Applicability of immobilized wood-rotting fungal biomass for biosorption of basic dye Alcian Blue

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ABSTRACT

In this study potential applicability of immobilised biomass of a wood-rotting dead macro-fungus *Fomitopsis carnea* are explored for the removal of the basic dye Alcian Blue. Effect of several parameters viz., temperature, pH and salt were studied in batch mode. In view of reutilization of the dye as well as the biosorbent, desorption/regeneration experiments were conducted. Desorption/regeneration studies could also be helpful in determining dye sorption mechanism. Studies indicate that the immobilized biosorbent could remove Alcian Blue efficiently. The experimental equilibrium data were modeled using the Langmuir equation. Dye uptake capacity of the biosorbent was observed to increase with rise in temperature and indicates chemisorption and/or ion exchange. The uptake was 11.1, 13.2, 16.4 and 24.2 mg/g at 10, 20, 30 and 40°C respectively. Higher removal of dye was also observed at higher pH. However, increased salt concentration from 0 mmol/L to 100 mmol/L reduced from 89 to 85%. Desorption of dye could be possible up to 51% using 0.1 M hydrochloric/acetic acids and thus suggests that ion-exchange and chemisorption could be the possible dye sorption mechanism.

Key words | biosorption, colored wastewater, fungus, immobilization, isotherm

INTRODUCTION

The increased use of synthetic dyes in many industries such as textile, paper and plastics, tanneries, pharmaceuticals, packed food, paint and electroplating industries in order to improve appearance of their products has resulted in generation of large quantities of colored wastewater (Maurya & Mittal 2006a). The presence of very small amounts (less than 1 ppm for some dyes) of dyes in water source could make them unacceptable for many uses. Colour acquired by receiving water bodies such as rivers or lakes inhibits growth of the desirable aquatic life necessary for self-purification by reducing penetration of sunlight, with a consequent reduction in photosynthetic activity. Water treatment cost of the utilities located downstream of coloured water bodies is high. Colour causing compounds can react with metal ions to form substances which are very toxic to fish and other aquatic life.

Removal of color in a cost effective and environmental friendly manner to an acceptable limit is a great challenge for environmental engineers. The conventional physico-chemical methods used for this purpose, such as coagulation and flocculation, chemical precipitation, oxidation, ion exchange, reverse osmosis and ultra filtration can be very expensive and sometimes not very effective too (Maurya et al. 2006). Biological treatment (use of microbial population) could be an alternative method to treat colored wastewater. However, these processes are very sensitive to the characteristics of the effluent, such as temperature, pH and chemical composition. Among treatment technologies, adsorption using activated carbon as adsorbent is rapidly gaining prominence as a method of treating aqueous effluent (El-Geundi 1991). However high cost of activated carbon leads to restrict its application at least in developing...
countries. Many studies have been undertaken to find low-cost sorbents, which includes bagasse pith (Nassar & El-Geundi 1991; McKay et al. 1988), maize cobs (El-Geundi 1991), sunflower (Sun & Xu 1997), fly ash (Gupta et al. 2000), peat (Ramakrishna & Viraraghavan 1996), saw dust (Singh et al. 1992; El-Nabarawy & Khedr 2000). However, these low-cost sorbents generally have low uptake, which means that large amounts of sorbents are needed. Therefore, there is a need to find an economical, easily available (in nature) and highly effective sorbent, which can be easily regenerated.

Since last few decades several types of biomass has been extensively investigated for the biosorption of various types organic and inorganic substances including heavy metals from aqueous phase. Unfortunately, biomass employed as biosorbents in these processes pose several undesirable properties, such as low mechanical strength, low density, and non-granular shapes etc. Thus, these undesirable properties of biomass lead to reduced efficiency of packed bed or fluidized bed reactor by clogging and short-circuiting. Thus, its field application is restricted only to the continuous stirred tank reactor followed by a biomass separation facility, which increases the overall cost of treatment. Immobilization of the biomass in a suitable matrix could enhance the physical properties of biomass and thus could be use in packed bed or fluidized bed reactor economically (Maurya & Mittal 2006b).

Thus, keeping above mentioned facts in mind, the experimental studies is focused to investigate applicability of immobilized wood-rotting fungal biomass for biosorption of the basic dye Alcian Blue. In batch experiments, the parameters like equilibrium isotherm, temperature (20 to 30°C), initial pH (2 to 9), salt concentration (0 to 100 mmol) have been studied. In addition, several desorbing agents like water; mineral acid (hydrochloric and sulfuric acid) and organic acid (acetic acid) at varying concentrations are evaluated to regenerate the spent biomass for reutilization.

Wood rotting dead macro fungal biomass (Fomitopsis carnea) was obtained from Kerala, India. It was naturally available in abundance as waste product of the forest.

**Preparation of biosorbent**

The wood-rotting fungus was manually plucked, washed with tape water. Sun dried fungus was powderized to a size below 75 µm using electric grinder. The powder biomass was dried in electric oven at temperature 50°C for 24 hours and stored in a desiccator.

For the immobilization of biomass a non toxic support matrix ‘Polyvinyl chloride (PVA)’ was employed. The detail method for immobilization is described elsewhere (Ariga et al. 1987; Maurya & Mittal 2006b). 5 g PVA was dissolved in 50 mL distilled water at 80°C. The cooled PVA solution was stirred using magnetic stirrer for 16 h and then 0.25 g powder biomass was added to the solution. The homogenous solution PVA and biomass was extruded into liquid nitrogen using peristaltic pump. As soon as the solution drop came in contact with liquid nitrogen, instantly bead was formed. The beads were kept in liquid nitrogen for at least 12 hours. Then the beads were freezeed and thawed at least four cycles. After slow drying about 4 to 5 days, the beads were kept at 40°C till the difference in weight between two consecutive days became negligible. The dried beads were stored in desiccator for further use.

**Biosorption isotherm experiment**

For the estimation of dye sorption capacity of the immobilized biosorbent at different temperature bottle point equilibrium isotherm experiments were conducted at 10, 20 and 30°C. 50 mL aqueous solution of Alcian Blue (initial dye concentration 100 mg/L) was taken in 100 mL wide mouth glass bottle, and varying amounts of biosorbent were added to each bottle. Before addition of biosorbent, the dye solution was maintained at desired temperature. Each sample was taken in duplicate. A control of two bottles that contains same dye solution but no biosorbent was also taken to account error of dye sorption in the inner surface of bottle. All bottles were loaded on an orbital rotary shaker (Remi, India) and shaken at 200 rpm at a constant temperature. Upon equilibration, the shaking was stopped,
and samples from each bottle were withdrawn with a glass syringe. The dye solutions were separated from the biosorbent filtering through 0.45-μm pore size membrane filter and equilibrium dye concentrations were measured using spectrophotometer.

The amount of dye adsorbed onto unit weight of adsorbent, \( Q_e \) (mg/g) was calculated using the mass balance equation given by:

\[
Q_e = \frac{(C_0 - C_e)}{M}
\]

or \( Q_e = \frac{(C_0 - C_e)}{M} \) (1)

Here, \( Q_e \) is the quantity of dye transferred (mg/g) onto the biosorbent, \( C_0 \) and \( C_e \) are the initial and equilibrium concentration of Alcian Blue (mg/L) respectively, and \( M \) is the dose of the biosorbent (g/L).

**Effect of initial pH**

To study the effect of initial on dye removal (%), equal amount of biosorbent (6 g/L) was added to the bottles containing dye solution (100 mg/L) at pH 2, 4, 7 and 9. The initial pH was adjusted using 0.1N HCl/NaOH. The bottles were shaken for 48 hours using an orbital rotary shaker at 35 ± 2°C. The solution was analyzed for remaining dye concentration.

The percent removal of Alcian Blue employing biosorbent was calculated as given below:

\[
\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100
\]

where \( C_0 \) and \( C_e \) are the initial and final dye concentration (mg/L) in the solution.

**Effect of salt (NaCl) concentration**

50 mL dye solution (100 mg/L) of varying concentration of NaCl (0, 1, 10, 100 mmol/L) was taken in wide mouth glass bottle and equal amount of biosorbent (9 g/L) was added to each bottles. The bottles were shaken using an orbital rotary shaker at a constant speed (200 rpm) and temperature (30 ± 2°C). Upon completion of 48 hours remaining dye concentration of the solution was measured and % removal was calculated using Equation 2.

**Desorption/regeneration experiment**

Desorption experiment was carried out in two phases. (a) Sorption: the predetermined weight of adsorbents were added to 1,000 mL dye solution (initial dye concentration 100 mg/L, shaking speed 200 rpm, temperature 30°C) and kept on orbital rotary shaker. Upon completion of 48 hours the equilibrium concentration of dye solution was measured. The dye-loaded biosorbent was separated from the dye solution. The dye loaded biosorbent was dried in oven at 40 ± 2°C until the difference in weight between two consecutive days became negligible. (b) Desorption: the predetermined amount of dye-loaded biosorbent (keeping the mass by volume ratio similar to the first phase experiment) was added to 50 mL solution of desorbing agents (distilled water, 0.1 M HCl, 0.1 M H₂SO₄, 0.1 M CH₃COOH) in 100 mL glass bottles. The glass bottles containing the mixture of dye-loaded biosorbent and desorbing agent were agitated for 48 h. Concentration of the desorbed dye was measured.

**RESULTS AND DISCUSSION**

**Biosorption isotherm**

The study of isotherms indicates the sorption capacities of the biosorbent for removal of sorbate from the solution at constant conditions. However, sorption capacity of a biosorbent for the particular sorbate varies with change in temperature and this variation could be used to understand the mechanisms involve in dye-biosorption interaction. Therefore, these experiments were conducted at four different temperatures (10 to 40°C). Experimentally obtained equilibrium isotherm data were analyzed using Langmuir isotherm to obtain the monolayer saturation capacity of the biosorbent at different temperatures. The mathematical equation of Langmuir isotherm is presented in Equation 3.

\[
Q_e = \frac{Q_m b C_e}{1 + b C_e}
\]

(3)

Where \( Q_m \) (mg/g) and \( b \) (L/mg) are the isotherm constants, represent monolayer saturation capacity of the biosorbent...
for the sorbate under study and head of adsorption respectively (Faust & Aly 1987).

Figure 1 shows the experimental equilibrium isotherm data along with the predicted values using Langmuir isotherm equation for the sorption of Alcian Blue on to immobilised biosorbent. The Langmuir isotherm constants, evaluated from the experimental equilibrium isotherm data at different temperatures with the correlation coefficients are presented in Table 1. According to Table 1, satisfactory regression correlation coefficients (>0.936) were found at all the studied temperatures. High correlation coefficients show that Langmuir models are suitable, for describing the biosorption equilibrium of Alcian blue and immobilised biosorbent, in the studied concentration range.

**Effect of temperature**

It is evidence from the Figure 1 and Table 1 that dye sorption capacity of the biosorbent is highly temperature dependent. As temperature was raised from 10 to 40°C, sorption capacity also increased from 11.1 mg/g to 24.2 mg/g. Inbaraj & Sulochana (2002) have reported similar results for the sorption of a cationic dye, Malachite Green onto the jackfruit-peel. Sorption increased from 164 mg/g to 234.4 mg/g, while as the temperature varied from 32°C to 50°C. Mall & Upadhyay (1995) have also reported an increase in the sorption of Methylene Blue onto boiler bottom ash. The favoured biosorption with temperature indicates sorption process is endothermic in nature (Singh & Srivastava 1999). Thus, the chemisorption and/or ion-exchange type of sorption-mechanisms may be operative (Maurya 2005).

**Effect of initial pH**

The effect of initial pH on Alcian Blue uptake was evaluated by measuring the uptake of dye at different initial pH 2, 4, 7 and 9; keeping other parameters constant (Figure 2). Uptake by the biosorbent increased from 31 to 70% with increase in pH from 2.0 to 9.0. Similar observations are reported for the sorption of cationic dyes by other workers (Gupta et al. 2000; Maurya et al. 2006). This behavior of dye sorption can be explained on the basis of surface charge of the biosorbent. It is reported that such biosorbents have net negative charge in aqueous phase (Kapoor et al. 1999). With increase in pH, the net electro negativity of the biosorbent increases due to the deprotonation of different functional groups present on the biosorbent surface (Harris & Ramelow 1990; Schiewer & Volesky 1995). Therefore, there is increase in attractive electrostatic forces between negatively charged biosorbent and positively charged Alcian Blue cation. Apart from the surface charge of the
biosorbent, concentration of protons is also very high at lower pH values (Muraleedharan 1993), and it decreases with increase in pH. Therefore, there is a possibility of competition between the protons and the positively charged dye molecule for the same sorption site.

**Effect of salt (NaCl)**

Figure 3 shows the negative effect of salt concentration on Alcian Blue uptake capacity of the biosorbent. Increase in salt concentration from 0 to 100 mmol/L, leads to decrease in dye uptake capacity from 89 to 85%. It may be due to competition of Na\(^+\) with positively charged dye molecule for the same binding sites on the biosorbent surface. Several authors (Ramelow et al. 1992; Donmez & Aksu 2002) have reported similar results for the sorption of heavy metals onto the biosorbent. The adverse effect of ionic strength on dye uptake suggested the possibility of ion-exchange mechanisms being operation in the biosorption process (Maurya et al. 2006).

**Desorption/regeneration experiment**

Desorption/regeneration characteristics of the biosorbent are an important parameter which could influence the overall treatment cost as well its environment degrading potential. Regeneration of spent biosorbent could also provide an option for recovery of spent dye and the biosorbent for reuse, which further contributes to the economy of wastewater treatment. Desorption studies can also provide a basis to understand the mechanism of dye biosorption (Mittal & Venkobachar 1989).

Desorption studies have been carried out in two phases. In first phase, the efficiency of several desorption agents (water, sulfuric acid, hydrochloric acid and acetic acid 0.1 M concentration) has been studied. The results of the first phase experiments could be helpful in selection of efficient desorption/regeneration media, besides delineating the biosorption mechanism. In second phase, effect of the strength of the regenerating agent has been studied.

Figure 4 indicates that dye could not be desorbed substantially (about 1%) using distilled water and thus rules...
out the possibility of physical sorption between the dye and the biosorbent. However mineral acids namely H₂SO₄ and HCl could desorb 37 and 51% respectively. This indicates ion-exchange may play an important role in the dye sorption (Mittal & Venkobachar 1989). It can also be observed from Figure 4 that acetic acid could also desorb up to 51% Alcian Blue dye efficiently and thus indicates chemisorption could be in operative as major mechanism in dye sorption process (McKay et al. 1987; Mittal & Venkobachar 1989; Maurya, 2005).

Figure 5 shows the effects of the strength of hydrochloric acid on desorption of dyes. It is observed that in all case there was an increase in desorption of dyes with the increase in strength of hydrochloric acid from 0.05 to 0.1 M. However, increased strength of the acid above 0.1 was not able to enhance desorption of dyes.

CONCLUSIONS

Immobilised biomass of wood-rotting dead macro-fungus (Fomitopsis carnea) was successfully applied for the sorption of Alcian Blue a ‘basic dye’ from aqueous phase solution. For immobilization of the biomass Polyvinyl Alcohol (PVA) was employed as a support matrix. Bottel point equilibrium isotherm experiment was conducted at various temperatures to estimate monolayer saturation capacity of the immobilized biosorbent at corresponding temperature. As temperature was raised from 10 to 40°C, dye biosorption increased from 11.1 to 24.2 mg/g. Higher sorption at higher temperature indicated that biosorption process was endothermic in nature and biosorption mechanism might be chemisorption and/or ion-exchange. Higher removal of dye was also observed at higher pH. However, increased salt concentration from 0 mmol/L to 100 mmol/L reduced removal rate from 89 to 85%. Desorption of dye could be up to 51% using 0.1 M hydrocholoric/acetic acids and thus suggests that ion-exchange and chemisorption type sorption could be the possible dye sorption mechanism. However, when higher strength hydrochloric acid (up to 1 M) was employed for desorption, no change was observed beyond 0.1 M.

REFERENCES


