Spent mushroom substrate: a crucial biosorbent for the removal of ferrous iron from groundwater

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Abstract

A new approach was carried out with the spent mushroom substrate (SMS) of *Pleurotus florida* on ferrous iron (Fe^{2+}) removal using live, dead and pretreated substrate. In this study, the various dosage levels of SMS namely, 0.25, 0.50, 1.0 and 1.50 g/50 mL were used for the removal of Fe^{2+} at different time intervals for 90 min. The effect of various temperatures and pH on Fe^{2+} removal was studied with optimized dosages and time intervals. The biosorption potential of *P. florida* SMS was checked against the iron-contaminated groundwater collected from in and around Salem, Namakkal and Dharmapuri districts of Tamil Nadu. The biosorption data were obtained and analyzed in terms of their kinetic behavior. Among the SMS of *P. florida*, the live SMS showed potential Fe^{2+} removal (100%) from aqueous metal solution in all the tested concentrations. SMS of *P. florida* showed high potential removal of Fe^{2+} in neutral pH, at room temperature and explored an efficient sorption ability (100%) in the tested water sample (SW10). The adsorption kinetic values fitted very well with pseudo-second-order when comparing with pseudo-first-order reaction. FTIR, SEM and EDX analysis proved the accumulation of Fe^{2+} by the SMS. The present study confirmed that the live SMS of *P. florida* may serve as a potential and eco-friendly biosorbent for removal of Fe^{2+} from the iron-contaminated water.

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Graphic abstract

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1 Introduction

Heavy metals are necessary for the growth and metabolism of living organisms at low concentrations, but several of them are poisonous at higher concentrations. Recent advances are necessary for treating the heavy

metal-contaminated water by efficient and low-cost technology [1]. The exploration of heavy metal-contaminated water has become an essential focus of environmental scientists in recent years. Likewise, the iron content, either ferric or ferrous exceed the limit of above 0.3 mg/L in drinking water leads to many human health disorders [2]. Generally, iron occurs in water as a soluble form (Fe^{2+}) and it becomes an insoluble form (Fe^{3+}) when it comes in contact with air. The presence of iron in water imparts the color, odor, makes the teeth and nail as black and weaker

as well as leads to roughness of skin and stickiness of the hair. Metal processing industries are prominently located in and around the Salem district, which are somehow being the sources of metal discharge that contaminates soil and water. A total reserve of over 500 million tonnes with an average grade of 38% iron is estimated for the major deposits occurring in various districts like Salem, Vellore, Namakkal, Dharmapuri, Villupuram, Tiruvannamalai, Thiruchirappalli and Perambalur [3, 4].

Physical and chemical processes like coagulation, flocculation, ion exchange, membrane separation and oxidation are available for the treatment of heavy metals. The above methods described are facing high cost, high sludge production, handling and disposal problems and technical constraints. Hence, it requires cost-effective and environmentally sound techniques for treatment of wastewaters containing metals. The process, adsorption is now documented as an efficient, economical and well-paid for heavy metal removal in wastewater. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Currently, non-living and microbial biomass are derived as biosorbents from natural sources [5].

During commercial mushroom production, the industry generates huge amount of spent mushroom substrate (SMS) as a waste byproduct. It is a mycelial unexploited left-over substrate after harvesting from the mushrooms. Day by day, the voluminous amount of SMS is generated in each mushroom industry since the mushroom plant are steadily growing. Lau et al. [6] reported that the production of 1 kg of mushrooms will generate 5 kg of spent residual material as SMS. In recent years, the mushroom industries are facing lots of tasks in storing and disposing the SMS. Each industry discards an average amount of about 24 tonnes of SMS per month [7]. Apparently, the obvious solution is to increase the demand for SMS through exploration of new applications for utilization. If SMS is to be recycled and reused, it would be a more economical and eco-friendlier.

The spent mushroom substrate has an inherent ability to absorb and or degrade toxins due to its high organic matter content and its diverse microbial populations. SMS of *P. pulmonarius* was used to treat petroleum, oil and grease and di (2-ethylhexyl) phthalate (DEHP)-contaminated soil and the results were very promising [8]. The SMS was most widely used as an organic tool for the bioremediation of acid mine drainage (AMD), which was an uncomplicated treatment system to treat effectively. Mushroom substrate can be a simple and cost-effective technology to treat the waste water containing heavy metals [9, 10]. In bioremediation, dyes were also successfully decolorized by crude enzymes present in the SMS [11].

Industrially produced heavy metal ions are considered as a major source of environmental contamination that

led to worsening of natural ecosystems and social health [12]. The iron is a priority heavy metal which poses a significant problem in groundwater due to its toxic nature. The removal of groundwater iron is essential for contaminated water before being utilized since large amount of iron both ferric and ferrous in drinking water often causes several health hazards in human being and other living organisms. Several authors captivated bio-adsorption as a sustainable low-cost technology on the removal of environmental contaminants [13, 14]. Wastes from edible mushroom and anaerobically digested seaweeds were used as a narrative biosorbent for the removal of heavy metals like cadmium, lead, chromium and copper [15, 16].

Adsorption efficiency of *Pitpappa* biomass was used for bioremediation process under single and binary metal systems [17]. The heavy metal biosorption was thrived in the multi component system on dried activated sludge with mechanism and surface characterization [18]. Metal ion removal was attained successfully in a horizontal rotating tubular bioreactor by a combined diffusion and adsorption models [19]. Adsorptive removal of heavy metals from aqueous solution was succeeded using chemically activated *Diplotaxis Harra* biomass [20]. Removal of iron from the waste ferrous sulfate by co-precipitation and magnetic separation is an alternative method [21]. In another study, Weizhi et al. [22] used a mixture of CO₂ and H₂O for the elucidation of ferrous iron through an oxidation process. So far, no reports have been studied on the adsorption of Fe²⁺ using *P. florida* SMS and this is the novel approach for the adsorption of Fe²⁺ using SMS of *P. florida*. Hence, the SMS of *P. florida* was subjected to adsorption of Fe²⁺ from the iron-contaminated water collected from different areas of Salem, Namakkal and Dharmapuri districts.

2 Materials and methods

2.1 Collection and processing of *P. florida* spent mushroom substrate

Mushroom industries generate a virtually inexhaustible supply of a co-product called spent mushroom substrate (SMS). It was used as a novel biosorbent for the adsorption of Fe²⁺ in aqueous solution. SMS of *P. florida* on the removal of Fe²⁺ contaminant was carried out using live, dead and chemically (sodium hydroxide, formaldehyde and orthophosphoric acid) pretreated SMS. These adsorbents were used in different dosage levels, such as 0.25, 0.50, 1.0 and 1.50 g/50 mL at different time intervals of 10, 20, 30, 40, 50, 60, 70, 80 and 90 min.

The *P. florida* spent mushroom substrate was collected from Panamarathupatti, Salem, Tamil Nadu, India, and it was air-dried and manually chopped into small pieces. This

Fig. 1 Spent mushroom substrate

SMS was stored at room temperature in a sealed plastic bag which was then placed in a dry and dark container (Fig. 1).

2.2 Collection of metal-contaminated water

The area selected for this present study covers around Salem, Namakkal and Dharmapuri districts. The site is located in the longitude of 78.14 °E and the latitude of 11.66 °N (Salem), the longitude of 78.17 °E and the latitude of 11.23 °N (Namakkal) and the longitude of 78.17 °E and the latitude of 12.13 °N (Dharmapuri) in Tamil Nadu, South India. Groundwater samples were collected in a sterilized plastic container from the iron-contaminated areas of Salem, Namakkal and Dharmapuri Districts of Tamil Nadu. The samples were carefully transported to the laboratory and stored at 4 °C until for the further analysis. Nearly 14 water samples were collected and analyzed for significant physicochemical characteristics and Fe^{2+} content using standard methods [23].

2.3 Adsorption of Fe^{2+} using SMS of *P. florida*

Prior to treat the groundwater, a batch mode study was carried out to optimize the efficiency of adsorbent on Fe^{2+} removal from aqueous solution at different environmental factors. The *P. florida* SMS was used as a potential adsorbent to remove Fe^{2+} from aqueous solution.

The stock solution of Fe^{2+} was prepared by dissolving 3.04 g of ferrous sulfate to 100 mL of double-distilled

water. From this stock solution, 1000 and 100 mg/L of ferrous stock was prepared by dissolving with the required volume of deionized water. From 100 mg/L stock solution, various concentrations of Fe^{2+} solution were prepared.

2.4 Effect of live adsorbent dosage on Fe^{2+} removal

For determining the optimal adsorbent dosage (live SMS) for Fe^{2+} removal, 50 mL of aqueous solution containing Fe^{2+} at various concentrations of 4, 6 and 8 mg/L were prepared in 250 mL conical flasks and inoculated with 0.25, 0.5, 1.0 and 1.5 g/50 mL of adsorbent dosages. Then the flasks were kept in a rotary shaker at 120 rpm for 90 min. About 1 mL of Fe^{2+} solution was taken at a regular interval of 10 min and analyzed Fe^{2+} content by standard method using UV–VIS spectrophotometer (Cyber lab UV100, USA) at 400 nm [23].

2.5 Effect of dead adsorbent dosage on Fe^{2+} removal

To enhance the adsorption rate of Fe^{2+} , the SMS of *P. florida* was autoclaved at 15 lbs for 15 min. Then the SMS was washed with generous amounts of deionized water, filtered using a muslin cloth and used as adsorbent for the biosorption process. The study was carried out as the protocol shown in live adsorbent.

2.6 Alkali treated SMS of *P. florida* and Fe^{2+} removal

As reported by Sathishkumar et al. [24], SMS of 15 g was transferred into 100 mL of 0.5 N NaOH solution for 30 min and washed with sterile distilled water and used as an adsorbent. Various concentrations of Fe^{2+} (4, 6 and 8 mg/L) were prepared from 100 mg/L of Fe^{2+} stock solution and inoculated with various NaOH treated adsorbent dosages (0.25, 0.50, 1.0 and 1.5 g/50 mL) in 250-mL conical flasks. Then the flasks were kept in a rotary shaker with 120 rpm at room temperature for up to 90 min. At a regular interval of 10 min, 1 mL of treated solution was taken and used to estimate the amount of Fe^{2+} .

2.7 Acid treated SMS of *P. florida* and Fe^{2+} removal

SMS of 15 g was transferred into 100 mL of 10% orthophosphoric acid solution for 30 min. After proper washing with sterile distilled water the substrate was used for adsorption study. Various concentrations of 4, 6 and 8 mg/L of Fe^{2+} were prepared from ferrous stock solution and inoculated with various acid treated adsorbent dosages (0.25, 0.5, 1.0 and 1.5 g/50 mL) in conical flasks. Then the flasks were kept under agitation with 120 rpm at room temperature for 90 min. At a regular interval of 10 min, 1 mL of Fe^{2+} solution was taken and estimated for the level of Fe^{2+} .

2.8 Formaldehyde treated SMS of *P. florida* and Fe^{2+} removal

About 15 g of filtered SMS was transferred into 100 mL of 15% formaldehyde solution for 30 min. For adsorption study, 4, 6 and 8 mg/L of Fe^{2+} was prepared from Fe^{2+} stock solution and inoculated with formaldehyde treated adsorbents at various dosages (0.25, 0.5, 1.0 and 1.5 g/50 mL) in conical flasks. Then the flasks were kept under agitation with 120 rpm at 30 °C for up to 90 min. At a regular interval of 10 min, 1 mL of Fe^{2+} solution was estimated for the level of Fe^{2+} .

2.9 Effect of various pH on biosorption of Fe^{2+}

Adsorption experiment was carried out at the pH ranges 3, 5, 7, 9 and 11. The acidic and alkaline pH of the medium has been maintained by adding the necessary amounts of hydrochloric acid and sodium hydroxide solutions, respectively. The parameters, particle size of the adsorbents and temperature optimized were kept stable while carrying out the study. During the experiment, 1 mL of aqueous solution was taken and analyzed the presence of Fe^{2+} .

2.10 Effect of various temperatures on biosorption of Fe^{2+}

The adsorption experiment was carried out at four different temperatures viz., 30, 35, 40 and 45 °C in a thermostated shaker machine (Neolab, India). The reliability of the temperature was sustained with an accuracy of ± 0.5 °C. The parameters, particle size of the adsorbents and temperature were kept optimum while carrying out the experiments. During the experimental study, 1 mL of aqueous solution was taken and analyzed for the presence of Fe^{2+} .

2.11 Fe^{2+} removal from groundwater sample (SW10) using different dosage of live SMS

Among the different samples collected from various places, the sample site SW10 showed high amounts of Fe^{2+} . Hence, SW10 sample was processed for adsorption in batch mode and column studies. For determining the optimal adsorbent dosage for Fe^{2+} removal, 50 mL of Fe^{2+} -contaminated water (SW10) was taken in 250-mL conical flasks and inoculated with various adsorbent dosages (0.25, 0.5, 1.0 and 1.5 g/50 mL). Then the flasks were kept under agitation at 120 rpm with suitable optimized conditions for 90 min. Every 10 min time interval the amount of Fe^{2+} was estimated.

2.12 Adsorption of Fe^{2+} by SMS of *P. florida* packed in column studies

This study was carried out using a column packed with live SMS at constant bed heights and constant flow rates with the collected Fe^{2+} -contaminated water sample (SW10). The column is made up of glass and 4 cm of internal diameters and 35 cm of height. In the column, the SMS bed height was adjusted into 10 cm and flow rate was fixed at 2.5 mL/min. The sample was collected from the outlet of a column at a time intervals of 10 min up to 3 h and analyzed the amount of Fe^{2+} concentration by standard method using UV–VIS spectrophotometer (Cyber lab UV100, USA) at 400 nm.

2.13 Determination of Fe^{2+} and significant physicochemical parameters in groundwater

The Fe^{2+} -contaminated water samples were collected from Salem, Namakkal and Dharmapuri districts and the significant physicochemical parameters such as color, odor, pH, total solids (TS), total suspended solid (TSS), total dissolved solid (TDS) and Fe^{2+} were analyzed by using standard prescribed methods [23]. Entire parameters were also determined in the treated water through the column study.

2.14 Adsorption kinetics study

Kinetic experiments using an untreated (live) *P. florida* SMS were conducted under similar conditions which was already mentioned above, and the samples were withdrawn at regular intervals for analysis. The pH of the solution was monitored continuously with a pH electrode and adjusted with 0.1 N HCl or 0.1 N NaOH solution, if deviations were observed.

In order to investigate the sorption kinetics of Fe^{2+} using live SMS of *P. florida*, the most commonly used pseudo-first-order and pseudo-second-order rate equations [25] were employed to fit the experimental data obtained from batch metal iron removal experiments.

A simple pseudo-first-order rate equation is expressed as

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1 t}{2.303} \quad (1)$$

where q_e and q_t are the amount of Fe^{2+} (mg/g) adsorbed at equilibrium and at time t , respectively, and k_1 is the first-order rate constant (/min). The value of k_1 was calculated from the slope of the plot of $\text{log}(q_e - q_t)$ versus t .

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models, and the most popular linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_t (mg/g) is the amount adsorbed at time t , q_e (mg/g) is the amount of Fe^{2+} adsorbed at equilibrium, k_2

is the second-order adsorption rate constant (g/mg/min), $h = k_2 q_e^2$ (mg/g/min) is the initial sorption rate. The application of the pseudo-second-order kinetics by plotting t/q_t versus t yielded the second-order rate constant k_2 .

2.15 Characterization of iron adsorbed SMS with FTIR, SEM and EDX

Live SMS after groundwater treatment was homogenized with distilled water and dried at 60 °C for 48 h. A FTIR instrument (Perkin Elmer Spectrum RX/FTIR system) was used to determine the functional groups of adsorbent. The pellet was prepared to be 1% w/w of the concentration of the SMS in KBr. Besides, the surface morphology of SMS

Table 1 Sampling area and number of Fe^{2+} -contaminated water

S. No	Districts	Sampling areas	Sample Code	Fe^{2+} concentration (mg/L)
1	Salem	Chalk hills	SW1	0.018
2	Salem	Kanjamalai	SW2	0.024
3	Salem	Thalamalai	SW3	0.017
4	Salem	Steel plant	SW4	0.028
5	Salem	Sithar Kovil	SW5	0.049
6	Salem	Dalmia Board	SW6	0.007
7	Salem	Panamarathu-patti	SW7	0.005
8	Salem	Bothamalai	SW8	0.008
9	Salem	Poolampatti	SW9	0.029
10	Salem	Mecheri	SW10	6.71
11	Namakkal	Kolli hills	NW1	0.044
12	Namakkal	Nainarmalai	NW2	0.011
13	Namakkal	Rasipuram	NW3	0.015
14	Dharmapuri	Theerthamalai	DW1	0.008

Fig. 2 Adsorption of different concentration of Fe^{2+} by various dosages of live SMS

and the sorption nature of Fe^{2+} were scanned with a scanning electron microscope (SEM) (Jeol JSM SEM 5500 LV) and energy dispersive X-ray analyser (EDX).

3 Results and discussion

The iron-contaminated water samples were collected from in and around Salem, Namakkal and Dharmapuri districts and studied their potential biosorption of Fe^{2+} using SMS of *P. florida*. Before treatment, the initial concentration of ferrous iron was analyzed in each water sample by standard method. The iron content (Fe^{2+}) seems to be higher in water samples collected from Mecheri region of Salem District (Table 1). The presence of iron in this area is mainly due to natural deposition of ores and operations of metal bearing industries. Since the industries generating metal-based wastes in the form of crusts, only the accessibility of iron was analyzed in each sample. Live, dead and chemically treated SMS were used as sorbents to remove such elements (Fe^{2+}) from aqueous solution to optimize adsorbent dosage, pH and temperature at different time intervals. SMS was selected as significant bio-adsorbent due to its physical versatility and metal sorbing ability [26].

3.1 Fe^{2+} removal using different concentrations of live SMS

The spent mushroom substrate of *P. florida* was used as a sorbent material for the removal of Fe^{2+} at different concentrations. The results of Fe^{2+} removal in aqueous solution noted that there was a maximum Fe^{2+} removal in all dosages (0.25, 0.5, 1.0 and 1.5 g) tested. At 4 mg/L concentration, maximum biosorption was observed in 1.0 g of SMS suspension during 90 min of exposure time and within 70 min of time a complete (100%) biosorption was observed at 0.5 g of SMS used (Fig. 2a). In aqueous solution containing 6 mg/L of Fe^{2+} , the dosage of 0.5 g of SMS adsorbed 100% of Fe^{2+} at 60 min and the maximum Fe^{2+} adsorption was observed at 80 and 90 min by 1.0 and 1.5 g of SMS, respectively (Fig. 2b). As a result, the dosage of 0.25 g of SMS adsorbed less amount of Fe^{2+} when compared to 0.5, 1.0 and 1.5 g of SMS. In the case of 8 mg/L of Fe^{2+} concentration, maximum of 96.5% biosorption was observed at 90 min in all tested dosages (Fig. 2c). The sorption rate of Fe^{2+} was higher when increasing the adsorbent dosage from 0.25 to 1.5 g. This may be due to its nature and extendable adsorbent dosage [27].

The evaluation seemingly is in agreement with observations recorded in the case of different fungal biomass [28] and Shokoohi et al. [29] who obtained 95% of iron adsorption with 0.9 g of dried biomass by activated sludge as dosage. The maximum removal (91.98%) of Fe^{2+} was observed

Fig. 3 Adsorption of different concentration of Fe^{2+} by various dosages of dead SMS

at one hour of contact time using the live biomass of *P. ostreatus* as adsorbent [30]. It has been demonstrated that mushroom mycelium and spent mushroom substrate are used as a potential biosorbents for the removal of heavy metals [31–33] and this fact has also been confirmed in this study. Fungi offer a wide range of chemical groups that can attract and sequester the metals in biomass [34, 35].

Fig. 4 Adsorption of different concentration of Fe^{2+} by alkali treated SMS

3.2 Fe^{2+} removal using different concentrations of dead SMS

The different concentration of autoclaved SMS was used for the removal of Fe^{2+} in aqueous solution. In 4 mg/L concentration of Fe^{2+} , the maximum biosorption was noted using 0.5, 1.0 and 1.5 g of SMS at 90 min of time interval, but within 40 min complete biosorption was observed at 0.25 g of SMS (Fig. 3a). In 6 mg/L of Fe^{2+} solution, the dosage 0.25 g of SMS adsorbed the maximum Fe^{2+} at 70 min, whereas 1.5 g dosage showed a maximum Fe^{2+} adsorption

Fig. 5 Adsorption of different concentration of Fe^{2+} by acid treated SMS

at 80 min exposure (Fig. 3b). Fe^{2+} at 8 mg/L, biosorption was observed at 70 min (Fig. 3c). The reduction of biosorption capacity in autoclaved *P. florida* SMS may be attributed to the loss of intracellular uptake. Mamun et al. [36] investigated the dead fungal biomass showed no obvious change in the metal adsorption capacity for first 4 h, 56.56% for Cu(II) and 22.30% for Cr(VI). Usually, dead biomass could be a good adsorbent of metal ions. It was reported that dead biomass is reasonable in wastewater treatment because they are less affected by toxic wastes and can be renewed and recycled for several times [37].

3.3 Adsorption of different concentration of Fe^{2+} by alkali-treated SMS

The efficacy of different concentration of alkali treated SMS on Fe^{2+} removal was studied. Increased dosage of alkali treated SMS is directly proportional to the removal of Fe^{2+} was observed. In the 4 mg/L of Fe^{2+} solution, the maximum adsorption of Fe^{2+} was achieved at the dosage of 1.5 g of SMS when compared with the other dosages. Among the tested dosages the maximum adsorption was attained by 20 min exposure period, moreover the complete Fe^{2+} removal was observed at 40 and 50 min in 0.5, 1.0 and 1.5 g of alkali treated SMS (Fig. 4a). In the 6 mg/L

Fig. 6 Adsorption of different concentration of Fe^{2+} by formaldehyde treated SMS

of Fe^{2+} solution, the dosage 0.25 g of SMS adsorbed less amount of Fe^{2+} when compared to 1.0 and 1.5 g of treated SMS (Fig. 4b). The maximum Fe^{2+} (90.1%) adsorption was obtained after 40 min in 1.0 g and at 60 min in 1.5 g of dosage. The complete Fe^{2+} was removed at 40 min in 1.5 g of treated SMS and at 60 min in 0.5 g of treated SMS, in 8 mg/L of Fe^{2+} aqueous solution (Fig. 4c).

3.4 Adsorption of different concentration of Fe^{2+} by acid treated SMS

The different concentration of acid treated SMS on Fe^{2+} removal was carried out at different Fe^{2+} concentrations. A complete biosorption was observed at 4 mg/L concentration in 1.5 g of SMS suspension during 40 min of exposure time and desorbed in 60 min (Fig. 5a). In 6 mg/L concentration, the dosage 0.25 g of SMS adsorbed less amount of Fe^{2+} when compared to 0.5, 1.0 and 1.5 g of SMS. The complete adsorption of Fe^{2+} was observed at 40 min in 0.5 and 1.5 g of acid treated SMS, whereas in 1.0 g, the maximum Fe^{2+} (100%) was observed at 60 min (Fig. 5b). At 8 mg/L concentration, maximum biosorption (87.62%) was observed at 40 min in 1.5 g of acid treated SMS and at 60 min in 1 g of SMS (Fig. 5c).

3.5 Adsorption of different concentration of Fe^{2+} by formaldehyde treated SMS

The different concentration of formaldehyde treated SMS on Fe^{2+} removal was studied in a batch mode study. At 4 mg/L concentration of Fe^{2+} solution, maximum (100%) biosorption was achieved in 0.50 g of SMS suspension used and the complete biosorption was observed during 50 min of exposure time in 1.0 g of SMS. The dosage of 0.25 g of SMS adsorbed less amount of Fe^{2+} when compared to 0.5, 1.0 and 1.5 g of SMS (Fig. 6a). In 6 mg/L of Fe^{2+} aqueous solution, the maximum Fe^{2+} was adsorbed in all tested dosages viz., 0.25, 0.5, 1.0 and 1.5 g for 40 min of contact time (Fig. 6b). In case of 8 mg/L of aqueous Fe^{2+} solution, the results showed that the increased dosage of formaldehyde treated SMS is directly proportional to the removal of Fe^{2+} . The dosage of 1.5 g of SMS adsorbed the complete Fe^{2+} at 30 and 40 min, whereas in 0.5 and 1.0 g entire Fe^{2+} was adsorbed in 80 and 60 min, respectively, (Fig. 6c).

3.6 Effect of live, dead and various pretreated SMS on the percentage removal of Fe^{2+}

Percentage adsorption of Fe^{2+} with different dosages of live, dead and chemically treated SMS was assessed. The dead SMS adsorbed Fe^{2+} ranging from 16.5 to 92.37%. Similarly, the alkali treated SMS showed adsorption about 18.4

Fig. 7 Adsorption of different concentration of Fe^{2+} by various pretreated SMS

to 98% Fe^{2+} . Acid and formaldehyde treated SMS removed Fe^{2+} significantly, they were ranged from 14 to 99% and 75 to 91%, respectively. Comparing to various treated SMS, the live SMS of *P. florida* showed maximum Fe^{2+} removal (85–100%) from aqueous solution in all the concentrations (Fig. 7). Hence, further study was carried out to remove Fe^{2+} using various concentrations of live SMS.

Removal of Fe^{2+} metal by test SMS was confirmed due to its nature and acid pretreatment. The assessments

Fig. 8 Adsorption of different concentration of Fe^{2+} using live SMS at various pH

apparently agreed with other studies captivated by many workers. The SMS used for Fe^{2+} removal is precisely evidenced the sorption mechanisms of heavy metals by the study carried out with *Mucor rouxii* [38], *Aspergillus fumigatus* [39] and *Aspergillus niger* [40]. As an indication, Javaid et al. [40] reported that the binding of H^+ ions to the fungal biomass after pretreatment are accountable for the adsorption of heavy metals. This shows that the acids destroyed the adsorbing groups and their positive ions (H^+) may covalently bind to the adsorbent surfaces. Therefore, the residual H^+ ions on the pretreated biomass may change the biomass electro negativity, resulting in a reduction in biosorption capacity.

Generally, mushrooms can act as an effective biosorbents of toxic heavy metals since they are growing in natural habitat having large, tough texture and conductive characteristics required for their development into sorbents, thus obviating for immobilization process which was required for other microbial sorbents [41]. The SMS including lignocellulosic materials decomposed and permeated by the fungal mycelium. High levels of residual nutrients and enzymes are still left in SMS [42]. Live SMS without any treatment has the advantage of including viable mycelia and several active enzymes produced by the fungi throughout the growing cycle. Consequently, this fresh SMS may perform more efficiently in remediation activities

than autoclaved and chemically treated SMS. Therefore, if *P. florida* SMS is to be used as an adsorbent, then their use as fresh (without treatment) products should also be considered.

3.7 Effect of various pH on biosorption of Fe^{2+}

The effect of pH on the removal of Fe^{2+} using SMS of *P. florida* as an adsorbent was studied with different pH ranging from 3 to 11. Increased the pH of the solution is directly proportional to the removal of Fe^{2+} . In 4, 6 and 8 mg/L of Fe^{2+} aqueous solution, maximum Fe^{2+} removal was observed at pH 7, 9 and 11 (Fig. 8). Biosorption level was gradually decreased in acidic pH. The complete adsorption of Fe^{2+} was obtained at pH 7 at 10 min of exposure time. This indicates that neutral pH was the best for the biosorption process of Fe^{2+} . pH in the medium affects the solubility of metals and the ionization state of the functional groups (carboxylate, phosphate and amino groups) of the fungal cell wall. These functional groups carry negative charges that allow the fungal cell wall components to be potent scavengers of cations [43]. Usually, the adsorption rate is pH dependent. Hence, the rate of Fe^{2+} adsorption was varied in different pH [44].

3.8 Effect of various temperatures on biosorption of Fe^{2+}

The effect of various temperatures (30 to 45 °C) on biosorption of Fe^{2+} by *P. florida* SMS was studied. In 4, 6 and 8 mg/L of Fe^{2+} aqueous solution, maximum Fe^{2+} removal was observed at 30 °C and gradually decreased in the study conducted at 40 and 45 °C. Biosorption efficiency was increased due to higher affinity of active sites for heavy metals ion attraction. It was found that the highest biosorption efficiency of Fe^{2+} was 100% in 4 and 6 mg/L and 98.62% in 8 mg/L. At the temperatures of 35, 40 and 45 °C, the adsorption effectiveness was found to be 95.5, 58.25 and 65.62%, respectively, at 8 mg/L Fe^{2+} concentration.

Based on the results obtained, the biosorption efficiency increased at 30 °C but decreased at 40 °C (Fig. 9). It was found that the highest biosorption efficiency obtained for Fe^{2+} at 10, 20 and 40 min of exposure time in 30 °C. This indicates that 30 °C was the suitable temperature for biosorption process and the results were in agreement in Horsfall and Spiff [45]. Biosorption was also affected with a lesser extent within the temperature ranges from 20 to 35 °C. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute [46].

Fig. 9 Adsorption of different concentration of Fe^{2+} using live SMS at various temperatures

Fig. 10 Adsorption of Fe^{2+} in SW10 sample using various dosages of live SMS **Fig. 11** Adsorption of Fe^{2+} in SW10 sample by column treatment **Table 2** Physicochemical parameters of SW10 metal-contaminated water

S. No	Parameters	SW10 Fe^{2+} -contaminated water	
		Before treatment	After treatment
1	Color	Blackish white	Pale white
2	pH	10.5	7.0
3	TS (mg/L)	5000	3000
4	TSS (mg/L)	1000	0
5	TDS (mg/L)	5000	4000
6	Fe (mg/L)	6.71	0

Table 3 Kinetic models of live SMS biosorbent on Fe^{2+} removal

Kinetic model	Live SMS of <i>P. florida</i>			
	4 mg/L	6 mg/L	8 mg/L	SW10
Pseudo-first-order				
k_1	0.03	0.07	0.03	0.06
q_e	7.78	11.48	14.9	12.74
R_1	0.97	0.96	0.93	0.63
Pseudo-second-order				
k_2	0.15	0.15	0.14	0.16
H	0.21	0.74	1.43	2.07
R_2	0.63	0.98	0.99	0.99

Fig. 12 Kinetic model for the removal of Fe^{2+} using live SMS of *P. florida*. **a** Pseudo-first-order kinetic model, **b** pseudo-second-order kinetic model

Fig. 13 FTIR spectra of *P. florida* SMS *P. florida*

3.9 Fe^{2+} removal from groundwater (SW10) using different concentration of live SMS

The ferrous iron content was determined in such sample ranges between 0.011 and 6.71 mg/L (Table 1). The SW10 sample was taken for further batch mode and column studies since it contain a maximum of 6.71 mg/L Fe^{2+} . In batch mode studies the different dosages of fresh *P. florida* SMS on Fe^{2+} removal from SW10 sample was observed. Among the dosages (0.25, 0.5, 1.0 and 1.5 g) used, the complete Fe^{2+} removal was observed in 0.5 and 1.0 g of fresh SMS by 20 and 30 min. The dosage 0.25 g of SMS adsorbed less amount of Fe^{2+} when compared to 0.5, 1.0 and 1.5 g of SMS (Fig. 10).

3.10 Adsorption of Fe^{2+} in groundwater sample (SW10) using live SMS packed column

Column mode adsorption studies are considered to be very important in treatment application point of view because of its economical to treat any wastewater in continuous mode than in batch mode. Column mode adsorption study was carried out to find the efficiency of the adsorbent for continuous removal of Fe^{2+} . Column study was carried out only with live *P. florida* SMS adsorbent, which showed the maximum adsorption of Fe^{2+} in batch mode studies. The fresh SMS effectively removed the Fe^{2+} from SW10 water sample and the results were presented in Fig. 11. The efficiency of a column mode experiment depends on the flow rate at which constant flow rate was maintained. Results obtained that increase in adsorption of Fe^{2+} due to column bed volume. It may be due to the

availability of more surface functional groups on bed volumes.

3.11 Physicochemical parameters of Fe^{2+} -contaminated SW10 water

The results of the physicochemical parameters such as color, pH, Total solids, Suspended solids, Dissolved solids and Fe^{2+} of SW10 sample were analyzed and the results are given in Table 2. All the values were reduced significantly in the water treated by live biomass.

3.12 Adsorption kinetics study

Kinetic studies for the adsorption of Fe^{2+} were studied using pseudo-first-order and pseudo-second-order equations. In order to find the best kinetic model, the fitting of experimental data to kinetic equations were tested and kinetic constants and correlation coefficients were determined which were shown in Table 3 and Fig. 12. Adsorption followed pseudo-first-order and pseudo-second-order reaction kinetics. Pseudo-second-order kinetic plot of t/q_t versus t gave the perfect straight line for the adsorption of the different concentrations of Fe^{2+} aqueous solution and iron-contaminated water (SW10) onto live SMS

Fig. 14 Characterization of SMS by SEM and EDX. **a** Surface morphology and internal structure of the SMS at 20 and 5 μm , **b** EDX analysis of SMS adsorbed with Fe

indicating that adsorption reaction can be approximated with pseudo-second-order kinetic model.

The Table 3 represents the pseudo-second-order rate constant (k_2), correlation coefficients constant (R) along with the experimental and calculated uptake capacity (q_e). The values of q_e denote the adsorption of Fe^{2+} which were higher. In many cases, the pseudo-first-order equation did not fit well to the investigation data over the entire range of contact time. The data sufficiently fits to the pseudo-second-order model with high correlation coefficients in the range of 0.98–0.99 are much higher than those for pseudo-first-order kinetics (0.63–0.97) and their calculated q_e values agreed well with the experimental q_e values. It concludes that the pseudo-second-order kinetic model fits for the biosorption of Fe^{2+} on the SMS of *P. florida*. This result was in agreement with Al-Anber [47] who reported that Lagergren pseudo-second-order model was fittest for the adsorption of iron from aqueous solution.

3.13 Characteristic features of *P. florida* live SMS

The FTIR spectrum and characteristic bands of SMS is shown in Fig. 13. SMS consists of complex organic and inorganic materials such as proteins, phospholipids and polymers etc. The C=O bonds have a stretching motion at 1740 cm^{-1} . The motion of asymmetric vibration belonged to CH_3 groups corresponds to 1450 cm^{-1} . The bands 1660 , 1540 and 1300 cm^{-1} represent the stretching motion of protein amide I, II and III, respectively. Besides, 1250 , 1080 and 1150 cm^{-1} signifies the motion of PO_2 anti-symmetrical, PO_2 symmetrical and C–O stretching, respectively. As reported by Kusvuran et al. [48], the mechanism of Fe adsorption occurs probably the presence of carboxyl and phosphorus group via ion-exchange, surface complexation and electrostatic interaction between functional groups. Figure 14a represents SEM pictures of live SMS. The image view of 20 and $5\text{ }\mu\text{m}$ are signified the interior structure of live SMS. From the view of these results, it concludes that SMS had a macroporous structure. The roughness of SMS surface is a particular importance for the Fe adsorption capacity. EDX examination also showed a confirmation on the accumulation of Fe by the SMS (Fig. 14b).

4 Conclusions

The *P. florida* SMS is a potential source for the adsorption of Fe^{2+} from iron-contaminated water. The live SMS of *P. florida* showed potential Fe^{2+} removal from aqueous metal solution in all the tested concentrations. The effect of various pH and temperature on Fe^{2+} removal was studied with optimized dosage and at time intervals. SMS of *P. florida* showed high potential removal of Fe^{2+} in neutral pH and

at the temperature of $30\text{ }^\circ\text{C}$. The biosorption potential of SMS was checked in Fe^{2+} -contaminated water collected from in and around Salem, Namakkal and Dharmapuri districts. The live SMS of *P. florida* explored 100% adsorption ability of Fe^{2+} in SW10 water sample. The biosorption data were analyzed in terms of their kinetic behavior and the adsorption kinetic values fitted very well with pseudo-second-order when comparing with pseudo-first-order reaction. Analysis of SMS by FTIR, SEM and EDX proved that the potential adsorption of Fe^{2+} . Currently, various physical and chemical methods are the accessible progress for the adsorption iron like heavy metals. However, they provide several adverse outcomes and often generated a large amount of secondary solid wastes. Hence, the present study is an open account for the adsorption of Fe^{2+} by *P. florida* SMS.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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