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Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye

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Abstract

Three kinds of filamentous fungi (*Rhizopus arrhizus*, *Trametes versicolor*, *Aspergillus niger*) were tested for their ability to adsorb Gryfalan Black RL metal-complex dye as a function of pH, temperature and dye concentration. *R. arrhizus* and *T. versicolor* exhibited the maximum dye uptake at pH 2.0 and at 25 °C while *A. niger* performed the highest dye biosorption at pH 1.0 and at 35 °C. Sorption capacity of each biosorbent increased with increasing initial dye concentration. Among the three fungi, *R. arrhizus* was the most effective biosorbent showing a maximum dye uptake of 666.7 mg g^{-1}. The Langmuir model described the equilibrium data of each dye–fungus system accurately in the concentration and temperature ranges studied. Kinetic analysis indicated that both adsorption kinetics and internal diffusion played an important role on controlling the overall adsorption rate for each fungus. Thermodynamic analysis verified that *A. niger* biosorption was endothermic while the others were exothermic.

Keywords: Biosorption; Fungi; Gryfalan Black RL; Metal-complex dye

1. Introduction

The impact and toxicity of dyes that are released in the environment have been very important and extensively studied. The source of such pollution lies in the rapid increase in the use of synthetic dyes because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dyes. More than 10,000 chemically different dyes are being manufactured. These dyes are mainly consumed in textiles, tanneries, pharmaceuticals, pulp and paper, paint, plastics, electroplating and cosmetics industries (Nigam et al., 2000). During the processing of dye manufacturing and dye application, up to 15% of the used dyestuff are released into the process water so the effluents from these industries are highly coloured (Slokar and Le Marechal, 1997; Forgacs et al., 2004). Standard wastewater treatments for colour removal appeared ineffective because of the chemical stability of most dye pollutants that makes them non-biodegradable. This led to the study of other effective methods, and many physical and chemical treatment methods including adsorption, chemical coagulation, precipitation, filtration, electrodialysis, and oxidation have been used for the treatment of dye-containing effluents. Some of these techniques have been shown to be effective, although they have limitations (Crini, 2006).

Biosorption is defined as the accumulation and concentration of organic and inorganic pollutants including metals, dyes and odour causing substances from aqueous solutions by the use of biological materials. These biological materials are typically live or dead microbial biomasses, which may be bacteria, fungi and algae. Biosorption in natural or uncontrolled situations typically involves a combination of active and passive transport mechanisms. The main attractions of biosorption are high selectivity and efficiency, cost effectiveness, good removal performance, possible regeneration at low cost, availability of known process equipment, sludge free operation and recovery of the

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sorbate. Raw materials which are either abundant (sea weeds) or wastes from other industrial operations (fermentation wastes, activated sludge process wastes) can be used as biosorbents. The use of dead microbial cells in biosorption is more advantageous for water treatment in that dead organisms are not affected by toxic wastes, they do not require a continuous supply of nutrients and they can be regenerated and reused for many cycles (Volesky, 2001; Sumathi and Manju, 2000; O'Mahony et al., 2002; Aksu, 2005; Won et al., 2006; Vijayaraghavan and Yun, 2006; Maurya et al., 2006). Textile dyes vary greatly in their chemistries, and their interactions with microorganisms depend on the chemistry of a particular dye, type of biomass, its preparation and its specific surface properties and environmental conditions. Since fungal biomass is non-pathogen to humans and animals and it can be produced cheaply using simple fermentation techniques or obtained as a waste from various industrial fermentation processes (for example citric acid and amylase fermentation processes may be a source for waste *A. niger*; waste *R. arrhizus* may be supplied from lactic acid and lipase fermentation processes; for obtaining waste *T. versicolor* oxalic acid fermentation process may be useful (Pandey et al., 2000)), it is widely used for the biosorption of dyes (Bidisha et al., 2006; Bayramoglu and Arica, 2007; Iscen et al., 2007; Kumari and Abraham, 2007). *R. arrhizus* (Aksu and Cagatay, 2006) *A. niger* (Fu and Viraraghavan, 2002), *N. crassa* (Akar et al., 2006) *P. chrysosporium* (Radha et al., 2005) are some of low-cost fungal materials which have been used as sorbents for the dyes.

Anionic water-soluble metal complex dyes are widely used in the textile and leather tanning industries for dyeing protein and polyamide fibres because of their excellent light fastness. Metals used in metallized dyes include mainly chromium, cobalt, and copper. Countless shades from greenish yellow to deep black can be generated by these dyes depending upon the metal, the dye ligands, and the combination of dye ligands in mixed complex dyes. The resulting wastewaters may contain a large amount of metal complex dyes. However, only a limited number of studies on the removal of metal complex dyes have been found in the literature (Ozacar and Sengil, 2005; Jozwiak et al., 2007). Moreover a few studies have been focused on the utilization of fungi for metal-complex dye biosorption (Blanquez et al., 2004) so the adsorptive properties of fungi for metal-complex dyes should be investigated. Gryfalan Black RL (G Black RL) was chosen in this study as it is one of the metal-complex derivatives belonging to the overwhelming majority of synthetic dyes applied in tanning and textile industries for dying wool, natural silk, polyamide and leather in Turkey.

2. Methods

2.1. Microorganisms and growth conditions

R. arrhizus and *A. niger* obtained from the US Department of Agriculture Culture Collection were the two filamentous fungi used in this study as biosorbents. The strains were cultivated in the media containing 17 g l^{-1} malt extract and 5.4 g l^{-1} soya peptone. The pH values of media were adjusted to 6.5–6.8 with dilute H_2SO_4 and NaOH solutions before autoclaving. Once inoculated, flasks were incubated on an orbital shaker at 100 rpm for 7 days at 25 °C. The white-rot fungus *T. versicolor*, obtained from Hacettepe University, Biology Department, Turkey, was another biosorbent used in this study. The growth medium contained the following ingredients as g l^{-1}; D-glucose (10.0); yeast extract (0.1); KH_2PO_4 (0.2), $NH_4H_2PO_4$ (0.5); $MgSO_4 \cdot 7H_2O$ (0.5) and 1 ml of $ZnSO_4$–$FeSO_4$ solution (prepared from 1.4 g l^{-1} $ZnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$). The pH of the medium was adjusted to 4.5 with dilute H_2SO_4 and NaOH solutions before autoclaving. Once inoculated, 250 ml Erlenmeyer flasks containing 100 ml of sterile medium were incubated on an orbital shaker at 100 rpm for 7 days at 30 °C.

2.2. Preparation of the microorganisms and G Black RL solutions for biosorption

After the growth period, the pellets of fungi were washed several times with distilled water, *R. arrhizus* pellets were inactivated in 1% formaldehyde solution (except *T. versicolor* and *A. niger*), and then dried at 60 °C for 24 h. For the biosorption studies, 10 g of dried biomass was suspended in 100 ml of double-distilled water and homogenized in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25, Germany) at 8000 rpm for 20 min and then stored in the refrigerator. At the beginning of biosorption, 10 ml dried biomass suspension was contacted with 90 ml of solution containing a known concentration of dye in an Erlenmeyer flask at the desired temperature and pH. For biosorption studies, Gryfalan Black RL (C.I. Acid Black 194, CAS No 61931-02-0) was used as received without further purification. Poland production dye was kindly supplied from Ersacolor, Turkey. The test solutions containing G Black RL metal-complex dye were prepared by diluting 1.0 g l^{-1} of stock solution of dye. The range of concentrations of prepared dye solutions changed between 50 and 1000 mg l^{-1}. The pH of each solution was adjusted to the required value with diluted or concentrated H_2SO_4 and NaOH solutions before mixing the sorbent or biomass suspension.

2.3. Biosorption experiments

Sorption studies were conducted in a routine manner by the batch technique. A number of stoppered Pyrex glass flasks containing a definite volume (100 ml in each case) of solutions of G Black RL dye of desired concentration, pH and temperature were placed in a thermostatic rotary shaker. The flasks were agitated at a 150 rpm constant shaking rate for 1 day to ensure equilibrium was reached. All the final solutions contained 1.0 g l^{-1} of biosorbent. Samples (5 ml) were taken before mixing the sorbent and dye bearing solution and at definite time intervals. The