Decolorization of Triphenylmethane Dyes using Immobilized Fungal Biomass

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Abstract

A dye is a colored soluble substance having affinity towards the substrate to which it is being applied. They are released as effluent from textile, leather, paper and other industries. Dyes causes turbidity thus interferes with photosynthesis of the phytoplankton. Other physical characteristics of the water include odour, change in dissolved oxygen, and salinity are also affected by dye contamination. Toxic nature of some dyes destroys fishes and microorganisms responsible for self-purification of water in streams. There are many classes of dyes in which triphenyl methyl dyes and azo dyes shows most toxic effects. Crystal Violet may cause cancer, it serves as eye irritant, shows harmful effects after inhalation or ingestion and also act as mitotic poison as well as clastogen. Ttriphenyl methyl dyes and some chemicals related to the dyestuff industries are nephrotoxic, hepatotoxic, cyanosis causing and carcinogenic. Currently removal of dyes from effluents is being done by the physico-chemical means. Such methods are often very costly and though the dyes are removed but accumulation of concentrated sludge creates a disposal problem. There is a need to find alternative methods of treatment that are effective in removing dyes from large volumes of effluents at low cost such as biological or a combination system. In present studies a wide verity of microorganisms were screened and a white-rot fungus *Phanerochaete chrysosporium* (MTCC 787) was found to be the best microorganism for decolorization of Crystal violet and Malachite green dyes. Immobilization of the microorganism was done over loffa sponge for efficient and repeated use of the biomass for removal of the dyes. Loffa sponge is an inert natural cellulosic fibber matrix, obtained from ripen fruits of *Loffa cylendrica*. Immobilization of the fungal biomass over the matrix improved efficiency of the biomass due to less dense fibber packing as compare to the free fungal biomass. Percentage decolorization through living and dead biomass of *Phanerochaete chrysosporium* was investigated and found to be 78.2% and 50.5% respectively in case of Malachite Green and 70.5% and 48% respectively in case of Crystal Violet dye. This deference indicates that metabolic activity is involved in dye decolorization along with adsorption. This is the first report of removal of triphenyl methyl dyes by loofa sponge immobilized *Phanerochaete chrysosporium* biomass.

Keywords - *Phanerochaete chrysosporium*, Loffa sponge, Crystal Violet, Malachite green, Dye decolorization.

Introduction

A dye is a colored soluble substance having affinity towards the substrate to which it is being applied. They are released as effluent from textile, leather, paper and other industries and causes water and land pollution if disposed in improper way and dye polluted water has very destructive impact on human health (Blackburn *et al*., 2004). Dyes causes turbidity thus interferes with photosynthesis of the phytoplankton and other physical characteristics of the water are also affected by dye contamination

(Banat *et al.*,1996). Toxic nature of some dyes destroys fishes and microorganisms responsible for self-purification of water streams thus harm self renewability power of river streams. There are many classes of dyes, in which triphenyl methyl dyes and azo dyes shows most toxic effects (Shore *et al.*,1996). Crystal Violet may cause cancer; eye irritation, shows harmful effects after inhalation or ingestion and also act as mitotic poison as well as clastogen. Ttriphenyl methyl dyes and some chemicals related to the dyestuff industries are nephrotoxic, hepatotoxic, cyanosis causing and carcinogenic.

Government legislation is forcing textile industries to treat their waste effluent. The conventional wastewater treatment systems are unable to remove recalcitrant dyes from the effluents. Currently removal of dyes from effluents is by the physico-chemical means. Such as membrane filtration (Mahanta *et al.*, 2008), advance oxidation (Shi *et al.*, 2007), photocatalysis (Lee *et al.*, 2006), coagulation (Chen *et al.*, 2007), and adsorption (Mahanta *et al.*, 2009), these methods are often very costly and accumulation of concentrated sludge creates a disposal problem. There is a need to find alternative methods of dye removal from large volumes of effluents at low cost. Biological or combination systems can fulfil these requirements. Textile industries consume large volumes of water and chemicals for wet processing of textiles. Many dyes are difficult to decolorize due to their chemical structure and synthetic origin.

In triphenylmethane dyes a central carbon atom is bonded to two benzene rings and one *p*-quinoid group (chromophore). The auxochromes are - NH_2, -NR_2 and –OH. Triphenylmethane dyes are widely used in the textile industries for dyeing of polyacrylon nitrile, nylon, modified nylon, wool, silk and cotton (Bekc *et al.*, 2008). Some of the triphenylmethane dyes are used in medicine; as biological stains, in paper and leather industry as colouring material.

Crystal Violet (CV) is a monovalent cationic triphenylmethane dye having molecular formula $C_{25}H_{30}N_3Cl$. It has extensive uses in human and veterinary medicine, biological stain and as textile dye. Malachite Green (MG) is a basic dye having chemical formula $C_{23}H_{25}N_2Cl$ also used in various biological strains and industries.

Biological processes are getting more attention as they are cost effective, environment friendly and do not produce large amount of sludge. Among biological processes, the adsorption technique is dreadfully attractive because of its, economic feasibility, simplicity of system design, good efficiency and easy operation and handling (Wong *et al.*, 2003). Present study was carried out to study of decolorization of Crystal Violet and Malachite Green dyes by immobilized microbial systems. Loofa sponge was used as the supporting matrix for the immobilization of selected microorganism. Loofa sponge is a natural fibrous matrix obtained from the ripened fruits of *Luffa cylindrical*.

Materials and methods

Microorganisms and culture medium

Phanerochate crysosporium MTCC 787, *Aspergillus nodulans* NCIM 1211, *Pseudomonas putida MTCC 4391, Bacillus licheniformis* MTCC 1483, *B. sublilis* MTCC 1427, *B. cereus* MTCC 8361, *Pseudomonas putida* and *Bacillus* strains were maintained by subculturing in every 3 weeks on slants containing Nutrient Agar. Nutrient Agar medium has the following composition: Beef extract 1.0 gL^{-1}, Yeast extract 2.0 gL^{-1}, Peptone 5.0 gL^{-1}, NaCl 5.0 gL^{-1}, Agar 20.0 gL^{-1}, pH 7.0. *Aspergillus nodulans* was maintained on Potato Dextrose Agar (PDA) slants having composition; Potato infusion of 200 gm potato, Dextrose 20 gL^{-1}, Agar 20 gL^{-1}, pH – 5.6. Maintenance media for *Phanerochate crysosporium* was Malt Extract Agar (MSA) media having the following composition; malt extract 20.0 gL^{-1}, Glucose 20.0 gL^{-1}, Peptone 1.0 gL^{-1}, Agar 20.0 gL^{-1}, distilled water 1000 mL, pH 5.5. The growth mediums for bacterial strains and for *Aspergillus nodulans* have same composition as maintenance media excluding "Agar"

component. For *Phanerochate crysosporium* growth media was consist of following ingredients D-glucose 10.0 gL^{-1}, KH_2PO_4 2.0 gL^{-1}, $MgSO_4.7H_2O$ 0.5 gL^{-1}, NH_4Cl 0.1 gL^{-1}, C_aC_{l2} .$2H_2O$ 0.1 gL^{-1}, thiamine 0.001 gL^{-1}, distilled water 1000 ml, pH - 4.5. All bacterial strains were incubated at 37°C at 100 rpm while fungal strains were grown at 25°C at 100 rpm in incubator shaker.

Materials

Malachite Green was obtained from S.D. Fine Chemicals, Mumbai, India. Crystal Violet (CV; was supplied by Merck, India. All microbial media ingredients were purchased from Himedia, India. A stock solution of Crystal Violet and Malachite Green 1000 mg/L was prepared in double distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions of stock solution. While in the experiments with living microorganisms, calculated amount of dye was added in growth media after the prior growth of microorganism in the flask.

Formulae and calculations

Calculation of uptake capacity

Dye removal can be expressed in two ways; first in terms of uptake capacity and second is percentage removal. Dye uptake capacity (q_e) of biosorbent is dye adsorbed per unit mass of the biosorbent (mg/g). q_e was calculated by using mass equilibrium equation, which is expressed as: (Ranjana *et al.*,2009).

$$q_e = (C_i - C_e)V/W \quad ...(1)$$

where qe is sorption capacity (mg/g) Ci is initial dye concentrations (mg/L) and C_e is dye concentrations (mg/L) in sample, V is the volume of the dye solutions in litter, and W is the weight of biosorbent in gram.

Percentage removal of dye from the solution can be calculated by using following formulae:

$$\% \text{ Decolorization of Dye} = \frac{C_i - C_e}{C_i} X\ 100 \quad ...(2)$$

Meaning of Ci and Ce is same as mentioned above.

Sorption isotherms

Langmuir sorption isotherm

The Langmuir sorption isotherm represents monolayer sorption pattern on the homogeneous surface without interaction between adsorbed molecules (Singh *et al.*, 2005; Kundu and Gupta, 2006). In Langmuir sorption isotherm assumption is that, the molecule bounded to a site does not influence the binding of another molecule to neighbouring site.

The linear form of the Langmuir isotherms is represented by the equation:

$$C_e/q_e = 1/Q^o b + C_e/Q^o \quad ...(3)$$

Where C_e is the equilibrium concentration of solute in solution (mg/L), q_e is uptake capacity of sorbent at equilibrium (mg/g), b and Q^o are the Langmuir constants related to the free sorption energy (L/mg) and maximum uptake capacity of biosorbent (mg/g) respectively. For good sorbents, values of 'Q^o' should be high and values of 'b' should be low (Kratochvil and Volesky,1998).

Freundlich Isotherm

The adsorption on heterogeneous surfaces described by the Freundlich sorption isotherm (Freundlich,1907). The Freundlich the isotherm be represented by the equation:

$$\log q_e = \log K_F + 1/n \log C_e \quad ...(4)$$

The intercept of the linear plot between log q_e and log C_e gives 'K_F' which is related with the adsorption capacity and slope gives, '1/n' that tells about the intensity of adsorption.

Thermodynamic evaluation of sorption process

The brief idea of thermodynamic parameters is required in order to study the changes in the reactions held during sorption process (Nouri *et al.*, 2007). Van't Hoff reaction isotherm helps in the Gibbs free energy change (ΔG, kcal/mol) calculations, which is represented by the given equation:

$$\Delta G = -RT \ln K_c \quad ...(5)$$

Where K_c is equilibrium constant, T is absolute temperature and R is the universal gas const ant (8.314 J/K/mol). The value K_c is can be determined from the following equation:

$$K_c = C_{Ae} / C_e \quad ...(6)$$

In which C_{Ae} is concentrations of adsorbed dye molecules on biosorbent and C_e is the remaining dye concentration in the solution at equilibrium in mg/L.

Van't Hoff plot (Plot of ln *Kc* vs. 1/*T*) was used to calculate enthalpy (ΔH, kcal/mol) and change in the entropy (ΔS, cal/mol/K) of adsorption (Liu and Liu, 2008) with the help of following equation:

$$\ln K_c = -\Delta Ho/RT + \Delta So/R \quad ...(7)$$

Where K_c is equilibrium constant, ΔH is enthalpy (kcal/mol), T is absolute temperature, ΔS is the entropy (cal/mol/K) of adsorption and R is the universal gas const ant (8.314 J/K/mol).

Immobilization of Phanerochate crysosporium on loofa sponge discs and its chemical treatment

Loofa sponge is a fibrous matrix of interconnected cellulosic fibbers. This is easily available in nature and can be obtained from the ripen fruits of *Luffa cylindrical*, commonly known as 'Torai'. The biomass of selected microorganism was immobilized over discs of loofa sponge by using method described by M. Iqbal (Iqbal *et al.*, 2005).

For pre-treatment, first excess of water was removed from immobilized fungal biomass using adsorbent paper and air drying. Oven drying of the immobilized biosorbent was avoided to prevent the risk of cracking and channel formation inside the immobilized biomass. For the pre-treatment, 5 gm of immobilized dry biomass was agitated with 500 ml 0.1 N NaOH for 24 hrs. at 120 rpm. After treatment, the biomass was separated out by filtration and washed thoroughly 5 to 6 times with excess of distilled water before use.

Batch biosorption experiments

Batch experiments with both living and dead biomass were conducted in 250 ml Erlenmeyer flasks. Microorganisms were grown in the 100 ml of culture media starting with 2 ml of seed culture as inoculum. After achieving the proper growth of the microorganism, the calculated amount of dye was aseptically added in the culture media and then the flasks were incubated at different temperature and shaking speed in temperature controlled orbital shaker. In the experiments with dead biomass, the biomass was first harvested from growth media by centrifugation at 10000 rpm for 10 minutes and then autoclaved and oven dried at 70°C for 12 hours. 100 ml of dye solution of different initial concentrations was incubated with the biomass at required conditions. Samples were collected at regular intervals and remaining dye concentration in the sample was measures through UV-VIS Spectrophotometer (Shimadzu UV-1600). OD of Malachite Green was measured at 595 nm and of Crystal Violet was measured at 585 nm wavelength. All the experiments were performed in triplicates and the average value was taken.

Result and Discussion

Selection of the suitable Micro organism for the decolorization of dyes

Experiments were performed with a number of microorganisms for selecting potential microorganism for dye decolorization. Figure 1 shows comparative dye decolorization capacity of microorganisms at their optimum growth conditions with 100 mg/L initial dye concentration.

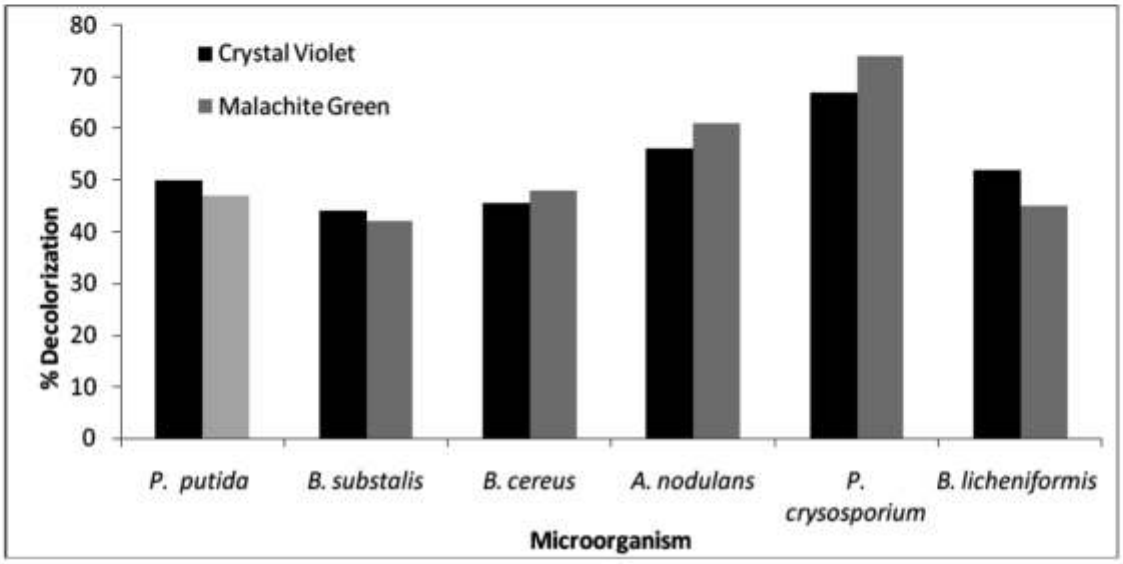

Figure 1: Dye removal capacities of different microorganisms. Experiments were conducted at 100 mg/L dye concentration with optimum growth conditions of the microorganisms.

The order of percentage dye removal capacity of the above mentioned microorganisms for Malachite Green was found to be *Phanerochaete chrysosporium* > *Aspergillus nodulans* > *Bacillus cereus* >*Pseudomonas putida* >*Bacillus licheniformis* >*Bacillus subtilis* and for Crystal Violet *Phanerochaete chrysosporium* > *Aspergillus nodulans* >*Bacillus licheniformis* >*Pseudomonas putida* >*Bacillus cereus* >*Bacillus subtilis.*

Phanerochaete chrysosporium was found to be the best microorganism among the organisms studied. *Phanerochaete chrysosporium* was selected for the further studies for removal of the dyes.

Effect of living and dead biomass of P. crysosporium on the dye decolorization:

Malachite Green and Crystal Violet removal studies were carried out using living and dead biomass of *Phanerochaete chrysosporium*. Results are shown in Figure 2 which indicates that the living microorganisms are much more effective than the dead biomass. Percentage decolorization for Crystal Violet was found to be 48% for dead biomass and 70.5% with living biomass and for Malachite green percentage decolorization was found to be 50.5% and 78.2% with dead and living biomass respectively.

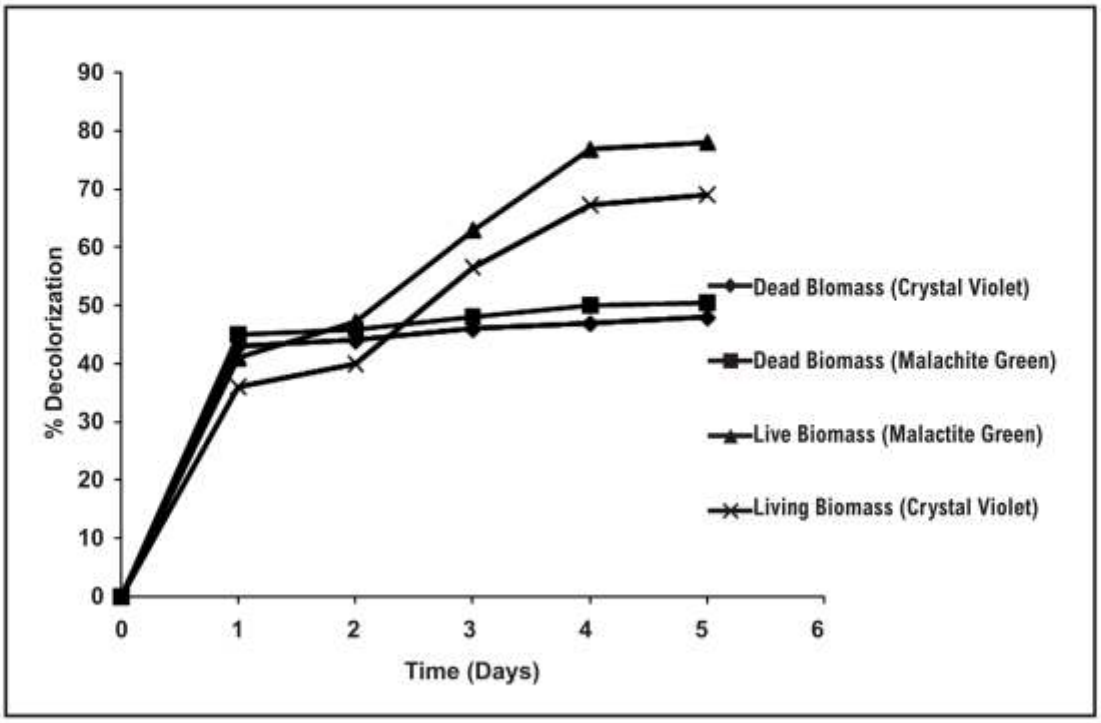

Figure 2: Malachite Green and Crystal Violet removal capacity of living and dead biomass of *Phanerochaete chrysosporium.*

The difference in decolorization capacities of dead and living biomasses may be due to the metabolic activities of the living biomass along with adsorption activities.

Although living fungal biomass was more effective in decolorization of dyes because of involvement of both the metabolic and adsorption phenomena, yet dead biomass of *Phanerochaete chrysosporium* of was further selected for the adsorption studies because of economic feasibility, easy maintenance and handling of the adsorption system based on dead biomass. There is also the possibility to chemically modify the surface characteristics of dead biomass according to the need.

Removal of dyes using immobilized microorganism

The microorganism was immobilized on loofa sponge and chemical treatment of immobilized microorganism was done to improve the dye adsorption capacity of the microorganism. Effect of immobilization and chemical modification on adsorption of CV and MG are shown in Figure 3. Dye uptake per unit weight of biomass was found to be much higher in case of immobilized *Phanerochaete chrysosporium* as compared to free fungal biomass. This is because of the fact that more surface area of the microorganism was available for adsorption of dyes as compared with the biomass pallets. Baig *et al.*, (1999) reported that carboxyl groups are mainly responsible for the binding of cations and the cation binding capacity of biomass surface will increase with increasing number of carboxylate ligands on the biomass surface. Mostly biomasses contain methyl ester groups over their surfaces which do not bind to cations significantly. However, base treatment such as sodium hydroxide can modify these methyl esters to carboxylate ligands, thus cation uptake capacity of biomass get increased (Feng Ning-chuan, 2010).

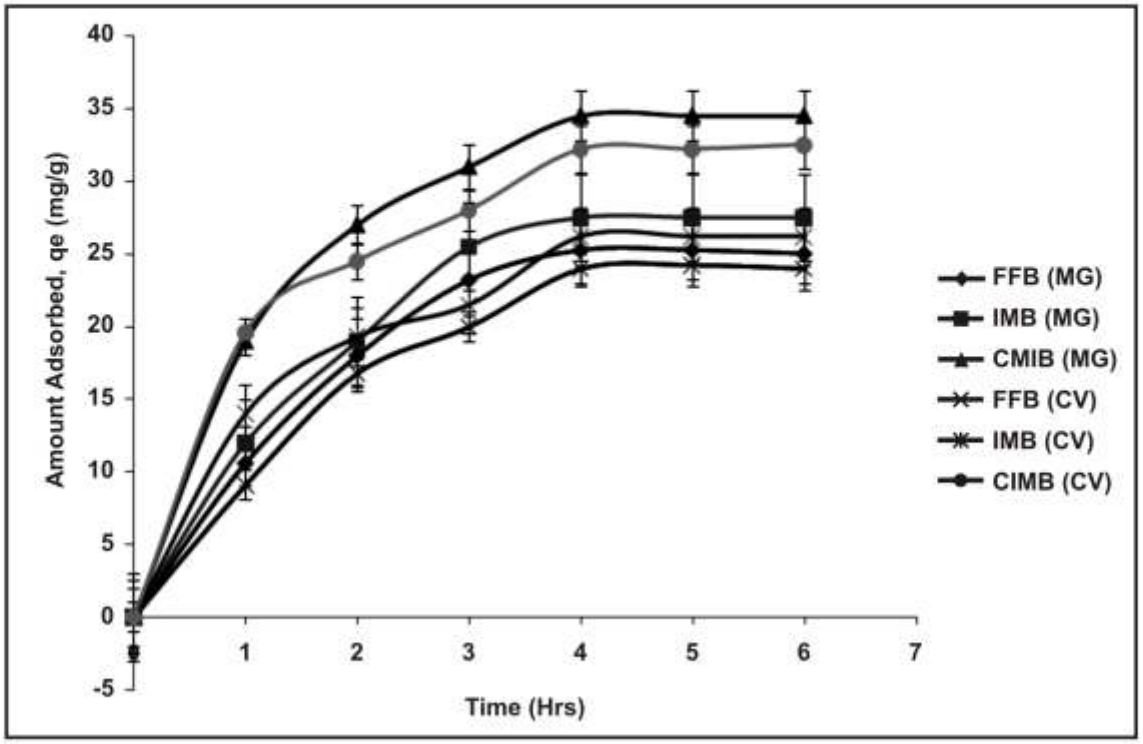

Figure 3: Dye uptake capacity of free, immobilized and chemically pretreatment *Phanerochaete chrysosporium*. (Biomass dose: 0.2 gm/100 mL, pH: 7, FFB = Free fungal Biomass, IMB = Immobilized Biomass, CMIB = Chemically Modified Immobilized Biomass, MG= Malachite Green, CV= Crystal Violet).

Effect of the dye concentration on adsorption

As the dye concentration increased from 100 mg/L to 1000 mg/L, the percentage decolorization decrease and dye uptake capacity (mg/g) of biomass increases, but at more than 400 mg/L the uptake capacity of biomass does not increase further. It may be due to the saturation of the biomass with all the sites captured by the dye molecules. The experiments were conducted with unmodified and chemically treated immobilized biomass at fixed biomass dose: 2 gm/L, pH: 7 and at 30°C. At these experimental conditions adsorption capacities of Crystal Violet and Malachite Green were found 29.6 mg/g and 31.4 mg/g of biomass respectively. On the basis of the above mentioned results 100 mg/L concentration of dyes were selected for further experiments.

Effect of the biomass dose

The experiments were performed by changing the biomass dose ranging from 0.05 to 1 gm/100mL, temperature: 30°C, pH: 7, dye concentration 100 mg/L for 4 hours of contact time. The percentage removal of dye increases with increase in biomass dose while dye uptake by per unit biomass and equilibrium time decreases. The percentage removal of dye increases with increase in biomass dose due to excess available adsorption sites and uptake capacity decreases because of the fact that the dye molecules were not sufficient to saturate all the active sites available for adsorption. In the light of both the facts the intermediate dose (0.2 mg/100 mL) was selected for further studies.

Effect of pH

The influence of pH on the MG and CV adsorption on chemically modified immobilized *Phanerochate crysosporium* biomass was studied. The experiments were conducted by varying the pH from 2 to 12, adsorbent dose 0.2 gm/100 mL, temperature 30°C, dye concentration 100 mg/L and contact time 4 hours. Figure 4 shows the effect of pH on equilibrium adsorption of the both dyes on the biomass surface.

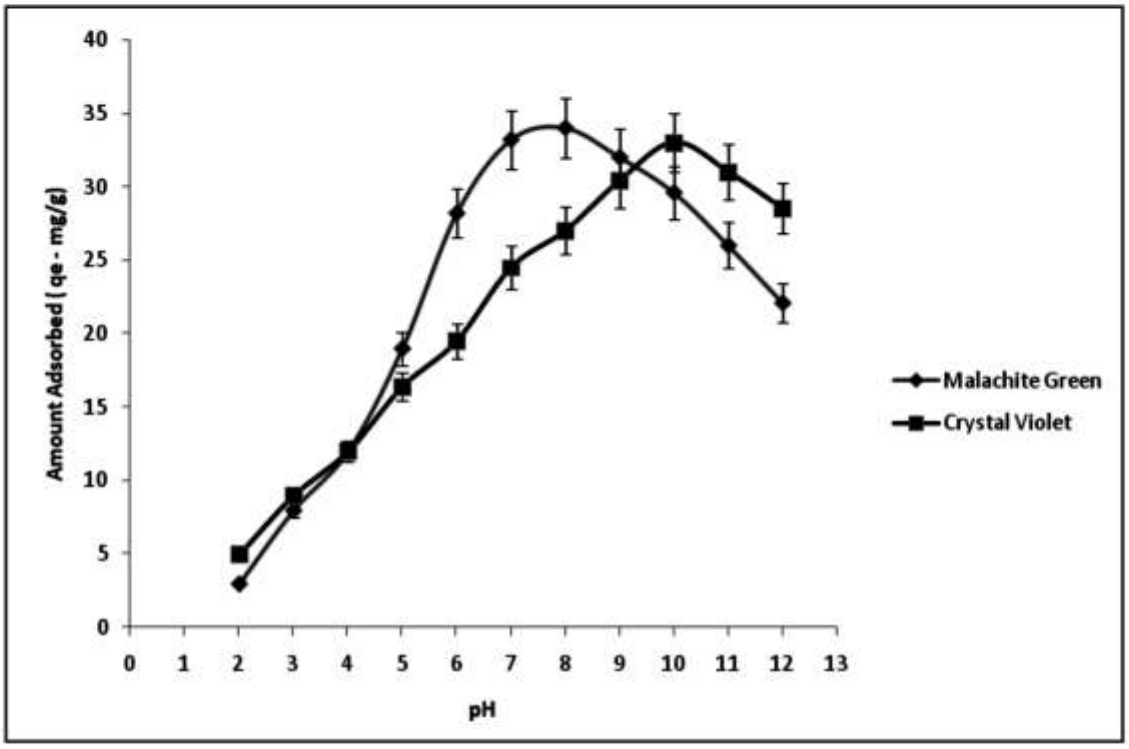

Figure 4: Effect of pH on the adsorption of Crystal Violet and Malachite Green by chemically treated immobilized biomass of *Phanerochate crysosporium* at adsorbent dose 0.2 gm/100 mL, temperature 30°C, dye concentration 100 mg/L and for 4 hours of contact time.

Maximum equilibrium adsorption of MG and CV was obtained at pH 8 and at pH 10 respectively. At lesser pH there was very small adsorption of dyes which may be due to the fact that H^+ ions competes with dye ions for the adsorption sites on the surface of biomass (Samiey *et al.*, 2010, Samiey *et al.*, 2010, Noroozi *et al.*, 2007).

Sorption isotherms

Figure 6(a) shows Langmuir isotherms for CV and MG adsorption over the NaOH treated loofa sponge immobilized biomass and Figure 6(b) represent Freundlich isotherms for the CV and MG adsorption. The calculated Langmuir isothermal and Freundlich isothermal adsorption parameters for the adsorption of MG and CV are summarized in Table 1. The Q^0 values gave approximate evaluation of the maximum adsorption capacity of biomass. It was revealed that NaOH treated loofa sponge immobilized Phanerochaete chrysosporium exhibited high adsorption capacity for both the dyes. Freundlich isotherm indicates that the value of 1/n is lying between $0.1 < 1/n \leq 0.5$ which supports that the biomass is an excellent biosorbent (Samiey *et al.*, 2010). The correlation coefficient is greater than $R^2 > 0.99$ for the

Langmuir isotherms. It indicated that adsorption of both MG and CV takes place mainly through monolayer adsorption pattern, moreover good correlation coefficient for Freundlich isotherm also supports the fact that there is some adsorption on heterogeneous surface in multilayer pattern.

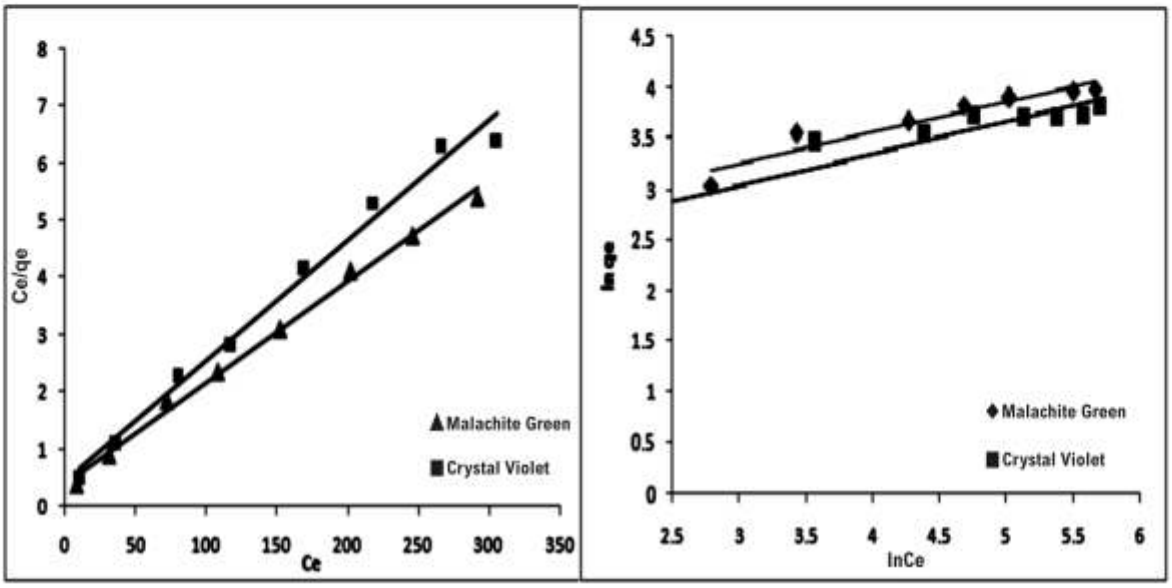

Figure 6: (a) Langmuir isotherm and (b) Freundlich isotherm for the adsorption of the adsorption of Crystal Violet and Malachite Green over chemically treated immobilized *Phanerochaete chrysosporium*.

Table 1: Different constants of Langmuir isotherm and Freundlich isotherm for adsorption of Malachite Green and Crystal Violet on the surface of *Phanerochaete chrysosporium*.

Biosorbent Chemically treated Immobilized biomass	**Langmuir Constants**			**Freundlich Constants**		
	Q° (mg/g)	b (L/mg)	R2	KF	1/n	R2
Malachite Green	58.8	0.0421	0.995	10.66	0.297	0.901
Crystal Violet	47.61	0.047	0.997	7.60	0.314	0.856

Thermodynamic study

Thermodynamic parameters for the Malachite Green and Crystal Violet adsorption are presented in Table 2, calculated using Van't Hoff plot (Plot of ln Kc vs. 1000/T) given in Figure 7. The negative values of ΔH and ΔG° for adsorption of MG and CV indicate that the adsorption process is endothermic and spontaneous, while the positive value of ΔS° indicates increased randomness at the solid-solution interface and good affinity of both the dyes towards the biosorbent (Sun *et al.*, 2008).

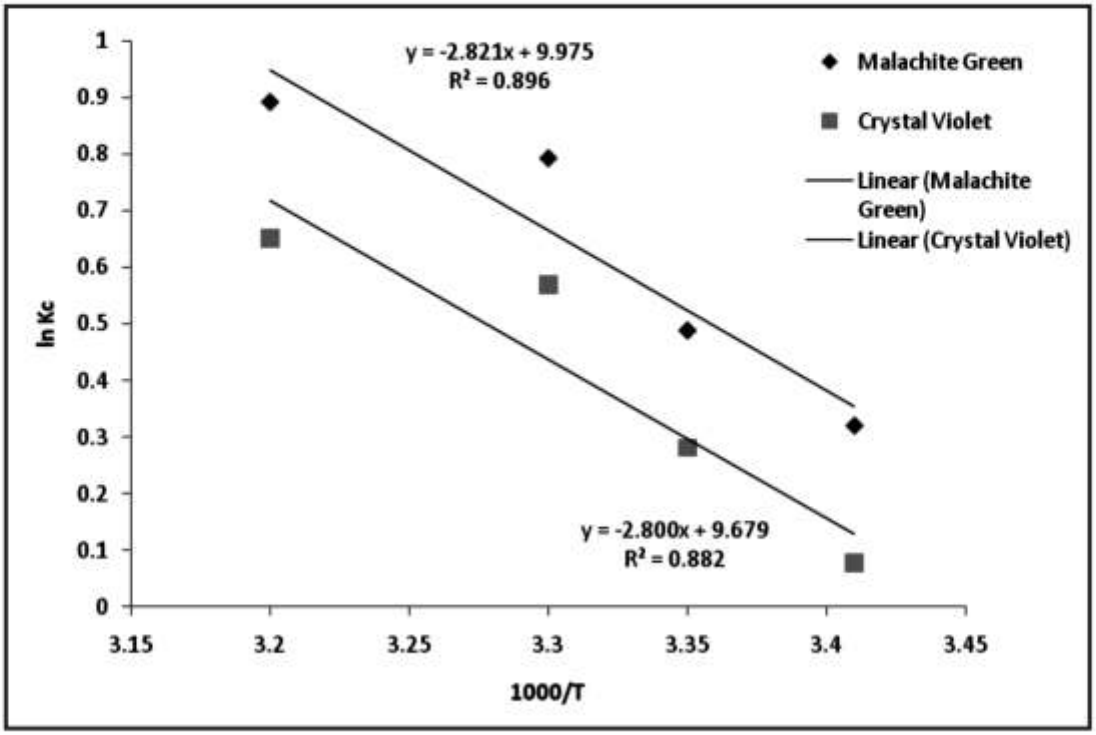

Figure 7: Van't Hoff plot, for the adsorption of Crystal Violet and Malachite Green over chemically treated immobilized biomass of *Phanerochate crysosporium.*

Table 2: Thermodynamic parameters for Malachite Green and Crystal Violet adsorption on of MG over chemically treated immobilized *Phanerochaete chrysosporium.*

Temperature in °K	-ΔG, kcal mol-1	-ΔH, kcal mol-1	ΔS, cal mol-1 K-1
Malachite Green			
293	0.779		
303	1.20		
313	2.07	23.445	82.89
Crystal Violet			
293	0.187		
303	0.697		
313	1.43	23.27	80.47

Conclusion

Phanerochate crysosporium was found to be the best microorganism among the microorganisms studied for dye decolorization. Further this study reveals that NaOH treated *Phanerochate crysosporium* dead biomass acts as an excellent biosorbent for Malachite Green and Crystal Violet dyes. *Phanerochate crysosporium* immobilization over loofa sponge improves dye uptake through biomass due to increase in

available surface for adsorption. Adsorption capacity of dead biomass of *Phanerochate crysosporium* was further improved by chemical pre-treatment with 0.1 N NaOH. Uptake capacity of biomass was increased from 25.25 mg/g to 34.5 mg/g for Malachite Green and from 24 mg/g to 32.2 mg/g of the biomass for Crystal Violet respectively after immobilization and chemical treatment of the biomass. Effects of various parameters viz. pH, temperature, initial dye concentration, contact time on uptake capacity were investigated and optimum conditions for the Crystal Violet adsorption was found as pH: 10, dye concentration: 100 mg/L, incubation time: 4 hrs. The maximum adsorption of Malachite Green was found to be at pH 8 and other conditions were found to be the same as for CV adsorption. Langmuir model better fits the equilibrium data for both the dyes, indicates the monolayer adsorption pattern of both the dyes over the biomass surface. Thermodynamic studies reveal that an adsorption phenomenon of Malachite Green and Crystal Violet on the treated biomass of *Phanerochate crysosporium* is an endothermic and spontaneous process.

Thus this study shows that immobilized and NaOH treated *Phanerochate crysosporium* can be used as an excellent biosorbent for removal of Crystal Violet and Malachite Green dyes from water sources.

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