Research Article

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Biosorption of malachite green by naturally grown algal biomass from Girna river, Jalgaon District, Maharashtra

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Abstract

The algal biomass was harvested from Girna river sites from Jalgaon District. The samples were assessed for the diversity of algal forms. The biomass was sun dried in laboratory and subjected to various chemical pretreatments. The dried powdered algal biomass was used in dyes biosorption studies. Chemical treatment to biomass was found to alter the biosorptive properties of biomass. Acid treatment was emerge as an effective treatment enhancing dye removal capacity of biomass (>90 mg of dye / g biomass). Kinetic studies indicated that the process was requiring <45min for >85% of sorption while process reached an equilibrium in <50 min of contact. Studies also revealed that that the biomass can be reused at least four times without altering the sorption properties. Certainly, these results have developed a trust with algal biomass, otherwise is a problem of algal blooms in rivers and ponds, in the treatment of dye waste waters.

Keywords Algal biomass, biosorption, malachite green, kinetics

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Introduction

Color is the first contaminant to be recognized in wastewaters and has to be removed before discharging into water bodies or on land. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and affects the aesthetic merit, water transparency and gas solubility in lakes, rivers and other water bodies. The removal of color from wastewaters is often more important than the removal of the soluble colorless organic substances, which usually contribute the major fractions of the biochemical oxygen demand (BOD). Methods for the removal of BOD from most effluents are fairly well established; dyes, however, are more difficult to treat because of their synthetic origin and mainly complex aromatic molecular structures. Such structures are often constructed to resist fading on exposure to sweat, soap, water, light or oxidizing agents (Poots *et al.*, 1976; McKay, 1979) and this renders them more stable and less amenable to biodegradation (Fewson, 1988; Seshadri *et al.*, 1994).Dye wastewaters discharged from textile and dyestuff industries have to be treated due to their impact on water bodies, and growing public concern over their toxicity and carcinogenicity in particular. Dyes usually have synthetic origins and complex aromatic molecular structures (Banat *et al.*, 1996). Treatment of dye eluents presents several problems mainly due to the toxicity and recalcitrance of dyestuffs. Discharge of dye eluents into the natural streams may be toxic to the aquatic lives (Kumar 2006). Color affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity. Dyes are synthetic aromatic water-soluble dispersible organic colorants, having potential application in various industries. The dyestuff usage has been increased day by day because of tremendous increase of industrialization and man's urge for color (Mohan et al., 2002). Some of the dyes are carcinogenic and mutagenic of aquatic ecosystems [Sivraj]. Malachite green, basic (cationic) dye, has been extensively used all over the world as a fungicide and ectoparasiticide in aquaculture and very dangerous and has highly cytotoxic property against mammalian cells [Bekci 2009]. The use of biomaterials as sorbents for the treatment of wastewaters will provide as a potential alternate to the conventional treatment and inexpensive ways of removing dyes from large volumes of eluents. Algae are ubiquitous naturally and serve as one of the biomaterials with high capacity for removing dye from contaminated waters.(Pansamriut,2006). Compare to physicochemical processes vs Biological processes have

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potential to convert or degrade the pollutant into water, carbon dioxide and various salts of inorganic nature. The isolation of potent species and there by degradation is one of the interest in biological aspect of effluents treatment Mohan et al., 2002). Malachite Green (MG) is a triphenyl methane dye shown in figure1 which is most widely used for coloring purpose, amongst all other dyes of its category (Gupta et al., 2004). MG has properties that make it difficult to remove from aqueous solutions. If the solution containing MG discharged into receiving streams it will affect the aquatic life and cause detrimental effects in liver, gill, kidney, intestine and gonads. In humans, it may cause irritation to the gastrointestinal tract upon ingestion. Contact of MG with skin causes irritation and redness and pain. Upon contact with eye will lead to permanent injury of human eyes and laboratory animals (Kumar et al., 2005). A total number of 539 taxa belonging to 4 classes are found in Jalgaon. These algae are distributed under 91 genera belonging to 32 families under 14 orders. The aim of present study is to apply potential of naturally grown algae for effective biosorption of malachite green and to reduce also the problem of river water.

Methods

Preparation of Biosorbent

The algal biomass was acquired from different sites of regional river Girna.The site for collection is shown in figure 1 The collected algal biomass was repeatedly washed with water to remove the impurities and dirt. Microscopy was done for evaluation of alge which showed abundance of *Nostoc* species. After this the biomass was dried in shadow for 2-3 days. After drying, the biomass sample was grinded to form powdered algal biomass, which was used for experiments.

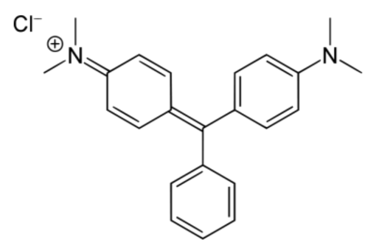
Analysis of Dye

The cationic dye used in this study was Malachite Green and its chemical nature was illustrated in the figure2. The lambda max (619nm) was determined using Shimadzu UV visible spectrophotometer. Stock solution of 1000ppm of dye was prepared and used for experimental study. At each time after Biosorption samples were filtered using filter papers. Percent decolorization was determined using formula

$$\% \text{ Decolorization} = \frac{(\text{OD Initial} - \text{OD Final}) \times 100}{\text{OD Initial}}$$

Figure 1 Site of sample collection

Figure 2 Chemical structure of malachite green



Batch adsorption experiments

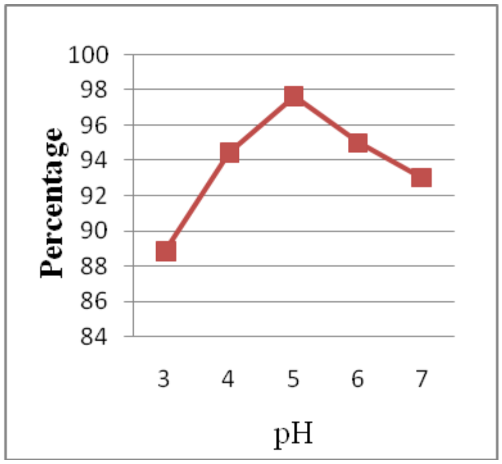
Adsorption experiments were carried out by agitating 5 g of PLS with 250 mL of dye solution for the desired concentration and pH in a horizontal shaker at 100 rpm for the time required to reach the equilibrium state (48 h). Studies were conducted at room temperature using a Dye concentration was estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, 619 nm, using a CamSpec M330 spectrophotometer. The samples were taken from the shaker at predetermined time intervals and the dye solution was filtered through a and then analyzed. Effect of pH, temperature and dye concentration on biosorption as well as reusability of algae for biosorption was studied.

Result

Effect of pH

In order to check the effect of pH on biosorption, the malachite green dye solution of fixed concentration was conditioned to different pH (ranging from 3 to 7). The malachite green solutions were then contacted with treated as well as untreated algal powders. The optical density (OD) of malachite green before and after decolorization was measured (619nm) using UV-visible spectrophotometer (Shimadzu, UV-1601) The sorption of dye as a function of initial pH (Figure 3) showed clearly that the solution pH had minimum role in biosorption of dye molecules by algal biomass. However, sorption increased with increase in solution pH up to pH 5 and then it was decreased. The results have indicated that pH 4 to 6 was an optimal range of pH for biosorption.

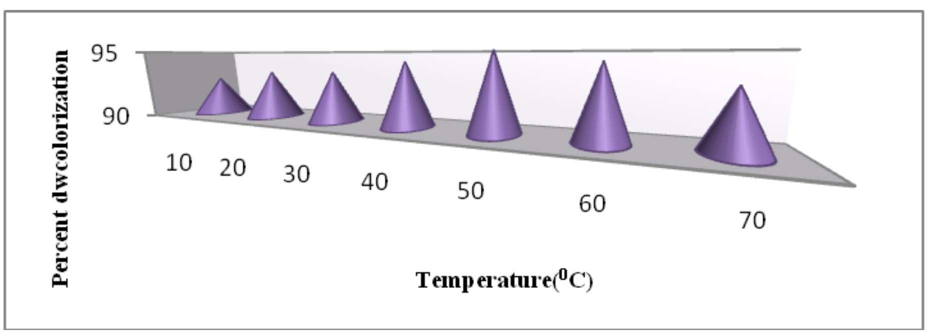
Figure 3 Effect of pH on biosorption



Effect of temperature

Bisorption experiment is carried out at different temperatures ranging from 10^0C to 70^0C.At all temperatures biosorption capacity was more than 90% showing that temperature has minimum role in biosorption process as well as can easily carried out at any temperature. However optimum temperature found was 50^0C shown in figure 4.

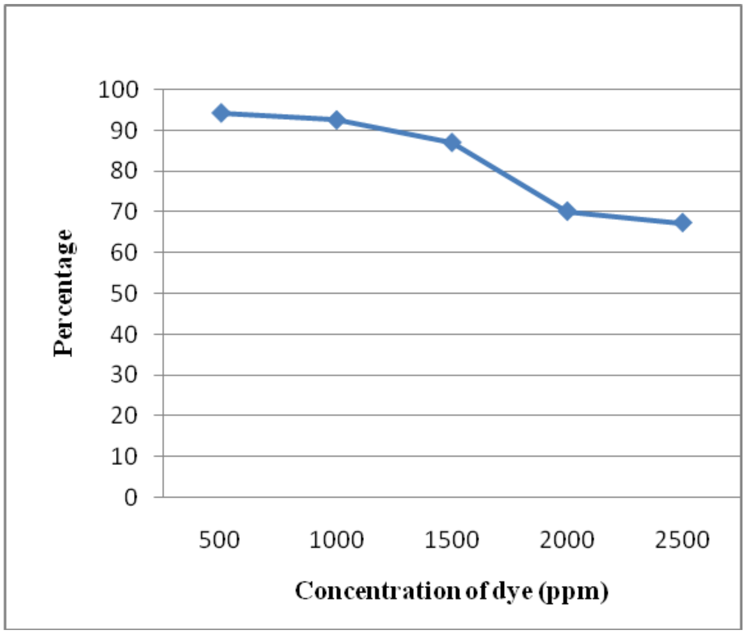
Figure 4 Effect of temperature on biosorption



Effect of dye concentration

The sorption of dye as a function of initial concentration indicated in figure5 showed that the concentration of solution played a vital role in biosorption of dye molecules by algal biomass. The uptake of dye (mg of dye/g biomass) was found decreased with increase in initial concentration, that could be attributed to early saturation of binding sites and less number of available binding sites on biomass. Under higher concentration there was very little biosorption of dye molecules. This is because of saturation of binding sites on the surface of algal biomass.

Figure 5 Effect of dye concentration on biosorption



Effect of dye loading capacity

The dye removal experiments performed in batch contact experiments may not give clear idea about the total dye loading capacity of biomass. In a batch experiment the biomass from one batch was separated by centrifugation and recharged with fresh aliquots of dye solution with same concentration. This would give us the reusability of biomass and total breakthrough capacity of biomass. The dye solutions with varying concentrations (500, 1000, 1500 mg/l) were used in separate experiments.

The results of biosorption saturation experiments are depicted in Figure 6. The general pattern seen from these figures indicated that algal biomass could be reused for subsequent cycles. The saturation of binding sites was seen earlier at higher dye concentrations. The drop in dye removal in fourth cycle could be because of saturation of binding sites. It could be also attributed to the loss of biomass during each cycle, reducing the net available number of sites. The total loading capacity of biomass can be calculated as cumulative dye removed from solutions during each cycle (mg dye bound/ g biomass). The binding capacity is an actual measure of biosorption efficiency of algal biomass. The dye loading capacity was increased with increase in initial dye concentration. The algal biomass was found to be effective among the pretreated biomass tested showing highest dye binding capacity of 97.13% at 100 ppm. As the dye initial concentration was raised from 100ppm to 2500 ppm dye loading capacity was decreased but repeats of each studied concentration was found to be effective dye loading capacity upto the studied 4 repreats.

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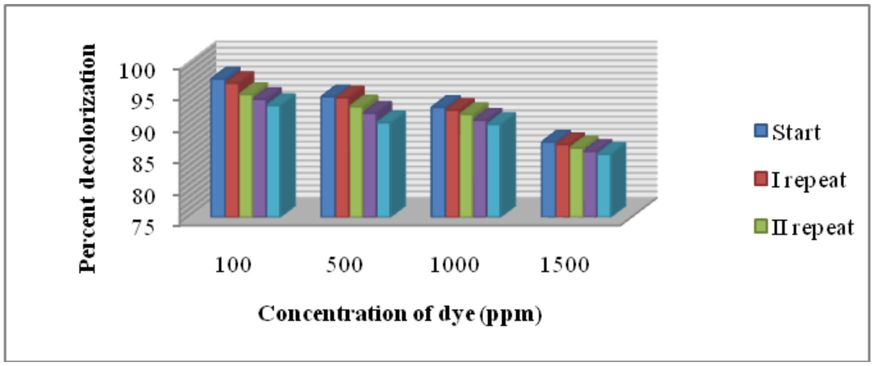
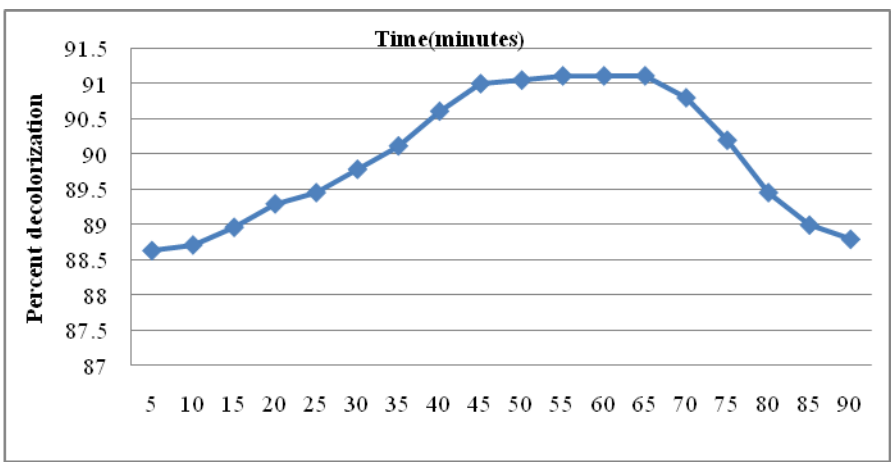
Figure 6 Binding capacity and reusability of algal biomass



Kinetics of dye biosorption by algal biomass

In practice, it is difficult to design a treatment process on the basis of the equilibrium position of the reaction because the reaction usually takes too long to go to completion. Therefore, time profile of biosorption process help to design the process. There are two types of rate of biosorption- 'overall rate of biosorption' and 'an intrinsic rate of biosorption'.Overall biosorption rates are the result of the intrinsic biosorption rate superimposed on the rate of the ions from the bulk solution to the actual biosorption sites. In order to study the dye biosorption kinetics, 2 g of the algal powder was contacted with 100 ml of dye solution (100 ppm) in 250 ml Erlenmeyer flasks. Flasks were incubated on rotary shaker at room temperature, 120 rpm. Samples of dye solutions were withdrawn from the flasks at different time intervals (5 to 60 min) and analyzed for absorbance at 619 nm. The data on kinetics of biosorption of malachite green by algal biomass are depicted in Fig. 6. It can be seen that 90 % of total adsorption was recorded in 45 min. The process reached equilibrium <50 min.

Figure7 Kinetic study of biosorption



Conclusion

The present study is an attempt towards the search for cheaper adsorbent system for removal toxic pollutants such as dyes. Removal and disposal of naturally grown algal mass is also an environmental concern of today. This study aimed at coupling these two major environmental problems. To summarize, algal biomass was found abundantly available in rivers streams specially in winter to summer seasons. All the samples have shown some potential towards removal of dyes from solutions. Chemical treatment to biomass was found to alter the biosorptive properties of biomass. Acid treatment was emerged as an effective treatment enhancing dye removal capacity of biomass (>90 mg of dye / g biomass). Kinetic studies indicated that the process was requiring <45 min for >85% of sorption while process reached an equilibrium in <50 min of contact. Studies also revealed that the biomass could be reused at least four times without altering the sorption properties. Certainly, these results have opened up new research area demanding further exploitation.

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