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Interaction of malathion, an organophosphorus pesticide with *Rhizopus oryzae* biomass

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ABSTRACT

Adsorption of malathion on *Rhizopus oryzae* biomass (ROB) with special reference to binding mechanism has been described. ROB has been found to adsorb ~85% of malathion from its aqueous solution as against 47–68% by other fungal biomasses. Hydrogen ion concentration does not influence the adsorption of malathion by ROB which follows Langmuir–Freundlich dual equilibrium isotherm model ($r^2 = 0.998$). Both physical and chemical interactions are responsible for binding of malathion on ROB. Scanning electron micrographs and EDXA spectra exhibit adsorption of the pesticide on cell surface of ROB. Studies with cell surface polysaccharides show that chitosan through its amine groups contributes largely in the adsorption of malathion. Extraction of lipids from ROB decreases its adsorption capacity to the extent of 36.37–94.02%, depending on the polarity of the solvent.

1. Introduction

Indiscriminate use of pesticides in agricultural activities leads to contamination of surface as well as ground water accumulation. Because of potential health hazard and entry into the human and animal food chain pesticide contamination has assumed alarming proportions [1–4]. In accordance with the EEC directive pesticide concentration in drinking water should be below 0.1 μg/L [5]. However, wide structural variations of the pesticides limit the efficacy of a single method towards attaining permissible level in drinking water. Conventional methodologies in this area such as chemical precipitation, ultrafiltration, reverse osmosis or electro-chemical treatment are found to be either inadequate and/or expensive [6]. In recent years hectic research activities based on adsorption phenomenon are going on to reduce the pesticide contamination in drinking water. Activated carbon is a highly effective adsorbent [7–10] but lack of cost effectivity prohibits its use in many countries including India. In addition to scientific preferences, economic considerations also play crucial role in the selection of appropriate biomass for pollution abatement. Thus intense research attention is now focused on cost effective, eco-friendly and easily available adsorbent particularly of biological origin. Different adsorbents such as agricultural byproducts, waste materials and microbial biomass have been utilized for removing different toxicants from wastewater [11–19].

However, the performance of a biosorbent depends on the characteristic properties of the biomass as well as the microenvironment of the target toxicant. The search for an appropriate and inexpensive biomass is a continuing process. The most effective and optimized utilization of a biomass demands a detailed understanding of the binding mechanism. Detailed investigations on the selective removal and/or recovery of metals, dyes, radionuclides as well as biocides using several types of algal, bacterial and fungal biomass have been reported [20,21].

Malathion, an organophosphorus pesticide (Fig. 1) of high selective toxicity is widely used in agriculture throughout the world [22–24]. It finds extensive application for controlling sucking and chewing insects including mosquitoes, aphids, turf insects, many floral and vegetable crops and fruits. To date adsorptive removal of malathion from wastewater has not been studied in detail and only a few reports are available in this regard [25–30]. The present article describes in detail the adsorption behavior of malathion on *Rhizopus oryzae* biomass with special reference to the mechanistic characteristics of the process.

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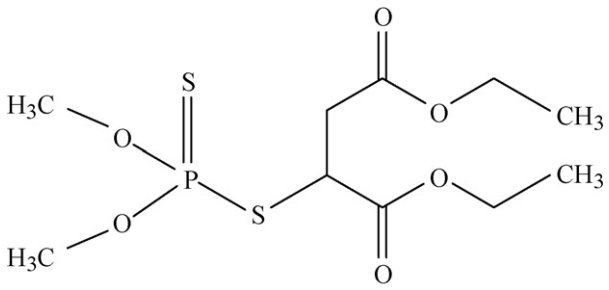

Fig. 1. Structure of malathion.

2. Materials and methods

2.1. Chemicals

Malathion used in this study was purchased from AccuStandard, INC, USA (purity 98%). Solvents are of HPLC grade and purchased from Marck, India. All the other chemicals and biochemicals were purchased from Merck, Germany. Ultrapure Millipore water (18.2 MΩ) was used as solvent.

Stock solution (2 mg/L) of malathion was prepared in dichloromethane. For preparation of the working solution, certain volume of the malathion solution was taken and the solvent was evaporated; required volume of water was added to get the desired aqueous solution.

2.2. Preparation of fungal biomasses

R. oryzae (MTCC 262), *Mucor rouxii* (MTCC 386), *Aspergillus viride* (MTCC 1782), and *Pleurotus sajor-caju* (MTCC 141) were obtained from the Institute of Microbial Technology, Chandigarh, India. *Termitomyces clypeatus* was kindly supplied by Dr. S. Sengupta, Indian Institute of Chemical Biology, Kolkata, India. *Aspergillus versicolor* was isolated in our laboratory [31].

The fungal strains were maintained on potato dextrose agar slant (20% potato extract, 2% dextrose, and 2% agar) and the biomasses were prepared following the procedures described earlier [32].

2.3. Estimation of malathion

Malathion was extracted from 20 mL of the supernatant containing 100 μL of saturated sodium chloride solution with dichloromethane thrice. The combined extracts were dehydrated by passing through sodium sulphate column and evaporated under reduced pressure in nitrogen atmosphere. Final volume of the solution was made up with *n*-hexane. Analysis of pesticide residue was performed using a gas chromatograph (Hewlett-Packard 6890 series) equipped with an auto sampler, nitrogen–phosphorous detector (NPD) fitted with a fused silica semi capillary (HP-5) column (30 m × 0.32 mm × 0.25 μm). The temperature program was 1-min hold at 160 °C initially, then raised at 10 °C/min to 250 °C and hold at 250 °C for 4 min and again raised to 270 °C at 10 °C/min and finally hold at 270 °C for 4 min. Detector temperature was 300 °C and the injector temperature and volume was 160 °C and 1 μl, respectively. The carrier gas was nitrogen (flow rate 10 mL/min).

2.4. Screening of biosorbent

Fungal biomass (0.05 g, dry weight) was added to 25 mL of malathion (100 μg/L, pH 6.0) solution taken in different 100 mL Erlenmeyer flasks and incubated at 30 °C for 24 h with shaking (130 rpm). At the end of incubation, biomass was separated by centrifugation at 10,000 rpm for 15 min. Malathion concentration in the supernatant was determined and the adsorption capacity of the biomass was calculated as described earlier [32]. Further experiments were conducted with *R. oryzae* biomass (ROB) only as it shows highest adsorption capacity towards malathion.

2.5. Effect of pH

The biomass was conditioned in 50 mM citrate-phosphate buffer solution of required pH (2.0–8.0) for 2 h with shaking. The conditioned biomass was then washed with deionized water and used for adsorption experiment as described above.

2.6. Equilibrium adsorption isotherm

This experiment was done at pH 6.0 using varied malathion concentrations (20–1500 μg/L). The other experimental conditions were same as described in the screening of biosorbent section.

2.7. Scanning electron microscopy

The sample for scanning electron microscopy (SEM) before and after malathion adsorption was prepared as described earlier [32]. Electron micrographs were recorded on FESEM (JEOL JSM-6700F) equipped with energy dispersive X-ray (EDX) analysis.

2.8. Fourier transformed infrared spectroscopic (FTIR) analysis

FTIR spectra of *R. oryzae* biomass before and after malathion adsorption were recorded on Shimadzu FTIR spectrophotometer using highly sensitive pyroelectric detector (DLATGS). Pressed pellets were prepared by grinding the samples with KBr in a mortar with 1:100 ratio and immediately analyzed in the region of 4000–400 cm^{-1} over 500 scan with a resolution of 4 cm^{-1}.

2.9. Modification of R. oryzae biomass

R. oryzae biomass (0.1 g dry weight) was incubated individually with 25 mL of xylene, benzene, petroleum ether (b.p. 60–80 °C), and chloroform at 30 °C for 2 h to modify the hydrophobic nature of the cell surface. Modified biomass was dried and used for adsorption following the procedure as described above.

2.10. Preparation of R. oryzae cell wall components

Different cell wall components like chitin, chitosan, mannan and glucan were isolated from the mycelia of *R. oryzae* following the procedure as described in our earlier publication [33]. In brief, lyophilized *R. oryzae* cell wall materials were autoclaved at 121 °C for 15 min after homogenizing in a waring blender with 1N NaOH (1:40, w/v). The alkali insoluble mass was thoroughly washed with water and refluxed with 100 volumes of 2% acetic acid (v/v) for 24 h at 95 °C. This was centrifuged and acid insoluble residue was washed with water, ethanol and acetone to obtain crude chitin. Chitosan was precipitated out from the supernatant by adjusting pH to 9.0; washed with chilled water, followed by ethanol and acetone and dried by lyophilization. Mannan and glucan were extracted from the lyophilized *R.oryzae* cell walls following the methods described by Northcote and Horne [34]. The isolated cell wall components were dried by lyophization. The isolated cell wall components (0.05 g) were used for adsorption experiments as stated above.

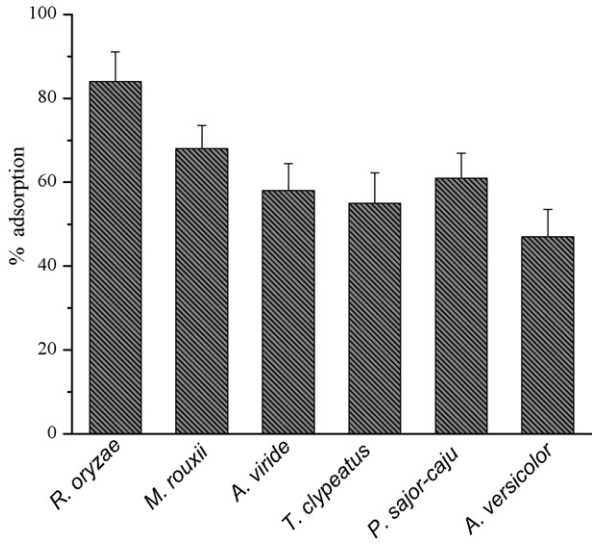

Fig. 2. Malathion adsorption on biomass of different organisms. Data represent an average of five independent experiments; ±SD shown by error bar.

3. Results and discussion

3.1. Screening of microorganism

R. oryzae biomass (ROB) has been found to be the most efficient biosorbent in the present study as it adsorbs ~85% of malathion from its aqueous solution in comparison with 47–68% by other fungal biomasses (Fig. 2). This difference in adsorption capacity may be attributed to difference in cell surface composition of the fungal strain [20].

3.2. Effect of pH

pH is an important parameter that influences the adsorption process by way of modifying the functional groups of the biomass. The effect of pH on adsorption of malathion was conducted in the pH range of 2.0–8.0. Adsorption of malathion by *R. oryzae* was found to increase only to a small extent with increase in pH values from 2.0 to 6.0 and then decreased (Fig. 3). We have shown earlier from zeta potential measurement that surface charge of ROB decreases from +5.4 to −36.45 mV corresponding to increase in pH values from 3.0 to 8.0 with zero point charge at pH 3.5 [32]. The net negative charge between pH 3.5 and pH 6.0 could develop from carboxylate groups that have pK values within 3.5–5.0 and beyond pH 6.0 suggests that the cell surface carries phosphate groups which have pK_2 (the second dissociation constant of phosphoric acid) values within 7–8 [32] The specific cell surface charges at different pH values are listed in Table 1. Since pH does not influence appreciably the adsorption of malathion, a neutral adsorbate by ROB indicates the importance of physical interactions over those of the ionic ones in this adsorption process [35,36].

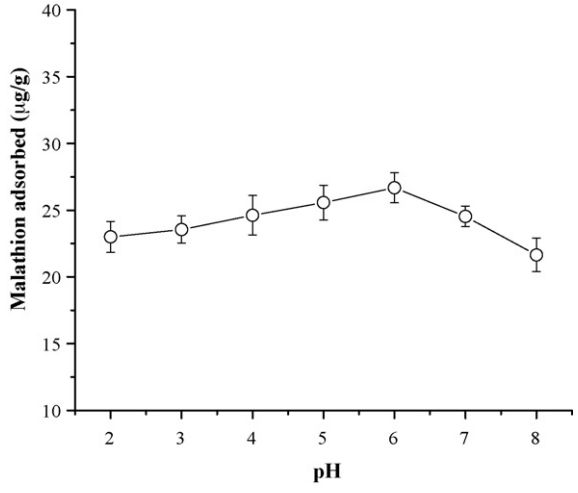

Fig. 3. Effect of pH on adsorption of malathion by ROB. Data represent an average of five independent experiments; ±SD shown by error bar.

Table 1
Cell surface charges (zeta potential) of *R. oryzae* biomass suspensions at different pH values.

pH	Cell surface charge (mV)
3.0	+5.41
4.0	−10.12
5.0	−15.61
6.0	−25.36
7.0	−35.32
8.0	−36.45

3.3. Equilibrium adsorption isotherm

In order to understand the adsorbate–adsorbent interaction, optimization of the use of the adsorbent and its adsorption capacity towards a particular adsorbate is necessary for studying the adsorption isotherm. Adsorption capacity of ROB towards malathion was determined by plotting the amount of malathion adsorbed by the biomass (q_e) against equilibrium concentration of malathion (C_e) in solution (Fig. 4) which shows that the adsorption capacity increases with increase in malathion concentration ultimately reaching equilibrium value. The adsorption capacity of ROB towards malathion was found to be 445.36 μg/g. To date we are not aware of any report dealing with adsorption of malathion with the microbial biomass. Gupta et al. [26] reported considerably lower adsorption capacity (2.08 μg/g) of malathion on bagasse fly ash. Adsorption process can better be understood by correlating the equilibrium adsorption data to different isotherm models such as Langmuir as well as Freundlich. Langmuir's model [37] deals with (a) the monolayer coverage of the adsorbate at specific homogeneous sites of the outer surface of adsorbent and (b) all adsorption sites are identical and energetically equivalent. On the other hand, the Freundlich model

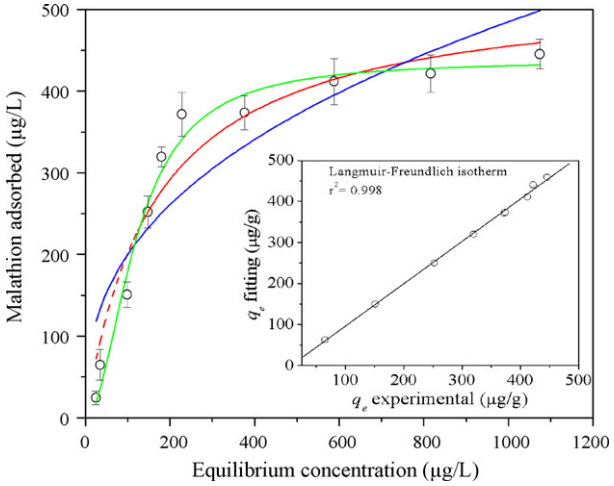

Fig. 4. Equilibrium adsorption isotherm of malathion, (inset) Langmuir–Freundlich dual model plot; –○–, experimental data; , Langmuir model; , Freundlich model; , Langmuir–Freundlich dual model. Data represent an average of five independent experiments; ±SD shown by error bar.

Table 2
Effect of different organic solvents on malathion adsorption by *R. oryzae* biomass.

Solvent used for biomass treatment	Amount of malathion adsorbed (μg/g of biomass)	Reduction in adsorption (%)
Control[a]	25.43 ± 1.01	–
Xylene	2.25 ± 0.11	91.15
Benzene	1.52 ± 0.06	94.02
Petroleum ether	6.28 ± 0.32	75.30
Chloroform	16.18 ± 0.81	36.37

Data represent an average of five independent experiments; ±SD shown by error bar.
[a] Biomass not treated with any solvent.

[38] describes the adsorption on a heterogeneous surface with uniform energy. The Langmuir (Eq. (1)) and Freundlich isotherm (Eq. (2)) models can be expressed as

$$q_e = \frac{a_L K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

where q_e and C_e are the concentrations at equilibrium in the solid (μg/g) and aqueous phase (μg/L), respectively, and a_L (L/μg) and K_L (L/g) are the Langmuir isotherm constants. $1/n$ is the heterogeneity factor and K_F (L/g) is the Freundlich constant. Analyses of the experimental data according to both Langmuir and Freundlich models reveal that the present adsorption process partially follows both of them (Fig. 4) indicating that both chemisorption and physisorption may take place simultaneously. Therefore, we have analyzed the experimental data following Langmuir–Freundlich dual model [30,39] (Eq. (3)),

$$q_e = \frac{K_{LF} C_e^{1/n}}{1 + a_{LF} C_e^{1/n}} \quad (3)$$

where K_{LF} and a_{LF} are the Langmuir–Freundlich isotherm constants.

The isotherm model graphs present in Fig. 4 show that malathion isotherm data exhibit the best fit to the Langmuir–Freundlich dual model, because of higher linear regression coefficient (r^2 = 0.998, inset Fig. 4). Thus, we conclude that the adsorption of malathion on ROB occurs through both chemical as well as physical interactions. We have reported earlier similar observation on the adsorption of mercury on *Aspergillus versicolor* biomass [31].

3.4. SEM-EDX analysis

Scanning electron microscopy has been used extensively as a tool for biosorbent characterization [40]. The surface morphology of the pristine ROB (Fig. 5A) is conspicuously different from that of the pesticide adsorbed species (Fig. 5B). The smooth surface of the pristine mycelia, turned rough and irregular after the adsorption process. Highly magnified images (Fig. 5C) of the postadsorbed ROB indicating by arrow demonstrate adsorption of malathion on the mycelial surface. EDX spectra of the fungal biomass before and after malathion adsorption were recorded in area profile mode. The presence of C, N, and O signals are due to X-ray emissions from the polysaccharides and proteins present on the cell wall of the biomass (Fig. 6A). On completion of the pesticide adsorption process, appearance of P and S peaks in addition to C, N and O indicate adsorption of malathion on the cell surface (Fig. 6B).

3.5. Interaction with lipids

Adsorption capacity of ROB towards malathion after treatment with different lipid soluble solvents reduces sharply to the extent of 94.02–36.37% (Table 2). Reduction in adsorption increases with decrease in polarity of the solvent. More than 90% reduction in adsorption of malathion by ROB after solubilizing the lipophilic

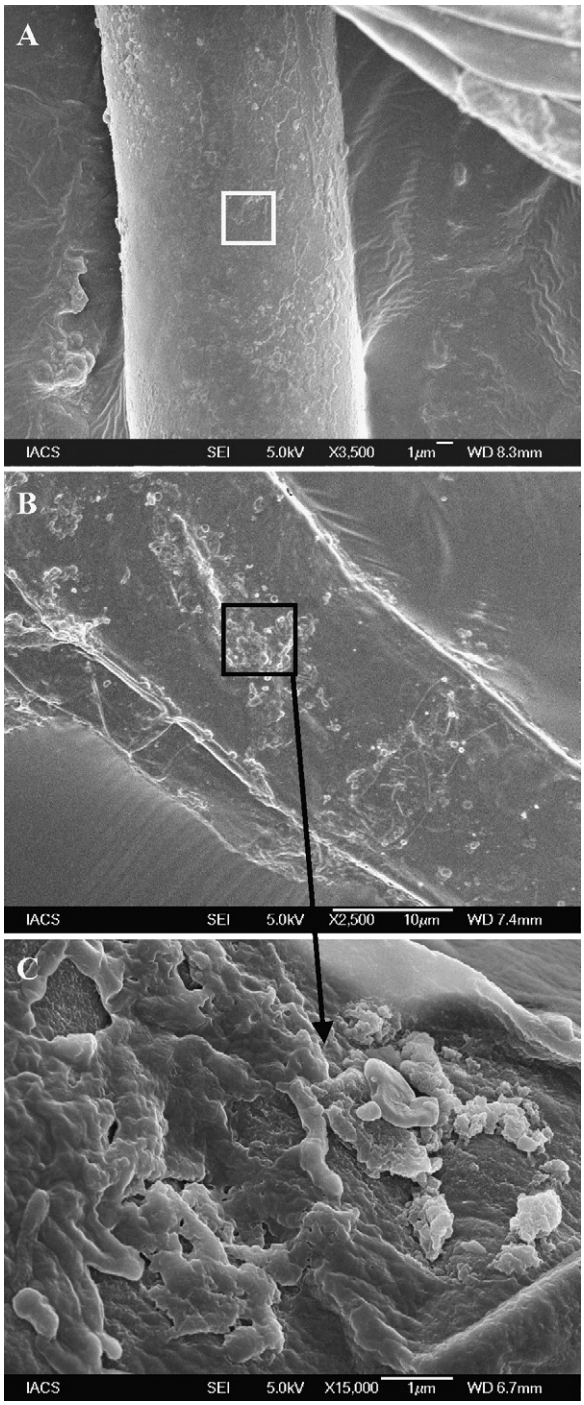

Fig. 5. SEM micrographs of ROB before malathion adsorption (A) and after malathion adsorption (B, low magnification; C, high magnification).

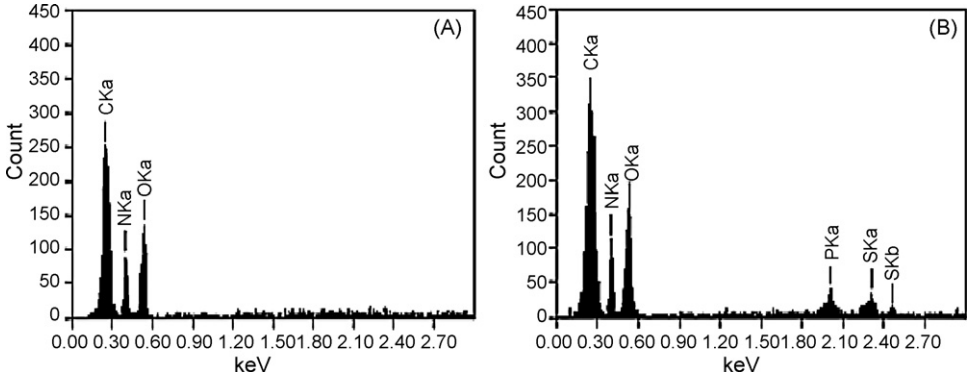

Fig. 6. EDX spectra of ROB before (A) and after (B) malathion adsorption. The spectra were recorded from the marked portion in images.

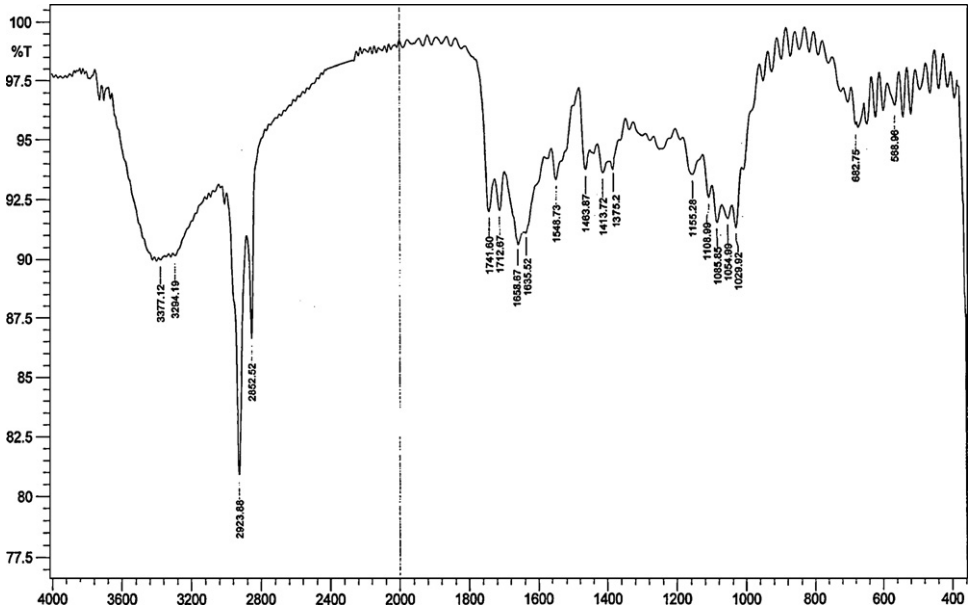

Fig. 7. FTIR spectrum of pristine *R. oryzae* biomass.

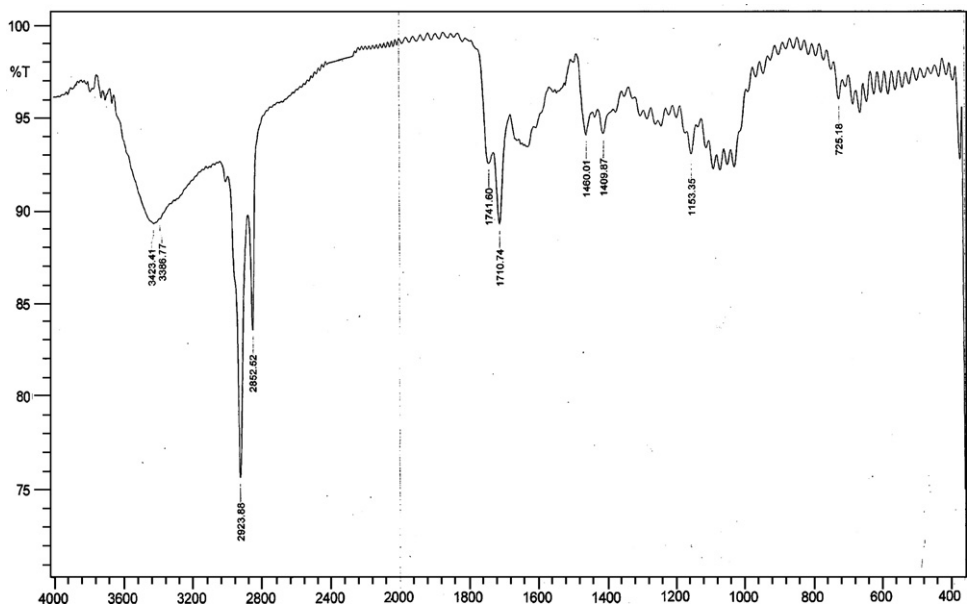

Fig. 8. FTIR spectrum of malathion adsorbed *R. oryzae* biomass.

Table 3
Adsorption capacity of malathion by different cell wall components.

Cell wall component	Adsorption (%)
Glucan	62.4 ± 2.26
Mannan	39.6 ± 1.05
Chitin	36.2 ± 1.38
Chitosan	80.7 ± 3.42

Data represent an average of five independent experiments; ±SD shown by error bar.

compounds suggests that the hydrophobic interaction plays the main role in the present adsorption process.

3.6. FTIR analysis

The FTIR spectrum of the *R. oryzae* biomass is also recorded to explain the binding of malathion with different active groups present in the cell surface as the functional groups have a unique energy absorption band [32,41,42]. The FTIR spectrum of the pristine ROB (Fig. 7) shows the absorption bands at 3377.12 and 3294.19 cm^{-1} which are the characteristics of amine and hydroxyl groups, respectively. The absorption band that appears at 2923.8–2852.5 cm^{-1} is due to the alkyl chains. The peak position at 1741.60 cm^{-1} may be ascribed to carboxyl groups, that at 1712.67 cm^{-1} to C=O of the carboxylic groups of the amino acids. The amide I band is primarily a C=O stretching mode and appears at the region around 1650 cm^{-1} while the amide II band is a combination of N–H bending and C–N stretching, being centered near 1550 cm^{-1}. The signal located near 1375.0 cm^{-1} is due to the amide III band and the strong band around 1100–1000 cm^{-1} corresponds to C–O bond, which is the characteristic peak for polysaccharides. The absorption spectra for amide band of the pesticide treated biomass (Fig. 8) are significantly different from that of the control biomass. The amide I and II bands present at 1658.67, 1635.52 and 1548.73 cm^{-1}, respectively, in the pristine biomass disappeared in the post adsorbed species. In addition to the signals present at 3377.12 and 3294.19 cm^{-1} in the control species, additional signals appeared at 3423.41 and 3386.77 cm^{-1} in the malathion adsorbed biomass. These data indicate the involvement of amine groups in the adsorption of malathion.

3.7. Adsorption of malathion by cell wall component

The cell wall of fungi including *Rhizopus* sp. contains 70–80% carbohydrates, *viz.* chitin, chitosan, β-1,3-D-glucans, β-1,6-D-glucans and small amount of mannoproteins and lipids. These are abundant sources of different functional groups like carboxyl, amine, hydroxyl, phosphate and sulphonate and play a significant role in metal and dye adsorption process [33,43–45]. Lièvremont et al. [46] showed that in addition to cell wall, other cellular components are involved in the adsorption of pentachloronitrobenzene (PCNB) from its aqueous solution by fungal biomass. To our knowledge there is no such report regarding the interaction of the pesticide molecule and the cell wall components. Earlier we have reported [33] the role of different cell wall components of *R. oryzae* in the adsorption of rhodamine B. Thus an attempt was made to explore the relative contributions of these components in malathion adsorption, and observed that chitosan, a polymer of glucosamine, and glucan adsorb ~81% and ~62% of malathion, respectively (Table 3). Adsorption capacity of phosphomannan and chitin (polymer of *N*-acetyl glucosamine) is lower in comparison with the above two fractions. The differences in the adsorption capacity may be attributed to the compositional variance of the saccharide moiety of the polymers constituting the cell wall. Adsorption of malathion by chitin is less in comparison to its deacetylated form, chitosan (Table 3) indicating the importance of amine group in the adsorption process. FTIR study (Figs. 7 and 8) also confirms the interaction of malathion with amine groups of the adsorbate. Recently, Deng et al. [47] showed the involvement of amine groups in the sorption of pentachlorophenol (PCP) and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution by polyethylenimine grafted *Penicillium chrysogenum*. However, these molecules are present in the fungal cell wall in a complex manner; as such all the active groups might not be available for interaction with malathion. Thus the interaction of malathion with ROB occurs in a very complex manner.

4. Conclusions

R. oryzae biomass is an efficient adsorbent for malathion, a widely used organophosphorous pesticide. Adsorption process follows Langmuir–Freundlich dual isotherm model indicating that both physical and chemical sorption takes place simultaneously. Scanning electron micrographs and EDX spectra indicate that malathion is adsorbed on the cell surface of the fungus. Amine groups of chitosan are mainly responsible for chemical interaction between malathion and *R. oryzae* cell wall. Hydrophobic interaction is the main cause of physical interaction as adsorption of malathion decreased to a great extent after removing lipids from ROB. *R. oryzae* biomass may be used for the removal of malathion from potable water.

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