Waste Management 38 (2015) 424–430

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

# Study of the degradation of methylene blue by semi-solid-state fermentation of agricultural residues with *Phanerochaete chrysosporium* and reutilization of fermented residues

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ARTICLE INFO

*Article history:*
Received 5 October 2014
Accepted 12 January 2015
Available online 31 January 2015

*Keywords:*
Methylene blue
Agricultural residues
Biodegradation
Adsorption
*Phanerochaete chrysosporium*
Reutilization

ABSTRACT

The degradation of methylene blue (MB) by semi-solid-state fermentation of agricultural residues rice straw with *Phanerochaete chrysosporium* and the reutilization of fermented residues was investigated. A maximum decolorization of 84.8% for an initial dye concentration of 0.4 g/L was observed at the optimal operating conditions (temperature 35 °C, pH 5). As compared to the previous results obtained using synthetic materials as substrate, the results in the present study revealed an excellent performance of the bioreactor in decolorizing the wastewater containing MB, which is due to this type of cultivation reproducing the natural living conditions of the white rot fungi. Among the two ligninolytic enzymes that are responsible to the decolorization, manganese peroxidase (MnP) activity was found better correlated with decoloration percentage. Our results also provide a first step to recycling the fermented residues for the removal of MB from aqueous solutions, the maximum adsorption capacity of the fermented residues reached 51.4 mg/g.



## 1. Introduction

Dyes are used in many industries, such as paper, plastics, food, cosmetics, and textile, in order to color their products. The presence of these dyes in water, even at very low concentrations, is highly visible and undesirable (Gong et al., 2009). Methylene blue (MB) is the most commonly used dye has caused greatly environmental pollution due to its toxicity (Zhang et al., 2011b). MB can negatively affect photosynthesis, and cause eye burns which may be responsible for permanent injury to eyes of human and animals (Tan et al., 2008). Furthermore, MB can also lead to heart rate increasing, vomiting, shock, Heinz body formation, cyanosis, jaundice, and tissue necrosis in humans (Vadivelan and Kumar, 2005). Therefore, the elimination of MB from industrial effluents represents a major ecological concern.

Microbial decolorization technique offers complete cleanup of colored effluent in a natural way as it mostly reduces the dyes to much simpler compounds of carbon dioxide, ammonia, and water by initiating cleavage of the bonds in the dyes (Singh and Pakshirajan, 2010). White rot fungi are the most efficient microorganisms in breaking down synthetic dyes, and the representative species *Phanerochaete chrysosporium* (*P. chrysosporium*) has been most extensively studied (Wesenberg et al., 2003). Two extracellular peroxidases, lignin peroxidase (LiP) and manganese peroxidase (MnP), produced by the fungus were considered to be responsible for the decolorization of dyes (Barr and Aust, 1994; Spadaro et al., 1992).

Based on the results of previous studies, semi-solid or solid fermentation system presents several advantages over the submerged one such as simpler techniques, superior productivity, less energy requirements and low wastewater output (Moldes et al., 2003). A variety of synthetic material like nylon-web, polyurethane foam, porous plastic material and silicon tube are common immobilization supports for the production of ligninolytic enzymes (Sedighi et al., 2009).

In this work, agricultural wastes rice straw was utilized as the immobilization support. About 300 million tons of straw is deserted or incinerated in China every year, which is not only destruction of soil and atmospheric environment, but also waste of resources (Xu et al., 2011). Compared with the conventional

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http://dx.doi.org/10.1016/j.wasman.2015.01.012
0956-053X/

solid fermentation system, this system has the following advantages: (1) as a type of renewable agricultural wastes, rice straw is especially abundant in nature, which makes the process more economical and environment-friendly (Ashori and Nourbakhsh, 2010; Bansal et al., 2012); (2) considerable amounts of ligninolytic enzymes were continually produced during the biodegradation of rice straw by *P. chrysosporium* (Cheng et al., 2014; Zeng et al., 2013a); (3) the rice straw after fermentation can be reused as efficient bioadsorbents for removing dyes from polluted wastewater, since *P. chrysosporium* would break its surface structures and generate more adsorption sites (Huang et al., 2008; Taccari et al., 2009); (4) *P. chrysosporium* can compete with other microorganisms when using rice straw as the nutrient, as the cellulose from these nutrients is not directly available to other microbes (Wesenberg et al., 2003).

The objective of this study was to assess the feasibility of employing a semi-solid fermentation system which including agricultural wastes rice straw and white rot fungus *P. chrysosporium* for the degradation of MB from industrial effluents. The degradation efficiencies of MB under different initial dye concentrations were investigated. The impacts factors of removal efficiency (pH values and temperature) and the activities of two main ligninolytic enzymes including LiP and MnP were evaluated. The reutilization of fermented residues for the removal of MB from aqueous solutions was also studied.

## 2. Materials and methods

### 2.1. Chemicals and strain

Rice straw used in this experiment was purchased from a farm in Yuelu District (Changsha, China). Rice straw was dried at 45 °C, and then it was ground to pass through a 4 mm nylon screen. The fungus *P. chrysosporium* strain BKMF-1767 was purchased from China Center for type Culture Collection (Wuhan, China). *P. chrysosporium* was maintained on potato dextrose agar (PDA) slants at 4 °C. Before the inoculation, the spores were gently scraped from the agar surface and blended in the sterile distilled water as spore suspension. The spore concentration was assessed by microscope with a blood cell counting chamber and adjusted to $2.0 \times 10^6$ spores per mL. Methylene blue ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$, FW = 373.9) was purchased from Sinopharm Chemical Reagent Co. LTD (Shanghai, China). All other chemicals used were of analytical grade. The dye effluent was prepared by dissolving MB in distilled deionized water to produce a stock solution of 1.0 g/L. From this, 200 mL volumes containing initial concentrations of 0.2, 0.3, 0.4, 0.5, and 0.6 g/L were prepared.

### 2.2. Culture conditions and sampling

The cultivations were carried out in semi-solid-state conditions, which are defined as the growth of microorganisms on solid materials in the presence of small quantities of free water (Rodríguez Couto et al., 2000). The moist insoluble substrates provide carbon, nitrogen, minerals and other nutrients, as well as anchorage for the microorganisms (Nigam et al., 2000). In this work, the cultivation was carried out in 500 mL flasks containing 60 g of rice straw powder and 200 mL of dye effluent in nitrogen-limited synthetic growth medium (Sedighi et al., 2009). In order to acquire the optimum condition for the decolorization, the experiments were carried out at varied initial conditions: pH 2–7 and temperature 20–45 °C. The pH of the growth medium was adjusted by using HCl or NaOH. To investigate the decolorization capacity of this semi-solid fermentation system at the optimum conditions, 5 experiment groups were started with different concentrations of MB (0.2, 0.3, 0.4, 0.5 and 0.6 g/L). Control without MB group was setup to investigate dynamic changes of enzymes activities. Each flask was stoppered and autoclaved twice for 20 min at 121 °C, then 5 mL spore suspension was inoculated in them at room temperature. The fermentation experiments were performed for 22 days. In the entire fermentation period, the humidity was maintained at 75%, which is optimal for ligninolytic enzyme production and supportive of fungal growth (Shi et al., 2008). To avoid the effects of sampling on fermentation, 3 alike conical flasks for each concentration were prepared in the same way. After inoculation, fermented straw was harvested from different sites in the flask every other day and mixed together homogeneously for routine analysis. All experiments were performed in three replicates.

### 2.3. pH determination

1 g of fermented straw was mixed with 20 g distilled water on a rotary shaker at 200 r $min^{-1}$ for 30 min and then centrifuged at 3500 r $min^{-1}$ for 15 min. The supernatant fluid was filtered through 0.45 μm filter papers and then pH of the filtrate was measured with a Mettler Toledo FE 20 pH meter.

### 2.4. Extracellular enzymes activity assays

1 g of fermented straw was mixed with 20 g distilled water on a rotary shaker at 200 r $min^{-1}$ for 30 min and then centrifuged at 3500 r $min^{-1}$ for 15 min. The supernatant fluid was filtered through 0.45 μm filter papers. Substrate filtrate was used for ligninolytic peroxidase activity analyses with a Shimadzu 2550 UV–visible spectrophotometer. LiP activity was measured as described by Sayadi and Ellouz (1995), one unit (U) of LiP activity was defined as the amount of the enzyme required to produce 1 mM veratryl aldehyde from the oxidation of veratryl alcohol per minute. Each reaction mixture (total volume 3 mL) contained 1.5 mL of 100 mM sodium tartrate (pH 3.0), 1 mL of 10 mM veratryl alcohol which was replaced by the same volume of sodium tartrate in the control mixture, 0.4 mL of enzyme extract, and 0.1 mL of 10 mM $H_2O_2$. The reaction was started with $H_2O_2$, and the formation of veratraldehyde was monitored at 310 nm. MnP activity was measured as described by Zhao et al. (2012), and one unit (U) of MnP was defined as the amount of enzyme required for producing 1 mM $Mn^{3+}$ from the oxidation of $Mn^{2+}$ per minute. Each 3-mL reaction mixture contained 2.4 mL of 50 mM sodium succinate (pH 4.5), 0.1 mL of 15 mM $MnSO_4$ replaced by 0.1 mL of sodium succinate in the control mixture, 0.4 mL of crude enzyme solution, and 0.1 mL of 10 mM $H_2O_2$. The reaction was initiated at 37 °C by adding $H_2O_2$, and the rate of $Mn^{3+}$-succinate complex formation was monitored by measuring the increase in absorbance at 240 nm.

### 2.5. Analysis of MB content

To determine the decolorization grade, 20 mL of ethanol were added to 1 g of fermented straw then shaken at room temperature for 2 h. Using this extraction mixture, even the dye adsorbed in the fermented residues could be recovered. The supernatant was measured for the determination of the concentration of residual MB. MB concentration is measured by using a Shimadzu 2550 UV–visible spectrophotometer at a maximum absorbance (664 nm) (Kim et al., 2014). Appropriate dilution was processed to ensure that the concentration of the solution was within the range of the standard curve.

### 2.6. Reutilization experiments

After 22 days fermentation, a desired amount of fermented residues was harvested and air dried at 50 °C for 24 h. Absorption experiments were performed by contacting 1 g fermented residues and 400 mL MB solutions (50, 100, 150 and 200 mg/L) in 500-mL flasks at 30 °C. The flasks were agitated in a shaking incubator at a constant shaking rate of 120 rpm. After 4 h, supernatants were measured for the concentration of residual MB. MB concentration is analyzed with a Shimadzu 2550 UV–visible spectrophotometer at a maximum absorbance wavelength (664 nm). The amount of MB removal in experiments, $Q$ (mg/g), was calculated according to the following equation:

$$Q = (C_0 - C_e)V_t/m \quad (1)$$

where $C_0$ and $C_e$ (mg/L) are the initial and final concentrations of MB in solution, $V_t$ (L) is the volume of the solution, and $m$ (g) is the mass of the total fermented residues.

### 2.7. Statistical analysis

Data are presented as the means of three replicates, and the standard deviations were used to analyze the experimental data. All figures if necessary were derived from origin 8.0. The obtained data were submitted to analysis of variance (ANOVA) and compared by Tukey's test ($p < 0.05$) using the software package SPSS (version 18.0).

## 3. Results and discussion

### 3.1. Effect of initial pH

Previous studies on dyes biodegradation by microorganism have indicated that pH is an important parameter affecting the biodegradation process (Xu et al., 2012; Zeng et al., 2013b). To obtain the optimum pH for dye biodegradation by *P. chrysosporium*, the fermentation started at different pH values ranging from 2.0 to 7.0. The effect of pH on decolorization of MB by *P. chrysosporium* is illustrated in Fig. 1. The maximum decolorization for MB studied in this work was observed at a pH 5.0 and the percentage decolorization decreased at both extremes of pH (<5.0 and >5.0). After 22 days fermentation, a maximum decolorization of 81.8% for an initial dye concentration of 0.4 g/L was observed when the temperature was 30 °C.

These observations indicate that the optimum initial pH for the fungus *P. chrysosporium* is 5.0. In order to acquire a precise understanding of the influence of pH to the decolorization, the variation in pH during the fermentation was studied. As shown in Fig. 1, there was a decline of pH during the primary stage of fermentation, after 8 days, the pH value increased slightly and later tended to stabilize. The variation in pH was due to the fact that the fungus produces organic acids such as oxalate during the initial growth period, which later decomposed by MnP (Li et al., 2011). It was noted that in medium fermentation stage, the pH of the substrate was around 4.5, which is exactly the optimum pH for MnP to carry out the catalytic reaction (Huang et al., 2008; Zhang et al., 2011a). On the other hand, pH 4.5 is also within the physiological pH range that is optimum for growth and lignin degradation (Tatarko and Bumpus, 1998).

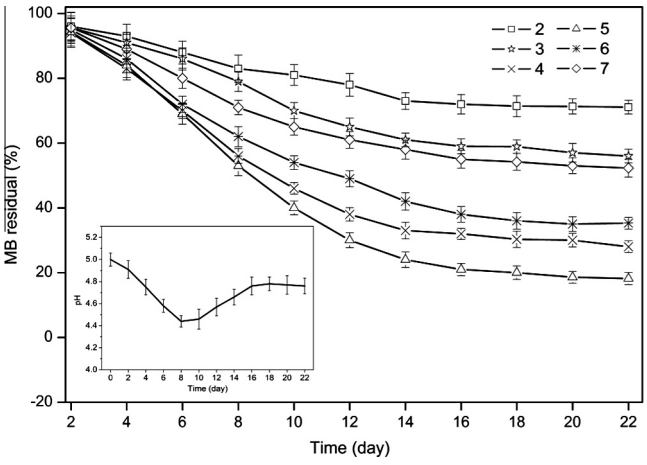


**Fig. 1.** Effect of initial pH (2–7) of the dye methylene blue (MB) on the percentage of decolorization by semi-solid state cultures of *P. chrysosporium* (*T*: 30 °C; initial dye concentration 0.4 g/L). The insert is the change of pH during the fermentation (initial pH 5.0). The bars represent the standard deviations of the means ($n = 3$).

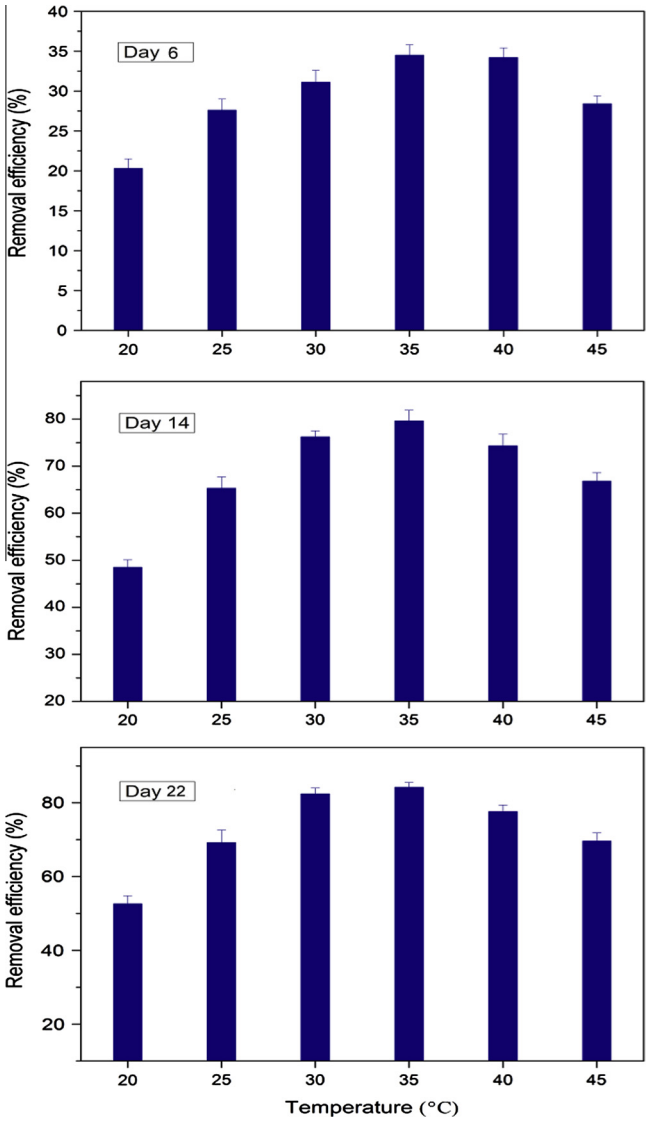


**Fig. 2.** Effect of temperature (20–45 °C) of the dye methylene blue (MB) on the percentage of decolorization by semi-solid state cultures of *P. chrysosporium* (initial dye concentration: 0.4 g/L; initial pH: 5). The bars represent the standard deviations of the means ($n = 3$).

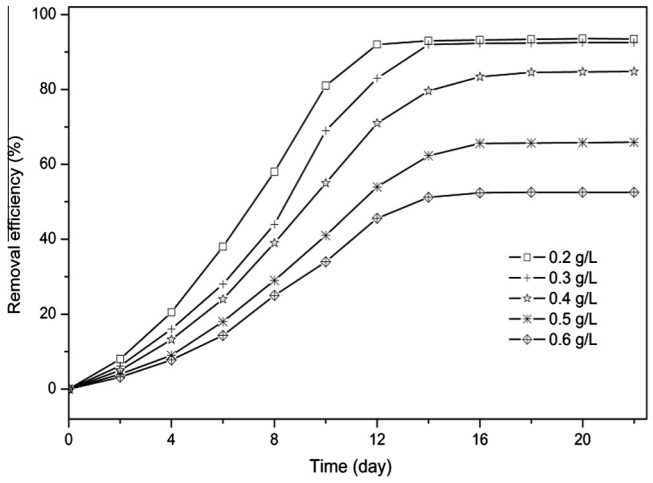


**Fig. 3.** Decolorization at the optimum conditions. The initial concentrations of methylene blue (MB) were varied from 0.2 to 0.6 g/L. Results are mean values of triplicate, and the standard deviations are below 5% ($n = 3$).

### 3.2. Effect of temperature

The effect of temperature on the biodegradation of MB was investigated at the temperature ranged between 20 and 45 °C at an initial concentration of 0.4 g/L. As seen in Fig. 2, at the end of the fermentation, the biodegradation of MB was noted to increase with the increase in temperature up to 35 °C and decreased with the further increase in temperature. A similar trend was observed on after 6 and 14 days of fermentation. Result showed that temperature affected removal rate of MB observably: during 22 days of 35 °C incubation 84.3% removal was achieved with merely 51.6% concentration decrease for the 20 °C incubation.

Our results here suggest that 35 °C is the optimum temperature for the decolorization. At higher (>35 °C) or lower (<35 °C) temperatures the decolorization activity of the fungus gets reduced, which is probably because the production and also the activity of peroxidases for decolorization were restrained under the adverse temperature. Hence, all further experiments were carried out at 35 °C.

### 3.3. Effect of methylene blue concentrations

In order to investigate the decolorization capacity of this semi-solid fermentation system, experiments were studied at the optimum conditions (pH 5, 35 °C), the initial concentrations of MB varied from 0.2 to 0.6 g/L. The results shown in Fig. 3 indicate that *P. chrysosporium* present excellent decolorization ability in this semi-solid medium, and most of MB was degraded after 22 days fermentation even at the initial MB concentration of 0.6 g/L. The decoloration percentages were 93.5%, 92.4%, 84.8%, 65.82% and 52.6% from the initial dye concentration of 0.2, 0.3, 0.4, 0.5 and 0.6 g/L, respectively. It is noticed that a low concentration of MB showed higher percentage of color removal compared to a higher concentration of MB: the decoloration percentage in 14 days at initial dye concentrations of 0.2 g/L was more than twice of that operating with an initial dye concentration of 0.6 g/L. We also observed that the decolorization was mainly occurred during the first 2 weeks. The decoloration percentage were 92.3%, 83.1%, 70.8%, 54.2% and 45.6% after 14 days from the initial dye concentration of 0.2, 0.3, 0.4, 0.5 and 0.6 g/L, respectively.

The data indicate that the dye concentration had a negative effect on the decolorization percentage. This is in agreement with the results obtained by Young and Yu (1997) when studying the decolorization of synthetic dyes by using ligninolytic enzymes. A general tendency is that high dye concentrations will cause a slower decolorization rate. The mechanism underlying this inhibiting effect may be higher dye concentration could inhibit the growth of *P. chrysosporium* and production of ligninolytic enzymes. Besides, high dye concentration implies less average attacks of ligninolytic enzymes to each dye molecule, and hence a slower color removal rate. Moreover, when ligninolytic enzyme activity reached the maximum, the decoloration percentage could also not increase with the increase of dye concentration. As it happens for all experiments, the rate of decolorization in the first two weeks was faster than that in the last week. We speculate that is caused by the decline in the quantity of fungi since the lack of nutrients and toxic metabolite accumulated in the medium.

As a summary of the results obtained previously, microbial decolorization process carried out in semi-solid/solid culture conditions using synthetic material as substrate obtained a maximum decolorization of 87% for an initial dye concentration of 0.2 g/L (Moldes et al., 2003; Sedighi et al., 2009; Singh and Pakshirajan, 2010). The process in the present study showed superior decolorization capacity, a decolorization of 92.4% for an initial dye concentration of 0.3 g/L was observed. This suggests that using rice straw as substrate is more suitable for carrying out the decolorization process. This is probably because rice straw contain lignin which induced production of ligninolytic enzymes and provided carbon and nitrogen source for the growth of *P. chrysosporium* (Rodríguez Couto et al., 2000).

### 3.4. Dynamic changes of enzymes activities

The ligninolytic enzymes production was investigated at different initial dye concentrations. The time course of enzymes activities of LiP and MnP was shown in Fig. 4. Among the two ligninolytic enzymes studied, MnP activity was found in large amounts in extracts while very low amounts of LiP activity was detected. The levels of LiP activity found in the culture were always less than 1 U/g dry straw. Maximum MnP activities, 10.0, 9.8, 9.3 and 7.9 U/g, respectively in cultures with 0, 0.2, 0.4 and 0.6 g/L of initial dye concentration, were obtained after 8 days of cultivation. Results presented in Fig. 4 show that the production of LiP reached the maximum value in 6 days, while the production of MnP did not reach the peak until day 8. After 10 days fermentation, LiP activities decreased significantly to undetected level, yet MnP activities remained at high values. As a whole, the culture with lower concentration of dye presented higher ligninolytic enzymes activities

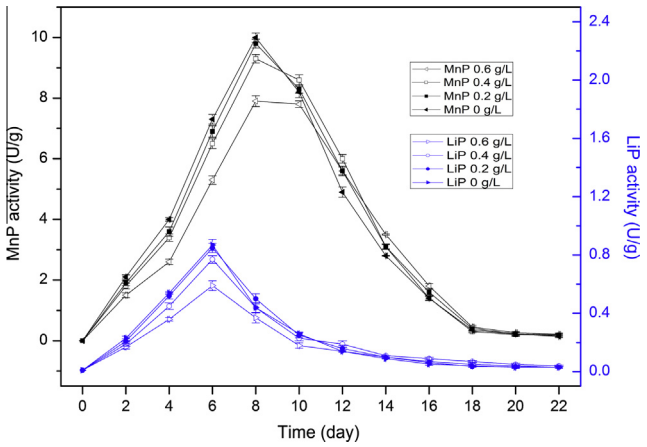


**Fig. 4.** Ligninolytic enzymes activities in semi-solid-state cultures of *P. chrysosporium* with different initial dye concentrations (0, 0.2, 0.4 g/L and 0.6 g/L). Enzyme activities are expressed in relation to the dry weight of fermented straw. The bars represent the standard deviations of the means ($n = 3$).

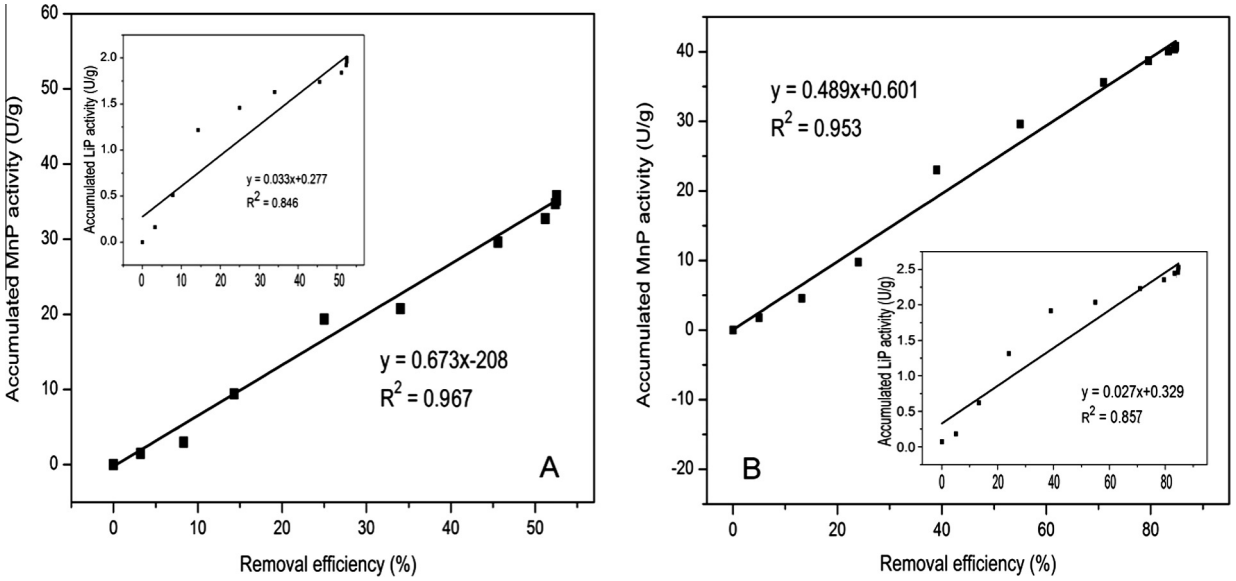


**Fig. 5.** Relationship between the percentage of decolorization and the accumulated ligninolytic enzyme activities. (A) Started with an initial dye concentration of 0.4 g/L; (B) started with an initial dye concentration of 0.6 g/L.

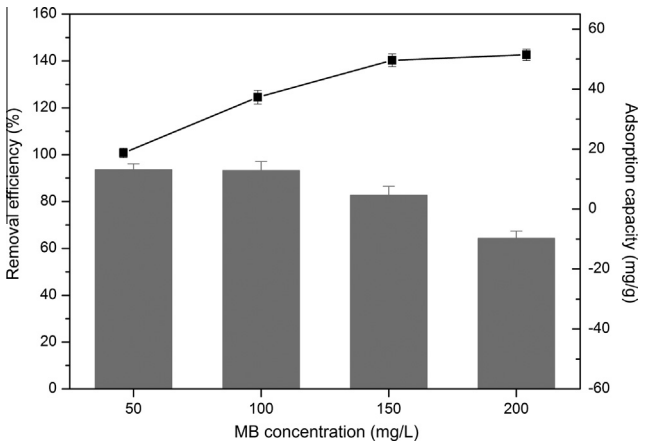


**Fig. 6.** The removal efficiency of methylene blue (MB) from aqueous solutions (50, 100, 150 and 200 mg/L) by the fermented residues (column), and the adsorption capacity of the fermented residues (solid line). The bars represent the standard deviations of the means ($n$ = 3).

during the fermentation. Besides, ligninolytic enzymes activities detected in the culture with low initial dye concentration were similar to those in control with MB group.

Taken together, our data indicate that the highest ligninolytic enzymes activities were appeared in the intermediate stage of the fermentation. A proposed reason is that ligninolytic enzymes were produced by *P. chrysosporium* during their secondary metabolism since lignin oxidation provides no net energy to the fungus (Wesenberg et al., 2003). Our results show that low concentrations of MB have little inhibition on the ligninolytic enzymes activities, which suggest that *P. chrysosporium* has the ability to growth with MB. In the present investigation, we observed that the culture with 0.6 g/L of initial dye concentration presented lower ligninolytic enzymes activities, it is probably attributable to the higher dye concentration formed an adverse environment for metabolism, energy and/or oxygen supplying system of *P. chrysosporium*.

To more directly examine the effect of ligninolytic enzymes on the dye decolorization, the relationship between dye decolorization and enzymes activities, the correlations between enzymes activities and the decoloration percentage were analyzed. As shown in Fig. 5, accumulated MnP activities and decoloration percentage were well correlated in cultures with 0.4 and 0.6 g/L of initial dye concentration ($R^2$ = 0.967 and 0.953), relatively lower correlations were observed between accumulated LiP activities and decoloration percentage ($R^2$ = 0.846 and 0.857). These observations suggest that MnP is possibly the main factor in the bio-decolorization process. Similar results have been observed in several other systems (Dorado et al., 1999; Michel et al., 1991).

### 3.5. Reuse of the fermented residues

After the fermentation, a considerable amount of residues were remained in the bioreactor. These residues mainly compose of the incompletely degraded rice straw and dead fungus cells. Previous study showed that up to 35 g protein from 100 g dry substrates were produced by *P. chrysosporium* after 30 days fermentation with wheat straw, and the fermented wheat straw fortified with additional nitrogen to achieve a C:N ratio of 20:1 (Nigam et al., 2000). The high protein and organic content of the digested residues may render them suitable substrate for soil conditioning or probable use as fertilizer (Nigam et al., 2000).

In this work, we studied the feasibility of employing the fermented residues for the removal of MB from aqueous solutions. To determine the adsorption ability of the fermentation residues, the absorption experiments were performed at 4 different concentrations (50, 100, 150 and 200 mg/L) of MB solutions. After 24 h contact, the remained amounts of MB are shown in Fig. 6. It was found that more than 90% of soluble MB was removed at the initial MB concentration of 50 and 100 mg/L, however, the removal efficiency decreased with the increase of the MB concentration, when the initial MB concentration reached 200 mg/L, the removal efficiency dropped to 64.3%, most probably because the limitation of functional groups (such as –COO and phenolic –OH) that are responsible for the adsorption. From another perspective, the total amount of removed MB increased with the increase of the MB concentration Fig. 6, the maximum adsorption amount of the fermented residues was 51.4 mg/g when the initial MB concentration was 200 mg/L. This comes about because dye concentration provides an driving force to overcome the mass transfer resistance between the solid phase and the liquid phase (Feng et al., 2013), with the increase of initial concentration of MB, the

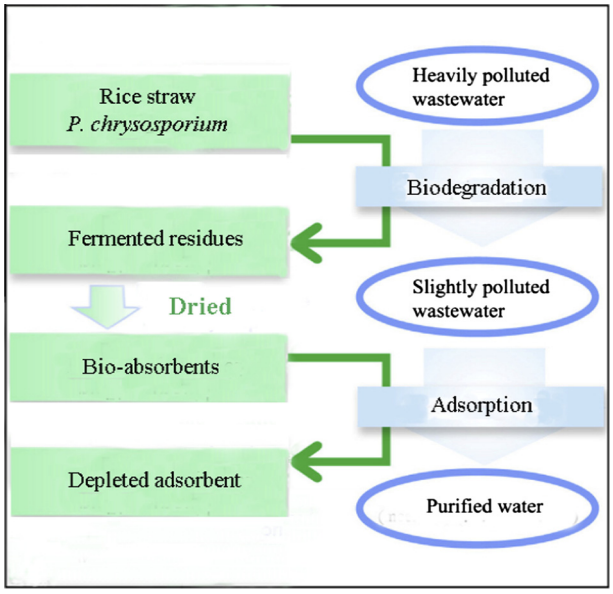


**Fig. 7.** A circulation system for dye polluted wastewater purification.

driving force increased, which consequently led to higher removal capacity.

Results showed that the residues from the decolorization showed a maximum removal capacity of 51.4 mg/g, which is over 4 times of the untreated rice straw (Feng et al., 2012). The significant improvement was mainly due to the increased specific surface area of rice straw, holes and cracks were formed on the surface of rice straw since lignin was selectively degraded by extracellular ligninolytic enzymes (Huang et al., 2008). Besides, a part of MB was adsorbed to the dead *P. chrysosporium* cells (Wesenberg et al., 2003). The adsorption capacity of fermented residues is not comparable to chemical modified rice straw (Feng et al., 2012; Zhang et al., 2011b). But the production of chemical modified adsorbents may cause more serious damage to the environment and also need more investment (Dawood and Sen, 2012). Thus, the reuse of the fermented residues to absorb dye from effluents could be a feasible treatment method. Taken together, we propose an economic, environmental friendly and recyclable dye removal system: step 1, removal of dyestuff from heavily polluted wastewater by semi-solid-state fermentation of rice straw with *P. chrysosporium*; step 2, removal of dyestuff from slightly polluted wastewater with dried fermented residues from step 1. Based on the above description, a schematic diagram of the dye removal system is shown in Fig. 7.

## 4. Conclusions

The results presented here show an approach to dye removal from effluents using white rot fungus and cheap agricultural residues. These initial studies have shown this semi-solid fermentation system is capable of processing heavily polluted industrial effluents, a maximum decolorization of 84.8% for an initial dye concentration of 0.4 g/L was observed at the optimal operating conditions (35 °C, pH 5). Our results also provide a first step to a cyclic utilization of fermented residues for the removal of MB from aqueous solutions, the maximum adsorption amount of the fermented residues reached 51.4 mg/g.

## Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (51378190, 50808073, 51278176, 51108178, 51408206), the Environmental Protection Technology Research Program of Hunan (2007185), the Fundamental Research Funds for the Central Universities, the Hunan University Fund for Multidisciplinary Developing (531107040762), a Project Supported by Scientific Research Fund of Hunan Provincial Education Department (521293050), the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17) and the Hunan Provincial Innovation Foundation for Postgraduate (CX2014B141).

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