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ARTICLE



Biosorption of Acid Red P-2BX by lichens as low-cost biosorbents

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ABSTRACT

The aim of this study is to examine the dye biosorption properties of lichen species called *Cladonia convoluta* and *Evernia prunastri*. Since lichens are extensively found in the environment, their suitability as a cheap adsorbent has been investigated in this study. The optimal parameters for textile dye biosorption were also determined. The dried lichen biomass showed better dye biosorption capacity than ash lichen biomass. *C. convoluta* had better dye biosorption capacity than *E. prunastri*. Dye biosorption rate was found as 71.41% at optimal conditions. This study concluded that *C. convoluta* was a successful and cheap biosorbent for treatment of water contaminated by Acid Red P-2BX dye.

KEYWORDS

Acid Red P-2BX; biosorption; lichen; wastewater treatment

Introduction

Treatment of wastewater after industrial use requires new and inexpensive approaches. Textile dyes are the primary contents of the textile wastewater and they are mutagenic and carcinogenic for living organisms [1]. Several physical and chemical methods have been used for wastewater treatment, but they are expensive and inefficient in textile dye removal [2]. Biological treatment methods have proved to be more effective, eco-friendly and cheaper [3]. Some studies concern bacterial [4], algal [5] and fungal [6] biomasses, but apart from this research there has been only one study that examined lichen [7] biomass for treatment of industrial wastewater.

Lichens are the most important examples of symbiotic life in nature. Lichen is the association of a mycobiont (fungus) and photobiont (green alga or cyanobacterium) [8]. The photobiont and mycobiont have some roles that support each other, and so many lichen species can adapt to the different environmental conditions. The photobiont supplies energy via photosynthesis to the mycobiont and the fungus provides water and a safe environment to the alga [9]. In addition, the mycobiont produces various lichen secondary metabolites that typically encrust the hyphal and algal surface of lichen during symbiotic relationship [10]. In the literature, lichens are recommended as indicators for heavy metal pollution [11]. There is only one reported study on the

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dye removal ability of lichen *Parmelia perlata* [7]. The aim of this study is to investigate the textile dye (Acid Red P-2BX) biosorption properties of lichen species *C. convoluta* and *E. prunastri* as a function of pH, biosorbent type, dye concentration, contact time, temperature and biosorbent dosage at a batch scale level.

Material and methods

Preparation of dye solution

Acid Red P-2BX (ARP-2BX) dye was supplied from the textile factory in Turkey. The stock dye solution (1000 mg/L) was prepared in distilled water. The stock solution was diluted to the desired concentrations for experiments.

Collection of lichens and biosorbent preparation

Two different lichen species (*C. convoluta* and *E. prunastri*) were tested for determination of their dye biosorption capacities. In the experiments, the lichens collected from the urban forest of Bilecik province (N 40° 11.5262', E 29° 57.962') were used and the collected lichens were prepared as biosorbent. Two different types of biosorbents were prepared for this study. The first group of biosorbents was cleaned by washing and, then the biomass was dried at 100°C during one night. The second group of biosorbents was kept in the ash oven for 30 min at 500°C. Both of the biosorbent groups were ground to make powder. To ensure that all of the powder particles were of equal size, they were passed through a 0.5-mm sieve and made ready for experiments.

Biosorption studies

All experiments were performed in Erlenmeyer flasks with 100 mL of dye containing solutions. To examine the effect of pH, the prepared experimental solutions with different pH values (2, 4, 6, 8 and 10) were used for dye biosorption. To test the efficiencies of two type of biosorbents as dried and ash, 1 g/L of biosorbents were added into the experimental solutions. In addition, the effect of contact time (30–1440 min), initial dye concentration, biosorbent dosage (1, 2 and 4 g/L) and temperature (25, 35 and 45°C) were investigated in experimental series.

Analytical methods

A spectrophotometer (Labomed INC. 22 model) at 535 nm (the wavelength of observing the maximum absorption peak for dye) was used to analyse the concentrations of dye in solution. The samples (2 ml) were taken at definite times and centrifuged (Hettich EBTA12 model centrifuge) at 4000 rpm for 3 min. The supernatant was used for dye analysis.

The dye biosorption rate (B%) was calculated from Equations (1) and (2):

$$\text{Biosorption rate (B\%)} = (C_o - C_f) / C_o \times 100 \quad (1)$$

$$q_m = C_o - C_f / X_m \quad (2)$$

q_m : the uptake of dye by a unit mass of biosorbent at any time (mg/g), C_o : initial dye concentration (mg/L), C_f : final dye concentration at any time (mg/L), X_m : the sorbent concentration (g/L).

FTIR analysis

The FTIR analysis was done by an Agilent Technologies, Cary 630 FTIR spectrophotometer. The dried biomasses of lichens (before and after biosorption) were ground into powders (blended with dry spectroscopic grade powders) and then pressed into small disks for FTIR measurements. Samples were scanned at the scan range of 400–4000 cm^{-1} .

Results and discussion

The selection of lichen species and the effect of pH on biosorption

In order to select the most effective lichen biosorbent, the different species were tested for dye biosorption. Optimal pH was found as 2 for both lichen species and biosorbent types (Table 1). The dried lichen biosorbents were also found to be more effective than ash lichen biosorbent for all species. Dried and ash lichen biosorbents were prepared with 100°C and 500°C, respectively.

C. convoluta showed more dye removal activity than *E. prunastri* (Table 1), and so *C. convoluta* was selected for further experiments. As seen in Table 1, ash biosorbents were not effective for both lichen species. It was reported that the high temperature as 500°C provided both the stability of biosorbent and increased surface area of biosorbent [12]. But, the results of our study showed that biosorbents dried at 100°C showed better dye biosorption activity

Table 1. The dye biosorption rate and capacities of lichen species (*C. convoluta*: C_o : initial dye concentration, B (%): biosorption rate, q_m : biosorption capacity).

Lichen	Type	C_o (mg/L)	pH	B (%)	q_m (mg/g)
<i>C. convoluta</i>	Dried	88.14	2	47.97	42.29
<i>C. convoluta</i>	Dried	88.71	4	34.94	31.00
<i>C. convoluta</i>	Dried	88.71	6	32.53	28.86
<i>C. convoluta</i>	Dried	87.71	8	34.04	29.86
<i>C. convoluta</i>	Dried	87.43	10	33.17	29.00
<i>C. convoluta</i>	Ash	86.71	2	46.62	40.43
<i>C. convoluta</i>	Ash	89.00	4	45.10	40.14
<i>C. convoluta</i>	Ash	88.29	6	46.28	40.86
<i>C. convoluta</i>	Ash	85.14	8	36.14	42.85
<i>C. convoluta</i>	Ash	63.71	10	20.04	13.00
<i>E. prunastri</i>	Dried	88.29	2	47.21	41.71
<i>E. prunastri</i>	Dried	88.71	4	34.46	30.57
<i>E. prunastri</i>	Dried	87.86	6	33.50	29.43
<i>E. prunastri</i>	Dried	87.29	8	33.55	29.29
<i>E. prunastri</i>	Dried	88.57	10	28.23	25.00
<i>E. prunastri</i>	Ash	88.15	2	45.22	39.86
<i>E. prunastri</i>	Ash	87.57	4	45.19	39.57
<i>E. prunastri</i>	Ash	88.00	6	45.13	39.71
<i>E. prunastri</i>	Ash	84.86	8	43.27	36.71
<i>E. prunastri</i>	Ash	60.29	10	23.10	14.29

than ash biosorbents dried at 500°C (Table 1). This study did not find that the use of ash as a biosorbent was successful. On the other hand, another research concluded that the increment in temperature caused degradation of some polymers in the surface and also dehydration of hydroxyl groups on the surface [13]. Recently, Zhao et al. [12] determined that the pyrolysis temperature caused reduction of the number of acidic functional groups such as the carboxylic functional groups on the surface. The results of this current study showed that the functional groups on the lichen surface that participated in the dye biosorption were exposed to thermal degradation and the biosorption rate was decreased. The dried biosorbent preparation was also more economic. Heating to 100°C took less energy than heating to 500°C. The biosorption of dye molecules was regulated by electrostatic attractions between oppositely charged molecules and surface functional groups [14]. In the solutions at low pH values, the surface of biosorbent, which was charged positively, interacted with the negatively charged dye molecules [15]. The optimal pH for biosorption of dye molecules on the surface of *C. convoluta* was found to be 2 (Table 1).

The effect of dye concentration

The effect of dye concentration on biosorption was examined. The augmentation of dye concentration resulted in *decreasing* of dye biosorption rate (Table 2). Recently, Kulkarni et al. [7] examined the dye biosorption capacity of lichen *P. perlata* and determined that the increment in the dye concentration caused the decreasing of dye biosorption percentage. Similarly, Bilal et al. [16] showed that biosorption capacity of microalgae was decreased by the *increase* of dye concentration. In addition, De Castro et al. [17] reported that dye biosorption by fungi *increased* dye concentration negatively. Lichen is an example of the symbiotic relationship between fungus and alga and it was expected that lichen showed properties similar to those of fungi or algae. The findings of this study were in agreement with others on dye biosorption with both fungi and algae. It was considered that the binding sites on the lichen were saturated with the dye molecules and further dye sorption was inhibited by increasing of dye molecules.

The effect of biosorbent dosage

In order to investigate the effect of biosorbent dosage on biosorption of dye by dried *C. convoluta*, different amounts of biosorbent dosages (1, 2 and 4 g/L) were tested for dye removal capacity. Figure 1 shows the results. Increasing adsorbent dosage caused an

Table 2. The effect of dye concentration on biosorption (C_0 : initial dye concentration, B (%): biosorption rate).

Lichen	Type	Co (mg/L)	B (%)
<i>C. convoluta</i>	Dried	54.71	63.71
<i>C. convoluta</i>	Dried	88.14	47.97
<i>C. convoluta</i>	Dried	139.57	26.29
<i>C. convoluta</i>	Dried	147.57	19.86
<i>C. convoluta</i>	Ash	63.43	45.27
<i>C. convoluta</i>	Ash	86.71	46.62
<i>C. convoluta</i>	Ash	139.29	14.26
<i>C. convoluta</i>	Ash	147.29	13.29

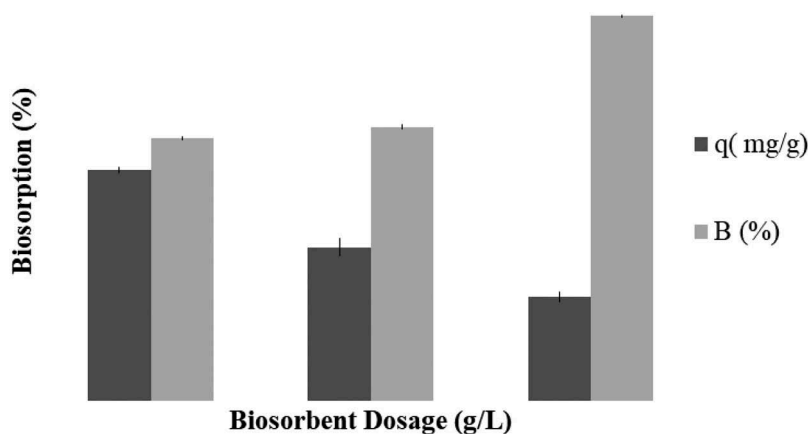


Figure 1. The effect of biosorbent dosage on biosorption (B, %).

increment of dye biosorption percentage. It was previously reported that dye removal was increased while the biosorbent dosage was raised [17].

The effect of temperature and contact time

The biosorption process was operated and then samples were taken at specific times for the examination of the time effect on biosorption. The equilibrium time was determined as 1440 min for dye biosorption by lichen (Figure 2).

In the results of the effect of temperature experiments, it was observed that biosorption rate was decreased by the increment of temperature (Figure 2). In a previous study, the effect of temperature on dye removal by lichen *P. perlata* was tested and it was shown that biosorption percentages were increased by the increment of temperature from up to 50°C [7]. But the results of the study showed that maximum decolourisation occurred at 25°C for *C. convoluta* (Figure 2).

FTIR analysis

Figure 3 shows the FT-IR spectra of *C. convoluta* before and after biosorption. The band presence at 3714 cm⁻¹ revealed the presence of -OH and -NH groups, but after biosorption, this band shifted to 3694 cm⁻¹ and a wide peak with moderate violence was observed. Changes starting from 700 cm⁻¹ indicate one or two weak aldehyde C-H peaks.

Biological wastewater treatment methods suggested the use of biological material for pollutant removal. Compared to other biological materials such as algae, fungi and other vascular plants, lichens have some advantages. They are the association of fungi and algae and can have more tolerance for toxic pollutants than fungi and algae. Wojtuń et al. [18] showed that lichens performed more heavy metal bioaccumulation capacity than vascular plants. The results of our study showed that lichens had an effective dye biosorption capacity and that they can be potential biosorbents for dye removal.

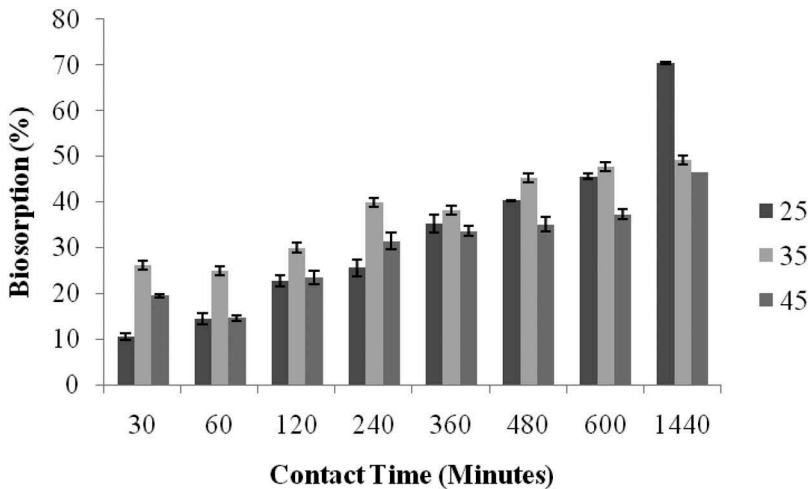


Figure 2. The effect of temperature (25, 35 and 45°C) and contact time (0–1440 min) on biosorption (%).

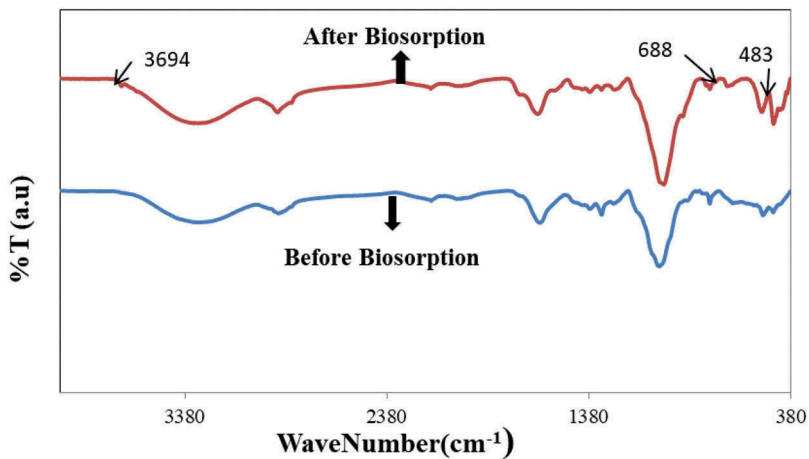


Figure 3. FTIR spectrum of lichen (dried *C. convoluta*) after and before dye biosorption.

Conclusion

This study concerns the determination of a capacity for biosorption of textile dye in two lichen species (*C. convoluta* and *E. prunastri*). It is clear that they are potential low-cost biosorbents. Two types of biosorbents were prepared from lichens. The first was dried at 100°C and the second was prepared as ash at 500°C. The dried lichen was found to be a more successful biosorbent than ash lichen. Further, *C. convoluta* performed more dye removal activity than *E. prunastri*. The optimal conditions for dye biosorption were also determined in this study. It was concluded that *C. convoluta* was acceptable as a low-cost biosorbent for removal of textile dyes from industrial wastewater.

Disclosure statement

No potential conflict of interest was reported by the authors.

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