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Short communication

Malachite green dye decolorization on immobilized dead yeast cells employing sequential design of experiments

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ABSTRACT

The use of low-cost, potential, locally available and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. Sequential Plackett–Burman design (PBD) model was used to screen out the most significant factors and Box–Behnken design (BBD) to study the combined effects of interaction between the variables selected by PBD. Second-order polynomial regression model was applied which was statistically validated using analysis of variance. Maximum decolorization 96.25% obtained at pH 6.88, dye concentration 188.01 mg/L and adsorbent dose 0.49 g (dead yeast cells) after 60 min. Kinetic studies showed that the adsorption follows pseudo-second order kinetics and maximum 61% desorption obtained. Negative values of Gibbs free energy change (ΔG°) showed that the adsorption was feasible and spontaneous and negative values of enthalpy change (ΔH°) confirmed exothermic adsorption.

1. Introduction

Synthetic dyes are extensively used in many industrial dyeing processes such as textile dyeing, paper printing, color photography, and as additives in petroleum products (Asgher and Bhatti, 2012). In the textile manufacturing industry, up to 50% of the dyes are lost after the dyeing process and about 10–15% of them are discharged in the effluents (Khambhaty et al., 2012). Dyes containing effluents from textile industries are highly colored and are therefore visually distinguishable (Mona et al., 2011). The complex aromatic structure of the dyes is resistant to light, biological activity, ozone and other degradative environmental conditions. The high stability and toxicity are the major problems in the treatment of dyes charged wastewaters (Asgher and Bhatti, 2012).

Efforts have been made to develop a single and economical method for the treatment of dyes in the textile wastewater, but still it remains a big challenge (Santos et al., 2008). Dye wastewater is usually treated by physical or chemical treatment processes. These include flocculation combined with flotation, electro-flocculation, membrane filtration (Amini et al., 2011), electro-kinetic coagulation, electrochemical destruction (Ma et al., 2009), ion-exchange, irradiation, precipitation, ozonation, and katox treatment method involving the use of activated carbon and air mixtures (Asgher and Bhatti, 2012); these technologies are generally ineffective in color removal, expensive and less adaptable to a wide range of dyes wastewater (Srinivasan and Viraraghavan, 2010). Adsorption has been observed to be an effective process for color removal from dye wastewater. Use of activated carbon has been found to be effective, but it is too expensive. Many studies have been undertaken to investigate the use of low-cost adsorbents such as peat, bentonite, steel-plant slag, fly ash, china clay, maize cob, wood shavings, and silica for color removal (Gupta and Suhas, 2009). However, these low-cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents. Therefore, there is a need to find new, economical, easily available and highly effective adsorbents (Srinivasan and Viraraghavan, 2010). Malachite green (MG) is a triphenyl methane dye used as parasiticide, fungicide, antiprotozoan and antibacterial agent (Srivastava et al., 2004). It is known to be highly toxic to mammalian cells and acts as a tumor-enhancing agent. It decreases food intake, growth and fertility rates, causes damage to liver, spleen, kidney and heart, and inflicts lesions on skin, eyes, lungs and bones. Hence it is necessary to remove it from effluent discharge (Bulut et al., 2008).

Saccharomyces cerevisiae MTCC 463 has been reported earlier for efficient decolorization of dyes, such as methyl red and malachite green (Zhisheng and Xianghua, 2005; Jadhav and Govindwar, 2006; Phugare et al., 2010). Commercial biotechnological processes such as brewing and distillation produce large quantity of waste biomass, either living or non-living (Phugare et al., 2010).

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Proper management of such waste is one of the serious issues nowadays. Utilization of waste beer yeast for the biosorption has been reported earlier (Phugare et al., 2010). In the present study, *S. cerevisiae* yeast cells left after ethanol production (Singh and Bishnoi, 2012) was used as sorbent for MG decolorization. Sorption capability of dye was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution (Gomes et al., 2011). So, Plackett–Burman design and Box–Behnken design (BBD) of response surface methodology (RSM) were used for optimization of conditions for maximum dye decolorization. Kinetic, thermodynamics and desorption studies were also studied.

2. Materials and methods

2.1. Adsorbent

Yeast *S. cerevisiae* MTCC 174 was used as adsorbent for dye removal in the present study. Yeast cells were collected from 3 L fermentor (BioAge, Mohali, India) after ethanol production from wheat straw hydrolysate as described in the previous paper (Singh and Bishnoi, 2012). The yeast cell suspension was washed with double distilled water, frozen at −80 °C in deep freezer for 24 h and lyophilized for 48 h and then heat killed. The dead *S. cerevisiae* cell suspension (as per PBD and BBD experiments) was added to 4% (w/v) sodium alginate solutions in 1:1 volume ratio and mixed thoroughly. The cell–alginate mixture was then cast into beads by dropping from a hypodermic syringe into cold sterile 0.1 M $CaCl_2$ solution. These beads had a diameter of approximately 3.0 mm and were hardened by keeping in the dilute (0.1 M) $CaCl_2$ solution for 24 h at 4 °C with gentle agitation (Behera et al., 2010). Finally, these beads were washed with sterile distilled water to remove excess Ca^{2+} ions and unentrapped cells before being used for the adsorption process. The same procedure was done with alginate solution without adding dead yeast cells.

2.2. Dye

Malachite green {4-[(4-dimethylaminophenyl) phenylmethyl]-*N*,*N*-dimethylaniline)} is a member of the triphenylcarbenium salts purchased from Qualigens Chemicals (India) and used without further purification. A stock solution of dye was prepared (1000 mg/L) and desired concentrations of the dye were obtained by further dilutions in distilled water. The initial pH was adjusted with 0.1 M sodium tartrate buffer (pH 2.0–4.0), 0.1 M sodium acetate buffer (pH 5.0), 0.1 M citrate phosphate buffer (pH 6.0–7.0) and 0.1 M borate buffer (pH 7.4–9.2).

2.3. Kinetic study

Kinetics of biosorption was studied by varying contact time from 5 to 180 min at 100 mg/L initial dye concentration and agitation rate 100 rpm while keeping other conditions constant (pH 7.0, temperature 30 °C). Samples were withdrawn after a regular time intervals in triplicate and analyzed spectrophotometrically at λ_{max} 617 nm. Percentage of dye removal and quantity of MG adsorbed on adsorbent at the time of equilibrium (q_e) were calculated using Eqs. (1) and (2), respectively.

$$\text{MG decolorization}\,(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (1)$$

$$\text{Adsorption capacity}\,(\text{mg/g})\, q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where C_0 is the initial dye concentration (mg/L) and C_e is the residual concentration of the dye (mg/L) at different time intervals, q_e is quantity of MG adsorbed on the adsorbent at the time of equilibrium (mg/g), V is volume (L) of solution and M is the mass of adsorbent (g) taken for experiment. Desorption of dye studied as 5 ml of 50% methanol was added to the dried, dye-saturated beads, shaken vigorously and left for 12 h. The dye extract solvent was then filtered into test tubes. This solvent/dye mixture was left for 1 h at 65 °C to evaporate the solvent. The remaining volume (water) in all test tubes was made up to 5 ml with distilled water and the concentration of desorbed dye was determined by spectrophotometer (Robinson et al., 2002).

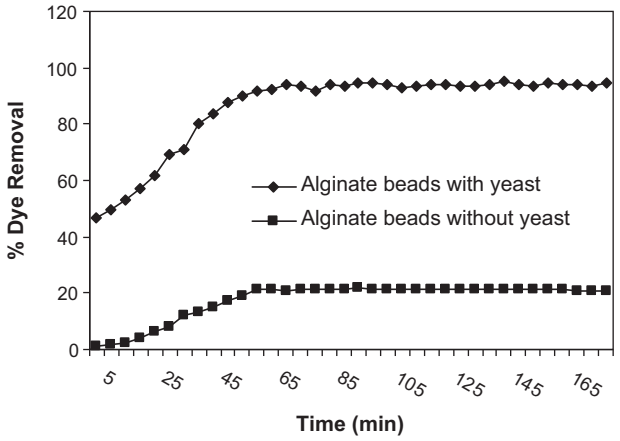

Fig. 1. Biosorption kinetics of MB dye on immobilized dead yeast cells at pH 7.0, temperature 30 °C, adsorbent dose 0.2 g and initial dye concentration 100 mg/L.

2.4. Statistical optimization study

2.4.1. PBD study

Plackett–Burman design was used to identify which variable(s) has a significant effect on percentage uptake of dye. Six variables (pH, contact time, sorbent dosage, initial dye concentration, agitation rate and temperature) were used in the present study. The designs and the percentage uptake for MG are shown in Table 1a. All experimental designs were carried out in triplicate and the mean value of the percentage uptake was taken as response. Experimental design and statistical analysis of data were done by using Design Expert Version 8.1.1 (trial version).

2.4.2. RSM study

Box–Behnken design and conducted experiments are shown in Table 1b. Experiments were carried out with three variables, and each variable varied at three levels for decolorization. The value of the dependent response was the mean of three replications. pH (4–9), adsorbent dose (0.1–0.5 g) and dye concentration (100–200 mg/L) were independent variables and MG decolorization was the response (dependent) variable. The second order polynomial model was fitted for decolorization using Eqs. (3) and (4) (Table 1b). The statistical analysis of the data was performed using "Design Expert" software (Trial version 8.1.1, Stat-Ease, Inc., Minneapolis, USA).

3. Results and discussion

3.1. Biosorption kinetics

Biosorption kinetics was studied for adsorption of MG of initial concentration 100 mg/L. Fig. 1 shows dye removal by dead yeast immobilized alginate beads and blank alginate beads. Fig. 1 shows that the rate of sorption decreases with increase of time and after