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Biosorption of Cr(III) ions from tannery wastewater by *Pleurotus ostreatus*

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Abstract

The article extends the study on the removal of Cr(III) ions by utilizing Basidiomycetous fungus *viz*., *Pleurotus ostreatus* (Jacq.) Quélet from aqueous solution. To predict the biosorption performance of the test fungus with actual wastewater of tannery, laboratory assays were conducted with synthetic pure metal-bearing solutions. Oven dried biomass of test fungus was utilized to evaluate the effect of pH, stirring intensity and initial metal ion concentrations. Results revealed optimum pH 4.5, stirring intensity 150 rpm, with increase in removal rate on increasing metal ion concentrations (4-20 mgL^{-1}) in the medium. The Langmuir and Freundlich models use to check the distribution of metallic ions between liquid and solid phase adequately described all experimental data on sorption capacity of the test fungus. On exposure of fungal biomass in tannery effluents 55% of biosorption efficiency for Cr(III) ions was obtained. To amplify this potential for prospective commercialization of biotechnology through the test fungus, the production of fungus was carried out on the economically cheaper substrates *viz.*, rice straw, wheat straw and cotton waste. The results clearly indicated among the agro-wastes (colonized) best removal efficiency was recorded for wheat straw (80-90%). Due to the low cost involved and simplicity of the technique, wheat straw colonized with *P. ostreatus* could be utilized as an excellent biosorbent for removal of Cr(III) ions from tannery wastewater containing low concentration of the metal.

Keywords: Biosorption, *Pleurotus ostreatus*, heavy metal, chromium, agro-waste.

Introduction

Like most of the developing countries, Pakistan tanning industry is also suffering from chromium pollution in wastewater (Gulfraz *et al*., 2002). Tanning process produces a very obnoxious and smelly waste, which contains chromium, sulphides, ammonia, chloride and other salts, in addition to large quantity of organic components. More than 160 tons per year of chromium is being discharged daily from nearly 237 tanneries clustered in Kasur, which is the biggest tanning area in country with most serious pollution. Over 62 percent of ordinary people and 72 percent of tannery workers have contracted one or more problems like cancer, respiratory infections, tuberculosis, loss of eyesight, liver and abdominal diseases, kidney and urine infection etc. Worse part being that, the majority of patients are under the age of 20 (UNIDO, 2001).

Under these circumstances, it is very important to develop and apply comprehensive methods of wastewater management that would facilitate the sustainable use of water resources, preserve environmental integrity and improve rural livelihood on a long-term basis.

Biosorption by Macromycetes has recently been projected for the remediation of wastewater containing toxic heavy metal ions. Macromycetes are a group of higher fungi belonging to division Basidiomycota characterized with the formation of visible fruiting bodies. The knowledge about the potential of Basidiomycetes to remove metal ions is limited to a few examples (Veit *et al*., 2005) in comparison with micromycetes and their role in this field has been known only for few decades (Mejstrik and Epsova, 1993). However, there are number of Basidiomycetes which have shown a great promise for heavy metal ions removal from wastewater (Bayramoglu *et al*., 2005, Akar *et al*., 2006, Pogaku and Kulkarni, 2006). The metal removal efficacy of these fungi can be further manipulated through their application as cost efficient commercial biosorbents by raising them on agriculture waste. Utilization of plant by-products as biosorbents would evoke tremendous interest to manipulate microbial resources along with natural products to evolve a benign technology. This alternative strategy in contrast to expensive and cautionary chemical based procedures opted as purification treatment for industrial effluents would likely to be more adoptable. Cultivation of fungi on agro-waste by solid state fermentation therefore not only fulfils the criteria of low cost production potential of the biosorbents in bulk quantity, but it also offers a number of advantages over submerged fermentation. These include higher yields with low cost carbohydrate source, lower operational cost and easy handling of the process (Gadd, 2001).

It has already been established that plant-derived biomasses demonstrated a high capability for toxic and precious metal removal and recovery (Iqbal and Akhtar, 2005, Pino *et al*., 2006, Qaiser *et al*., 2007). However, the biosorption potential of Basidiomycetes preparation on agro-waste especially for industrial heavy metal ions removal has not been extensively attempted. Keeping in view economic feasibility of this process, the aim of present study was to develop a new, efficient and cost-effective biosorbent for the removal of Cr(III) ions from tannery wastewater in Pakistan. For this purpose, first phase of the study included assessment of biosorption potential of *P. ostreatus* biomass. For large scale industrial application fungal biosorbent mass cultivated on agro-waste was evaluated for its biosorption potential from tannery wastewater.

Materials and Methods

Sampling

Wastewater samples were collected from treatment lagoon (contain tannery wastewater after preliminary and primary treatment) in the Tanneries Treatment Plant, Kasur. To ensure accuracy and precision, triplicate effluents samples were drawn from the sampling point. The samples were given proper treatment for storage at $4^{o}C \pm 1$ by acidification with 1.5 mL conc. HNO_3 to pH < 2 per liter of the samples (Tayim and AlYazouri, 2005).

Procurement, growth and maintenance of test fungal strain

The pure culture of *P. ostreatus* (FCBP 317) was obtained from the First Fungal Culture Bank of Pakistan, Institute of Mycology and Plant Pathology, Punjab University, Lahore and maintained on 2% MEA, for utilization in biosorption studies.

Biomass Production of Test Fungal Species

Mycelial biomass of the test fungus was grown in liquid medium (2% ME, 20 g malt extract/1000 L) in flasks by taking active inocula from preserved stock culture. Inoculated flasks were incubated for 12-15 days under controlled temperature of $25 \pm 1^{o}C$ in stationary phase. After the incubation period, the biomass of the test fungus was separated from culture broth by filtration and subjected to successive washings with double distilled deionized water with finality of the culture broth removal. The biomass was dried in oven at $60 \pm 1^{o}C$ for 24 hours and homogenized in a blender to break the cell aggregates into smaller fragments of 0.5-1mm diameter (mesh size 150 μm). The dried biomass was preserved in airtight jar to be used in biosorption test series.

Batch Biosorption Experiments

Batch experiments were performed by taking 0.2 g of oven dried biomass of test fungus in 250 mL flask containing 100 mL of 14.35 mg L^{-1} (selection of particular concentration was based on quantitative assessment of metal present in tannery wastewater) of Cr(III) solution at 150 rpm and $25^{\circ}C$ for 3 hours. To study the effect of initial pH on metal ions biosorption by *P. ostreatus* biomass, the pH values of the contact solutions were adjusted in the range of 2.0–6.0. The effect of stirring intensity on metal ions sorption was monitored at low (50 rpm), medium (100 rpm) and high (150 and 200 rpm) speed of agitation using non-agitated system as the control. Effect of initial metal ion concentration was investigated by changing the initial concentration of Cr(III) ions within the range of 4-20 mg L^{-1} at constant pH and temperature. After each experiment, the mixture was filtered through Whatman filter paper No.1 and the residual metal ions concentration was determined using Atomic absorption spectrophotometer (Model, Varian AA 1275 series).

Biosorption assay with tannery wastewater

From the biosorption optimization assays, the best pH and rpm were selected for reassessment of effective biosorption of Cr(III) ions in synthetic solution and tannery wastewater by the test fungal species. For this purpose, three systems were designed i.e., System-I, II and III. The comparative biosorption assessment model description in three different component metal ions systems is depicted in Table 1.

Table 1: Comparative assessment systems for biosorption assays

System-I	System-II	System-III
System-I: related to synthetic solution of Cr(III) ions and employed during biosorption optimizing assays.	**System-II:** related to synthetic solution of Cr(III) ions and employed during verification of optimized biosorption assays.	**System-III:** consisted of Tannery Wastewater (TWW-III) employed at varying optimized conditions.

After each experiment, wastewater samples of tannery, owing to high content of organic load were digested. Acid digestion of the samples was carried out in 250 mL flasks containing HNO_3 +

$HClO_4$ (1:1). Residual metal ion concentrations were determined spectroscopically.

Agro-waste colonization by fungal mycelia

Rice straw, wheat straw and cotton waste were used for mycelial cultivation of *P. ostreatus*. For this purpose substrates were soaked overnight in water for softening and drained while maintaining moisture content at 70%. Measured amount of each three substrates was filled in plastic bags measuring 20 x 30 cm and were inoculated with test fungal species after autoclaving. The inoculated bags were kept in an incubator at 25^{o}C for 12-15 days.

The prepared material (bags completely colonized with fungus mycelia) was dried by two methods i.e. oven and sun drying to compare and contrast the biosorption efficiency of fungus preparation. Oven drying was carried out at 60^{o}C for 24 hours and for sun drying prepared material was exposed directly to sun light for 12-14 hours during the months of May and June from 12pm-5pm. Loss in water was determined by calculating the dry weight of material. All differentially treated agro-waste bags prepared by solid state fermentations were passed through 150 μm mesh size to obtain approximately same particle size (0.5-1mm diameter) for further use in biosorption assays.

The batch biosorption experiments were conducted with prepared material (colonized and uncolonizeed agro-waste) under pre optimized biosorption conditions in same way as mentioned earlier.

Biosorption data evaluation

All the experiments were run in triplicates and controls were also run on same pattern without addition of biomass.

The amount of metallic ions biosorbed per g of biomass (q) and the efficiency of biosorption (E) were calculated using following equations.

Where, C_i = initial concentration of the metallic ions (mg L^{-1}); C_f = final concentration of metallic ions (mg L^{-1}); m = dried mass of the biosorbent in

$$q = \left(\frac{C_i - C_f}{m}\right)V, \quad E = \left(\frac{C_i - C_f}{C_i}\right)*100$$

the reaction mixture (g); V = volume of the reaction mixture (mL).

The data pertaining effect of initial concentrations of metal ions on biosorption capacity of fungi was calculated by using Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) adsorption isotherm.

Langmuir model $$\frac{q_{eq} = q_{\max} bC_{eq}}{1 + bC_{eq}},$$

Freundlich model $$q_e = K_F (C_e)^{1/n}$$

Where, $\boldsymbol{q_{eq}}$ = metallic ions adsorbed per unit of weight of adsorbents at equilibrium (mg g^{-1}); $\boldsymbol{q_{max}}$ = maximum possible amount of metallic ions adsorbed per unit of weight of adsorbents (mg g^{-1}); $\boldsymbol{b}$ = constant related to the affinity of binding sites for metal ions (L mg^{-1}); $\boldsymbol{C_{eq}}$ = equilibrium concentration (mg L^{-1}); $\boldsymbol{K_F}$ **and** $\boldsymbol{n}$ = Freundlich characteristic constant of the system.

Results

Physicochemical analyses

The results obtained on physicochemical analyses of the tannery wastewater are shown in Table 2. All analytical techniques employed were item standard methods (APHA, 1995).

Effect of pH

Results obtained on effect of pH on the biosorption potential of the test fungus for Cr(III) ions showed considerable increase in Cr(III) uptake capacity and efficiency at pH > 3.5, the maximum being at pH 4.5 (2.27 mg g^{-1}/31.70%) followed by subsequent reduction in metal ions uptake with parallel results at pH 5.0 (1.97 mg g^{-1}/27.52%) and 5.5 (1.95 mg g^{-1}/27.10%) (Fig.1). Reduction in metal ions removal was more conspicuous at higher acidic pH values i.e., 2.0-3.0 exhibiting biosorption capacity in the range of 0.46-0.89 mg g^{-1}.

Effect of stirring intensity

The biomass of *P. ostreatus* depicted progressive increase in uptake capacity on mounting rotation speeds as compared to control (without shaking) (Fig. 2). The highest Cr(III) ions removal capacity and efficiency was recorded at 150 rpm (1.97 mg g^{-1}/27.52%), with slight reduction at 200 rpm (1.72 mg g^{-1}/24.05%) and lowest at 50 rpm (1.17 mg g^{-1}/16.37%). Therefore, biosorption potential of the test fungus for Cr(III) ions increased in order of 150 rpm > (27.52%) 200 rpm (24.04%) >100 rpm (21.53%) > 50 rpm 16.37%) > control (9.66%).

Effect of initial concentration of metal ions

The graphical presentation of the effect of initial metal ion concentrations on biosorption capacity of the test fungus is depicted in Fig. 3. Results demonstrated that biosorption capacity of the test fungus for Cr(III) enhanced as the initial concentration of metal ions was increased in the medium (4-20 mg L^{-1}). At the lowest dose of metal ions (4 mg L^{-1}), the test fungus demonstrated 1.02 mg g^{-1} biosorption capacity, which increase on increasing concentration between 8-20 mg $L^{-1.}$

Kinetics of biosorption, Langmuir and Freundlich adsorption isotherm

Data evaluation according to the Langmuir and Freundlich constant along with the correlation coefficient (R^2) calculated from the corresponding plot for the biosorption of Cr(III) ions by the test fungus is presented in Table 3. The results presented in Fig. 4A & B indicates both models, Langmuir and Freundlich, fit reasonably well in the experimental data.

Biosorption assays with Tannery wastewater

Under optimized conditions of pH (4.5) and stirring intensity (150 rpm), the biosorption potential recorded by *P. ostreatus* was observed with parallel results (1.98 mg g^{-1}/ 55.05%) in both MS-II and TWW-III, which were significantly greater than MS-I (1.50 mg g^{-1}/ 41.92%) (Fig. 5A & B).

Biosorption assays with colonized and uncolonized agro-waste

Data acquired on biosorption capacity and efficiency on agro-waste biosorbents i.e., with and without mycelial colonization in general, illustrated that all biosorbents removed Cr(III) ions efficiently from tannery wastewater. However, colonized agro-wastes exhibited greater biosorption potential as compared to un-colonized. Among three agro-wastes, wheat straw (with and without fungal colonization) exhibited a significantly high biosorption capacity (1.42-1.63 mgg^{-1}) and efficiency 80-91% (Fig. 6 A&B). Sorption capacity and efficiency was further improved significantly under sun dried wheat straw treatment (1.63 mg g^{-1}/91%) in comparison to oven dried straw (1.54 mg g^{-1}/86%). Cotton waste (colonized and uncolonized) exhibited ~80% removal efficiency for Cr(III) ions. On the contrary, rice straw demonstrated low biosorption capacity and efficiency ranging between 1.25-1.35 mg g^{-1} and 67-75%, respectively.

Discussion

Presently the biomass of *P. ostreatus* exposed to Cr(III) ions solution, exhibited maximum sorption capacity in the pH range 4.0-4.5, above and below that range substantial decline in metal uptake was evidenced which represents the pH factor being highly sensitizing element Akar *et al*., 2006). The investigations revealed that low pH (4.0 and below) limits the biosorption Cr(III) ions on fungal biomass surfaces, probably due to the ion exchange between metallic species and competition effects with oxonium (hydronium) ions to some extent in the biosorption mechanism (Zhou, 1999). However, maximum uptake between pH 4.0-4.5 recorded in present investigation could possibly be related to reduction in metal ions solubility promoting adsorption and favouring complexation (Guibal *et al*., 1992). The reduction in metal ions uptake displayed by the fungus at pH > 5.5, can be explained on the basis that at higher pH values the metal ions may accumulate inside the cells, and or the intra-fibular capillarities of the cell walls by a combined sorption microprecipitation mechanism, therefore biosorption experiments are meaningless at higher pH (Beveridge, 1986).

The effect of agitation speed between 50-200 rpm as compared to non-agitated, on removal of metal ions by *P. ostreatus,* revealed that uptake potential generally increased with elevating agitation speed. The non-agitated condition, as well as lower speed probably cause inefficient dispersion of biomass particles in the liquid medium and increase resistance in external mass transfer (Chergui *et al*., 2007). Similarly, Dilek *et al*. (2002) proposed that at lower stirring speed the biomass granules agglomerate and may take more time to reach equilibrium. This indicates that a shaking rate in the range of 100-150 rpm is sufficient to ensure that all the surface binding sites are made readily available for metal ions uptake by *P. ostreatus*.

The fungus subjected to varied concentrations of Cr(III) ions from 4-20 mg L^{-1}, exhibited an increase in sorption capacity on increasing metal concentration and maximum uptake was evident at the highest applied concentration. This assessment is in line with previously reported data on sorption of Cu (II) ions by *P. chrysosporium* (Say *et al*., 2001) and in other fungi in many other similar studies (Arica *et al*., 2004, Veit *et al*., 2005, Sheng *et al*., 2007). There is evidence that at high metal concentration the number of ions sorbed is more than at low metal concentration, where more binding sites were free for interaction (Mukhopadhyay *et al*., 2007).

Isotherm analyses indicate that the data acquired on sorption capacity of test fungal species under the effect of initial concentration of metal ions fits appropriately in both models i.e., Langmuir and Freundlich. The Langmuir model predicts the formation of an adsorbed solute monolayer, with no side interactions between the adsorbed ions. The Freundlich model considerers the existence of a multilayered structure (Cossich *et al*., 2002). This observation implies that monolayer biosorption, as well as heterogeneous surface conditions may co-exist under the applied experimental conditions. Hence, the overall sorption of Cr(III) ions on the biomass is rather a complex phenomenon, involving more than one mechanism, including ion exchange, surface complexation and electrostatic attraction. In Freundlich model, value of *n* corresponds to distribution of bonded ions on the sorbent surface is greater than unity, indicative of a constant partitioning of sorption mechanism, where sorbate can easily penetrate into the sorbent and therefore shows good adsorption (Loukidou *et al*., 2004).

The optimized conditions selected for the test fungus from biosorption assays were applied to conduct experiment for removal of Cr(III) ions present in tannery wastewater. Results obtained revealed no indication of any reduction in biosorption efficacy of the test fungal species for Cr(III) ions despite the fact that the tannery wastewater carried differential impurities in the form of nutrients, anions and cations i.e., Na^+, Mg, Ca^{2+}, K^+, Cl^-, SO_4^-, CO_3^- and HCO_3^- along with high pertaining values of TDS, BOD and COD. Similar findings were recorded by Matheickal and Yu (1999) while investigating the effect of light metal ions Na^+, K^+, Mg^{2+} and Ca^{2+} on the biosorption of Pb (II) ions by *Durvillaea potatorum* and *Ecklonia radiata*. They found that biosorbents had much higher relative affinity for heavy metals than for light metals.

In experiments carried out to evaluate the Cr(III) ions removal potential of some agro-wastes colonized with *P. ostraetus* mycelia, the biosorption potential of both colonized and un-colonized agro-wastes was confirmed (Fig 6A & B). However, better sorption potential was exhibited in the case of colonized agro-waste which may be attributed to the likely chemical changes in plant residue cell wall components by fungal lignin and cellulose degradation, simultaneously resulting in solubility of the polymer core. Thereby making further provision of supplementary binding sites for metal ions by setting out fragments of varying sizes (Reid, 1985). The high biosorption potential in wheat straw could be due to loose mycelium colonization on this straw, allowing maximum exposure of binding sites for metal biosorption. The reduced metal sorption capacity by rice straw and cotton waste and associative fungal mycelium could possibly be due to increased compaction of agro-waste with fungal mycelium leading to blockage of some micro-pores in crop residues, making it difficult for the metal ions to reach the adsorption sites. Since adsorption takes place micro-pores (Motoyuki, 1990), any reduction in microspores means less availability of metal adsorption sites. Comparative assessment of the influence of two types of biomass, sun-drying both colonized and un-colonized masses displayed better biosorption efficacy as compared to oven dried biomass. Enhanced Cr(III) ions removal capacity was recorded in the case of colonized straw as compared to un-colonized. It may be due to variation in moisture retention of the substrate after colonization with fungus. Besides, oven drying might have denatured some important chemical groups/sites essential for biosorption on the cell wall of biosorbents (Huang *et al*., 1990), which remain intact in case of natural drying under sun.

Conclusion

The present study concludes that *P. ostreatus* has the potential to remove Cr(III) ions from tannery wastewater under specific conditions of pH and stirring speed. The experimental data is well modelled with the Langmuir and Freundlich sorption isotherm equations. The performance of this macromycetous fungus can be further enhanced by culturing them on agro-wastes such as wheat straw. The present study opens new vistas for management of heavy metal contaminated industrial effluent using low cost and environmental friendly biological methods.

Table 2: Physico-Chemical Characterization of Tannery Treatment Plant.

Sr.#	Parameters	Tannery Wastewater, Current status	*NEQS Acceptable limits	**WHO Acceptable limits
1.	Copper (II), mg L^{-1}	1.21	1.00	0.20
2.	Chromium (III), mg L^{-1}	14.35	1.00	0.10
3.	Nickel (II), mg L^{-1}	0.05	1.00	0.20
4.	Zinc (II), mg L^{-1}	0.54	5.00	2.00
5.	pH Value (acidicity/basicity)	8.5-9.5	6.0-10	No guideline
7.	Biochemical Oxygen Demand (BOD) at 20°C, mg L^{-1}	500	80	No guideline
8.	Chemical Oxygen Demand (COD), mg L^{-1}	4000	150	No guideline
9.	Total Dissolved Solids (TDS), mg L^{-1}	1510	3500	No guideline

*****National Environmental Quality Standards (NEQS) for liquid Industrial Effluents
******World Health organization Standards (WHO) for drinking water

Table 3: Isotherm model parameters for the biosorption of Cr (III) ion onto biomass of *P. ostreatus*

Isotherm model parameters for the biosorption of Cr(III) ions onto biomass of *P. ostreatus*							
Test fungus	q_{exp} **(mg g^{-1})**	**Langmuir**			**Freundlich**		
		q_m **(mg g^{-1})**	b **(mg L^{-1})**	R^2	K_F	n	R^2
P. ostreatus	1.97	2.36	0.36	0.92	1.41	2.30	0.94

● ------ Biosorption capacity, ● —— Biosorption efficiency

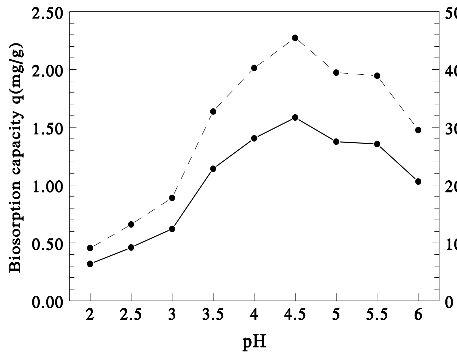

Fig. 1 Effect of pH on biosorption potential of the *P. ostreatus* for Cr(III) i

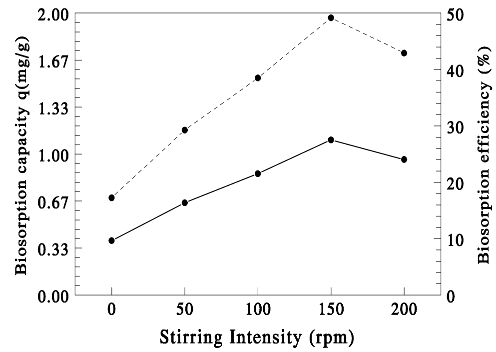

Fig. 2 Effect of stirring intensity on biosorption potential of the *P. ostreatus* for Cr(III) ions.

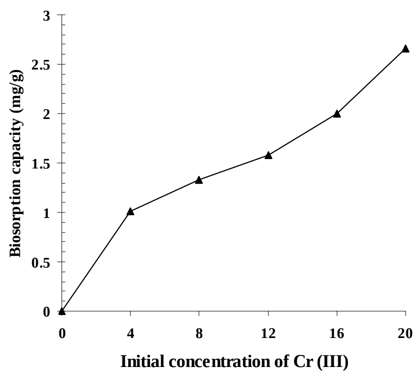

Fig.3 Biosorption capacity of *P. ostreatus* for Cr(III) ion at various initial concentrations

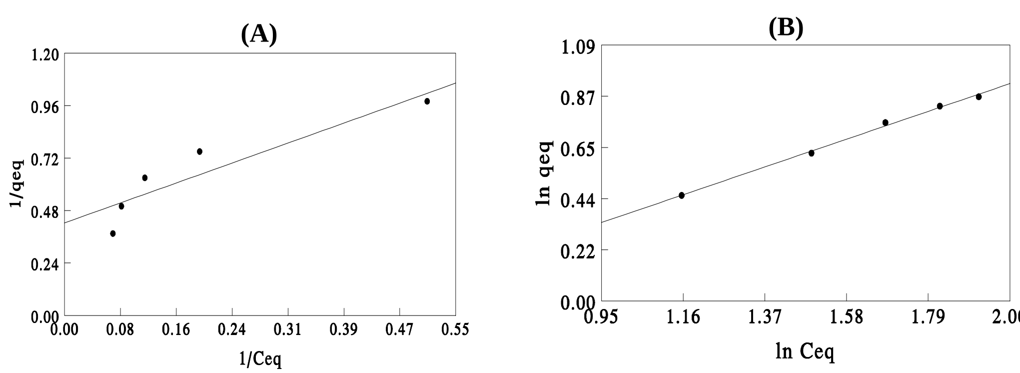

Fig. 4 A & B: The linearized Langmuir (A) and Freundlich (B) adsorption isotherm for Cr(III) ions biosorption by *P. ostreatus*.

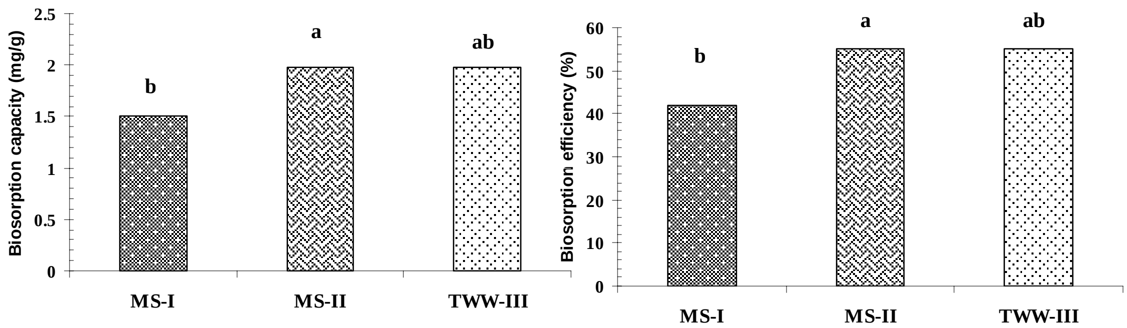

Fig. 5 A & B: Comparison of biosorption capacity (A) and efficiency (B) of the *P. ostreatus* for Cr(III) ions in Metal System-I (MS-I), Metal System-II (MS-II) and Tannery Wastewater-III (TWW-III).
Initial concentrations of Cr(III) ions in three systems: 14.35 mg L^{-1}. Biosorption conditions: MS-I, at pH 5.0, 150 rpm for 3 hours. MS-II and TWW-III, at pH 4.5, 150 rpm for 3 hour.
Values with different letters at the top show significant difference ($P \leq 0.05$) between different systems in their metals removal efficacy as determined by DMR Test.

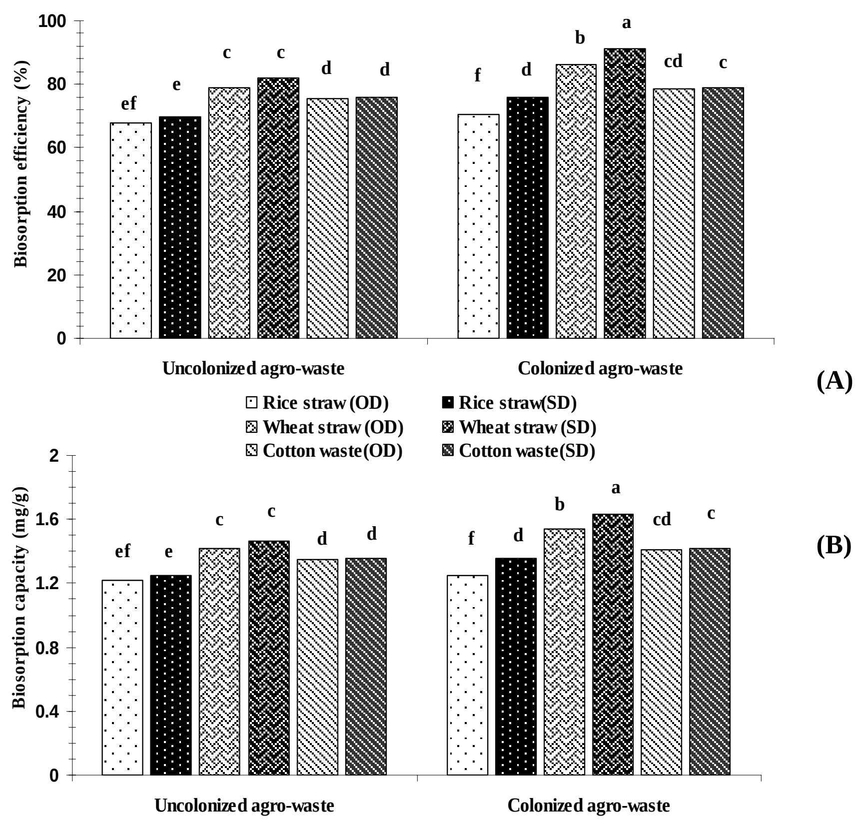

Fig. 6 A & B: Biosorption capacity (A) efficiency (B) of uncolonized and colonized agro-waste for Cr(III) ions from tannery wastewater.
Initial concentration of Cr(III) ions in the effluents: 14.35 mg L^{-1}. Biosorption conditions: pH, 4.5 at 150 rpm for 3 hour. All experiments were conducted at biomass dose @ 0.8 g 100 mL^{-1} at $25^{o}C$. **OD**: oven dried, **SD**: sun dried.
Values with different letters at the top show significant difference ($P \leq 0.05$) between colonized and uncolonized agro-waste in their metals removal efficiency as determined by DMR Test.

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