of different design variables such as the presence of *L. minor* and/or algae; (b) assess the influence of the design variable on water quality parameters; (c) assess and compare the dye and COD removal of four classes of dyes (Acid Blue 113, Reactive Blue 198, Direct Orange 46 and Basic Red 46) with each other; and (d) monitor the effect of dye accumulation as a function of the relative growth rate of *L. minor*.

2. Materials and methods

2.1. Dyes and nutrients

Four dyes were used in this study: Acid Blue 113 (AB113), Reactive Blue 198 (RB198), BR46 and Direct Orange 46 (DO46), which were supplied by Dystar UK Limited (Colne Side Business Park, Huddersfield, United Kingdom) except for AB113, which was obtained from Sigma-Aldrich Company UK Limited (The Old Brickyard, New Road, Gillingham, United Kingdom). The studied azo dyes are different in structure, molecular weight, mode of applications and number of azo bonds (Table 1).

The fertiliser TNC Complete, which is an aquatic plant nutrient supplied by TNC Limited (Spotland Bridge Mill, Mellor Street, Rochdale, United Kingdom), was used in this study. The corresponding ingredient composition was as follows: nitrogen (1.5%), phosphorus (0.2%), potassium (5%), magnesium (0.8%), iron (0.08%), manganese (0.018%), copper (0.002%), zinc (0.01%), boron (0.01%) and malybdenum (0.001%). Ethylenediaminetetraacetic acid, which is used as a source for copper, iron, manganese and zinc, was also provided by TNC Complete. One millilitre of fertiliser was added to 10 l of dechlorinated tap water.

Dye stock solutions were arranged for each dye by dissolving 5 g of a dye in one litre of distilled water and stored in the dark at 4 °C. The synthetic wastewater applied in this project was prepared by mixing the dye solution with dechlorinated tap water and fertiliser (TNC Complete), providing a 5-mg/l concentration for each dye.

2.2. Experimental set-up phases

The experiment was carried out at the university using plastic containers (length, 33 cm; width, 25.5 cm; depth, 14 cm) located outside. Twenty containers simulating shallow ponds were allocated for each dye. An additional 20 containers without dyes (controls) were also monitored. The containers were manually operated; e.g., contaminated inflow water was added by the operator. It follows that there were no physical inflow or outflow structures in the containers.

In the first phase between 10 July 2014 and 11 August 2014, each container was filled with tap water to the desired level of 6.9 cm depth, which is equivalent to 5 l. Subsequently, 200 healthy *L. minor* plants were added to each container, and the system was fed weekly with water and fertiliser (for composition; see Section 2.1). The plant was collected from a small pond close to Cowpe Reservoir (Cowpe, Rossendale, United Kingdom).

In the second phase between 11 August 2014 and 15 December 2014, the system was kept outside for acclimatisation and monitoring purposes. During this period, the plants grew very well, and some algae started to develop in most systems naturally, which were detected by using Leica DM750 LED Biological Microscope with ICC50W Camera Module-5.0 Mega Pixel (New York Microscope Co., Lauman Lane, Hicksville, New York, USA). Algal species were identified with the help of standard textbooks such as Nakada and Nozaki (2015). From 9 September 2014, dyes at a concentration of 5 mg/l were added to undertake initial tests to examine plant survival (data not shown).

On 15 December 2014, the third phase was started. The experiment was performed under controlled laboratory conditions by moving 69 containers (simulated pond environments) to the Maxwell Building (The University of Salford). The experiment comprised 14 ponds for each dye and 13 ponds without any dye. The set-up consisted of four treatment groups. The first group comprised *L. minor* and algae (LA Pond), the second one used only *L. minor* (L. pond), the third group used only algae (A Pond) and the fourth group represented the control without using *L. minor* and algae (C. pond). Four replicates for each group and two replicates for each control were used.

The group of artificial ponds containing only *L. minor* as well as the control group without any plants were kept free of algae. Considering that *L. minor* grows very rapidly, the surface areas of the ponds were frequently covered preventing sunlight from reaching any traces of algae in the *L. minor* ponds. However, any visual traces

Table 1
Characteristics of dyes used in this study.

Number	Colour index name	Molecular composition	Molecular weight (g/mol)	λ_{max} (nm)	Chemical class
1	Acid Blue 113	C32H21N5Na2O6S2	681.6	566	Diazo
2	Reactive Blue 198	C41H30Cl4N14Na4O14S4	1304.8	625	Diazo/Oxazine
3	Basic Red 46	C18H21N6	321.4	530	Monoazo
4	Direct Orange 46	C12H10N3NaO3S	299.2	421	Monoazo

Note: λ_{max}, wavelength at maximum absorption; C, carbon; H, hydrogen; N, nitrogen; Na, sodium; O, oxygen; S, sulphur; Cl, chlorine.