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REVIEW

Removal of pollutants using spent mushrooms substrates

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Abstract
Due to increasing environmental pollution, there is a need for cheap and effective methods to remove pollutants from water. Mushrooms can be used as a green adsorbent in modified and natural forms to remove pollutants such as dyes and heavy metals. The use of edible mushrooms is not judicious because edible mushrooms have good nutritive and medicinal properties. Alternatively, the use of spent mushroom substrates is advised. This review discusses the potential of spent mushroom substrate as a source of immobilized mushroom mycelium, which is produced in large amounts after harvesting of mushroom fruit bodies. In laboratory conditions, *Agaricus, Pleurotus, Lentinus, Calocybe* and their spent mushroom substrates are efficient adsorbents allowing 70–90% of removal of pollutants. The efficiency of spent mushroom is similar to that of mushroom. Chemisorption and physisorption processes are involved in the adsorption process. Langmuir isotherms reveal the involvement of monolayer adsorption irrespective of the use of mushroom fruit bodies or spent mushroom substrate. Fourier-transform infrared (FT-IR) analysis reveals the presence of carboxyl, hydroxyl, amino group in the adsorption of pollutants, dyes and heavy metals.

Introduction

Globally, the production and per capita consumption of mushroom has increased at a rapid rate for last 5 decades. According to the United Nations Food and Agriculture Organization statistics, the average annual growth rate of edible fungi is 5.6% worldwide. During 1997–2012, annual per capita consumption of mushrooms increased from about 1 kg to over 4 kg. The main producer and consumer of mushroom is China (Royse 2014). In India, more than 40,600 tons of mushrooms produced annually (Pandey et al. 2014). Mushroom cultivation is one of the environmental friendly ways to recycle agricultural and agro-industrial wastes for the production of mushroom fruit bodies or mycelium with good nutritive and medicinal properties. In 2016, market value of cultivated edible mushroom species is about 30–34 billion dollars and medicinal mushroom species is 10–12 billion dollars. Therefore, it is billion dollar agribusiness which cannot be shut down.

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The problem related to mushroom cultivation industries is the disposal of waste generated after the harvesting of mushrooms. The mushroom substrate, left over after harvesting of mushroom fruit bodies, is called as spent mushroom substrate. The disposal of spent mushroom substrate in environment-friendly way is a great challenge for the mushroom industries. In Iran, there is an increase in the mushroom production industries which are generating more than 50,000 tons of spent mushroom substrate annually. The generation of spent mushroom substrate was generally two times higher than the mushroom harvested. According to Oei (1991), two tons of spent mushroom substrate remains from each ton of mushroom harvested. Now, efforts have been made to increase the mushroom production like the use of different substrate combinations and optimization of processes, which not only increased the biological efficiency and production capacity of mushroom but also reduced the generation of spent mushroom substrate.

Mushrooms are also known for their potential as adsorbent for the adsorption of pollutants from the industrial effluent and soil (Table 1). However, there are critics in using nutritive and medicinal species of mushroom in the adsorption of pollutants. To solve this issue, either non-edible varieties of mushroom or spent mushroom substrate of edible mushroom varieties have been used.

Table 1 Removal of pollutants by adsorption on the biomass of mushroom

S. no.	Mushroom spp.	Accumulated pollutants	Remarks	References
1	*Ganoderma lucidum*	Copper	Highest uptake capacity in mushroom for copper	Muraleedharan et al. (1995)
2	*Pycnoporus sanguineus*	Heavy metals	Removal of heavy metals lead, copper, and cadmium from aqueous solution was investigated in fixed-bed column studies. Besides the removal of heavy metals, column can be used even after a number of adsorption and desorption cycles	Zulfadhly et al. (2001)
3	*Agaricus bisporus* and *Lentinus edodes*	Cadmium	Adsorption of cadmium from aqueous solutions by these edible mushrooms	Mathialagan et al. (2003)
4	*Phanerochaete chrysosporium*	Cadmium	Used in two ways: (i) immobilized on Loofa sponge disk and (ii) free fungal biomass. Immobilized biomass could be regenerated and metal recovery can be done and reused in ten biosorption–desorption cycles without significant loss of capacity	Iqbal and Edyvean (2005)
5	*Agaricus macrosporus*	Zinc, copper, mercury, cadmium or lead	In supplemented and non-supplemented acid medium, greatest differences in biosorption capacity were seen for living biomass	Melgar et al. (2007)
6	*Inonotus hispidus*	Arsenic	*I.hispidus* biomass was feasible, spontaneous and exothermic under examined conditions and therefore, can be used for arsenic adsorption	Sarı and Tuzen (2009)
7	*Pleurotus platypus*, *Agaricus bisporus* and *Calocybe indica*	Cadmium and lead	*P. platypus* showed the highest metal uptake potential for cadmium, whereas *A. bisporus* exhibited maximum potential for lead. Milky mushroom showed the lowest metal uptake capacity for both the metals	Vimala and Das (2009)
8	*Tremella fuciformis* and *Auricularia polytricha*	Cd, Cu, Pb, and Zn	The humid *T. fuciformis* biomass is able to reduce heavy metals concenas compared to dry biomass	Pan et al. (2010)
9	*Mushroom*	Crude oil	These have ability to adsorb crude oil and heavy metals	Emuh (2010)
10	*Pycnoporus sanguineus*	Oil removal	Oil removal from water using mushroom	Srinivasan and Viraraghavan (2010)
11	*Pleurotus ostreatus*	Cadmium	*P.ostreatus* has good biosorption capacity	Tay et al. (2011)
12	*Agrocybe aegerita; Pleurotus ostreatus; Hericium erinaceus*	Copper	Adsorption affected by the initial concentration of Cu^{2+}, adsorption time, and concentration of mushroom powder	Huo et al. (2011)
13	*Pleurotus sajor-caju*	Heavy metal Zn	Mushroom fruit body is effective in reducing the concentration of heavy metals and zinc	Jibran and Milsee Mol (2011)
14	*Boletus edulis, Macrolepiota procera* and *Xerocomus badius*	Mercury	Data obtained by CV-AAS and inductively coupled plasma atomic emission spectroscopy were highly biased for mercury adsorption	Jarzynska and Falandysz (2011)
15	*Trichoderma sp.*	Mancozeb pesticide	*Trichoderma* sp. remove macozeb from soil	Ahlawat et al. (2010)

Table 1 (continued)

S. no.	Mushroom spp.	Accumulated pollutants	Remarks	References
16	*Tricholoma lobayense*	Congo red dye	Langmuir isotherm was fitted to the sorption equilibrium data, and the maximum adsorption capacity was 147.1 mg/g at 25 °C.	Tian et al. (2011)
17	*Pleurotus tuber-regium*	Heavy metals	Biosorption potential of *Pleurotus tuber-regium* in contaminated with some heavy metals and the effect of such heavy metals on the pileus development of *Pleurotus tuber-regium* were investigated and found good	Oyetayo et al. (2012)
18	*Galerina vittiformis*	Cadmium, chromium, copper, lead, zinc	This mushroom adsorbs the heavy metals and possesses various cellular mechanism spent mushroom substrates that may detoxify heavy metals	Damodaran et al. (2013, 2014)
19	*Auricularia polytricha*	Emulsified oil	*A. polytricha* fruit body was a fast, film-diffusion-controlled physical process for oil biosorption as depicted by multifactor effectiveness study, kinetic study, and scanning electron micrographs	Yang et al. (2014)
20	*Pleurotus ostreatus*	Malachite green	The highest percent removal of dyes was 89.58% and the largest biosorption capacity reached 32.33 mg/g.	Chen et al. (2014)
21	*Pleurotus eryngii*	Copper	Efficient in removing copper from the solution	Kan et al. (2015)
22	*Agaricus campestris, A mellea,C. inversa, C. nebularis, M. procera, B. aestivalis, B.edulis, L.deterrimus, T.portentosum, T. terreum*	Nickel, chromium, lead, cadmium, mercury	Heavy metal contents in the mushrooms are mainly affected by species and their lifestyle. All mushrooms species were bioexclusors of nickel, chromium, and lead	Širić et al. (2016)
23	*Pleurotus ostreatus*	Dyes	It is able to decolorize dyes	Skariyachan et al. (2016)
24	*Lepiota hystrix*	Copper and lead	This mushroom biomass has a good potential to be used in removal of metal ions and can be used up to three adsorption/desorption cycles without losing efficiency	Kariuki et al. (2017)

Spent mushroom substrate possesses leftover mycelium of the mushroom which can be utilized as a source of immobilized mushroom mycelium. Burning and landfill are the most adopted techniques for the disposal of spent mushroom substrate but are not environment friendly. Many researchers have analyzed the efficiency of mushrooms (Kariuki et al. 2017; Kan et al. 2015; Damodaran et al. 2014) and spent mushroom substrate (Md-Desa et al. 2016; Siasar and Sargazi 2015; Kamarudzaman et al. 2015) as adsorbent of pollutants, dyes and heavy metals along with evaluating the environmental impacts. This chapter describes the potential of mushroom and spent mushroom substrate in the adsorption of pollutants. This article is an abridged version of the chapter published by Kulshreshtha (2018) [chapter 9, In book: Green Adsorbents for Pollutant Removal] in the book series Environmental Chemistry for a Sustainable World (https://www.springer.com/series/11480).

Mechanism of adsorption

Generally, binding of metals, pollutants and dyes to the mushrooms and spent mushroom substrate depends on the four mechanisms: (i) adsorption (ii) ion exchange (iii) complexation and (iv) precipitation. Physical adsorption is based on the electrostatic forces and Van der Waals forces. Occasionally, cation transport system transports the metal ions bearing the same charge and ionic radius along with the other required ions for metabolism. It has been reported that mushroom biomass develops mechanisms to resist the heavy metals through the secretion of chelating substances that are able to bind with metal ions. Further, metal ions accumulation is reduced due to the alterations in the metal transport system. Another mechanism to develop resistance includes the binding of metal ion to intracellular molecule such as metallothionein or accumulates in intracellular organelles like vacuole or mitochondria (Ayangbenro and Babalola 2017).

The principal mechanism of heavy metal binding is related to physical binding and chemical binding of metal ions to the spent mushroom substrate. However, ion exchange can be observed as an important phenomenon in adsorption. Occasionally, bivalent metal ions are exchanged with counter ions of polysaccharides.

As mentioned earlier, complexation plays an important role in the adsorption process. It is based on the surface charge of spent mushroom substrate and mushroom. Mushroom possesses chitin, a negative charge compound in the cell wall, which provides negative charge to the surface of mushroom mycelium. Both possess negative charge due to the presence of carboxyl, amino, thiol, amide, imine, thioether, phosphate, which provide them ability to make complexes during metal–ligand and adsorbate–adsorbent interaction (Javanbakht et al. 2014).

Precipitation, a metabolically independent process, is a chemical reaction between the metal and cell surface of mushroom and spent mushroom substrate. This leads to the deposition of heavy metals into solution and on the surface of mushroom mycelium.

In the living mushroom mycelium, adsorption process depends upon the metabolic processes, while dead biomass of mushroom passively binds metal ions by various physicochemical mechanisms. Nevertheless, complete knowledge of metabolism-dependent processes is required in order to optimize and maintain the adsorption in the living system. In the living biomass, metabolic activities are affected by rate of respiration, the products formed during metabolism and nutrient uptake which further affects adsorption, ion exchange, complexation and precipitation.

In the case of organic pollutants, adsorption is based on chemical structure such as molecular size, charge, solubility, hydrophobicity and reactivity. In addition to adsorption and complexation, permeation of spent mushroom substrate biomass may contribute to the adsorption process.

Hydrocarbons are hydrophobic compounds, insoluble in water, however, can be associated with nonpolar environment. They can be adsorbed on the surface of organic substances and spent mushroom substrate biomass. Lipophilic, hydrophobic compounds can pass through cell membranes and adsorb into organic matrix of spent mushroom substrate (Javanbakht et al. 2014). In the case of dye adsorption, chitosan, extracted derivative of chitin, is better than naturally occurring mushroom chitin. Dyes adsorbed on the surface of chitosan by various mechanisms that include surface adsorption, chemisorption, film diffusion and pore diffusion; and chemical reactions like adsorption complexation and ion exchange. The main group involved in the adsorption of dyes is amine group; however, hydroxyl group may also contribute in the process (Javanbakht et al. 2014). It is pertinent to note that effectiveness of the substrate in adsorbing the pollutants is more important than the mechanism involved in the adsorption.

Mushroom as a green adsorbent

Mushrooms can be served as green adsorbent which can accumulate pollutants from the surroundings and reduce their concentration (Udochukwu et al. 2014). The role of mushroom in adsorption of pollutants, dyes and heavy metals has been assessed by many researchers (Table 1). The mushroom mycelium can be used in the live or dead form. Live form of mycelium requires the maintenance of appropriate condition in order to maintain the viability. However, dead biomass can be used in a variety of conditions as it is not affected by pH, temperature, salinity (Kulshreshtha et al. 2014).

Preparation of mushroom and its mycelium as adsorbent

Mushroom and its mycelium are required in bulk amount for the adsorption purpose. Therefore, mushrooms can be collected in bulk amount from the natural environment or can be cultured in the laboratory. In the laboratory, mushroom can be cultured by solid-state fermentation process and submerged fermentation process in the fermenter or Erlenmeyer flask. In solid-state fermentation, substrate is prepared from agricultural or agro-industrial wastes which lead to the formation of fruit bodies of mushroom. In contrast, mushroom culture in Erlenmeyer flask or fermenter leads to the production of mycelial biomass of mushroom (Fig. 1).

Mycelium of mushroom can be cultured in an Erlenmeyer flask containing malt extract medium, and incubated at 25 °C, 125 rpm in an incubator shaker for 21 days. For harvesting the mycelium, broth was separated by filtration technique and discarded. Adsorbent can be prepared from the harvested mycelium or collected mushrooms by autoclaving for 15 min at 121 °C, 18 psi pressure, which is followed by oven drying for overnight at 60 °C. It can be ground into fine particles and then sieved to get particles of uniform size, i.e., lesser than or equal to 150 µm. This adsorbent can be used immediately, or preserved for a longer time in silica-filled desiccators (Abdul-Talib et al. 2013).

Modified mushroom for adsorption

Recently, Xu et al. (2016) produced an adsorbent by using *Pleurotus cornucopiae* and further, used for the adsorption of hexavalent chromium ions from the aqueous solution. To prepare adsorbent from the *Pleurotus cornucopiae*, it was washed with deionized water for several times, which was followed by drying at 50 °C for 3 d and grinding in a pulverized mill and sieve through 40-mesh, 60-mesh, and 100-mesh in order to get uniform particles of specific sizes. The surface of this dried mycelium was modified by chemical treatment to increase its adsorption capacity. Fourier-transform infrared spectroscopy analysis revealed that amine, hydroxyl, and carboxyl groups provide binding sites for adsorbate. These groups played an important role in adsorption when modified *Pleurotus cornucopiae* was

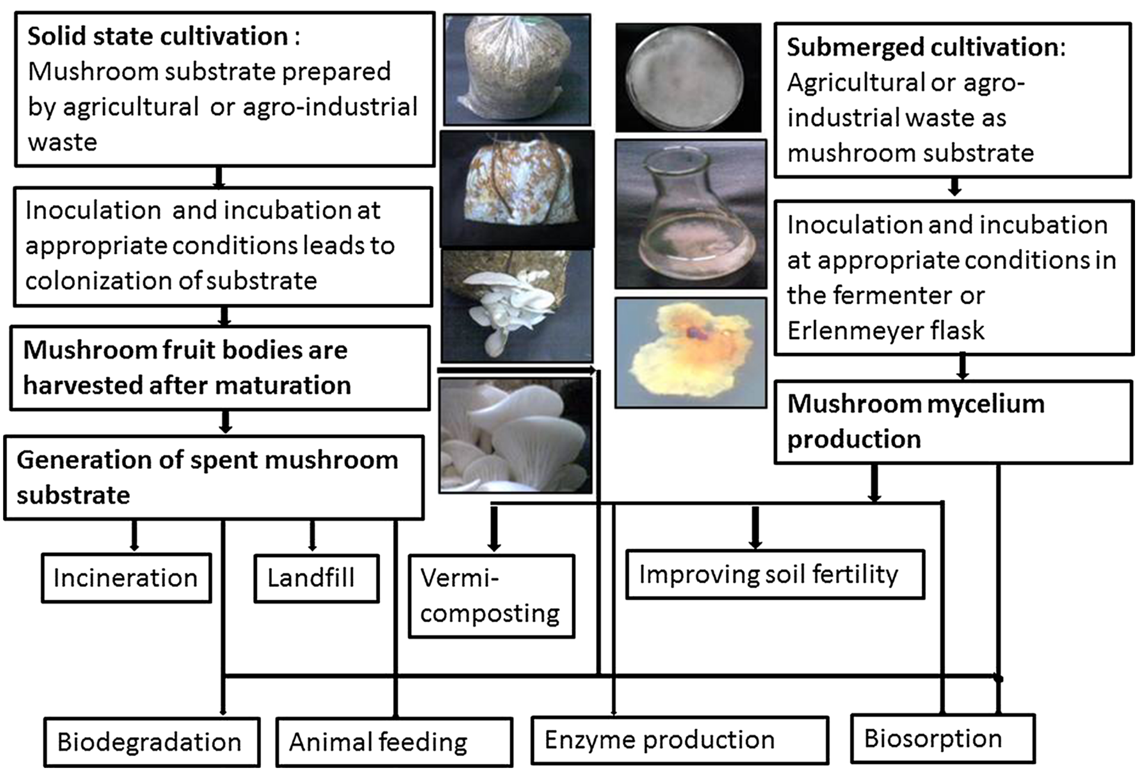

Fig. 1 Applications of the mushroom produced by submerged and solid-state cultivation method. Submerged fermentation and solid-state cultivation provides mycelial biomass and fruit bodies, respectively, which can be used for consumption. Disposal of spent mushroom compost by landfill and incineration is not an environment-friendly approach. Environment-friendly applications of spent mushroom compost include preparation of vermicompost, improving soil fertility, biodegradation or biosorption of pollutants, used as animal feed and for producing enzymes

used for the adsorption of hexavalent chromium ion. The increased dosage of this adsorbent increased the efficiency of adsorption of chromium ions. Under the optimum controllable factors like pH, temperature; hexavalent chromium removal efficiency of 75.91% was achieved. This adsorption was best fit to the Freundlich isotherm model (Xu et al. 2016). A detailed study at pilot scale and industrial scale plant is required to assess the potential of modified *Pleurotus cornucopiae* biomass in the adsorption of chromium ions so that technology can be implemented for industrial effluents.

In another experiment conducted by Xie et al. (2015), *Lentinula edodes* was treated with a mixture of sodium hydroxide, ethanol, and magnesium chloride. The effect of this treatment was assessed on adsorption capacity. Adsorbent was prepared by the approximately same procedure as mentioned in the aforesaid paragraph. In this study, initial concentration of heavy metals was 50 mg/L; adsorbent dosage was 5 g/L. This magnesium chloride-modified *Lentinula edodes* was used to adsorb cadmium and copper ions from the aqueous solution with high adsorption capacities of 51.64 ± 0.65 and 59.03 ± 0.64 mg/g, respectively, which was reported to be greater than that of raw biomass. A huge number of binding sites were exposed after the treatment of *Lentinula edodes* with magnesium chloride which helps in the adsorption of metals. In the adsorption of copper and cadmium ions, both physisorption and chemisorption were reported to involve. These processes are based on electrostatic interaction, ion exchange, and complex formation. The study of thermodynamic parameters revealed that the process was endothermic and spontaneous. The data were fitted well to pseudo-second-order kinetic model which revealed the involvement of chemisorption process. This study also focused on the recovery of heavy metals from real industrial effluent. The adsorption and heavy metal recovery efficiency was 90% and 80%, respectively (Xie et al. 2015). Therefore, magnesium chloride-treated spent mushroom substrate was found to be better than raw culture of *Lentinula edodes* in effective adsorption and desorption of heavy metals from the real industrial effluent.

Limitations of using mushroom in adsorption

Harvesting the mushroom mycelium for removal of pollutants is not a feasible option, especially in developing and undeveloped countries because the primary focus of mushroom cultivation is to provide protein-rich food to the people. Secondly, mushrooms also have anti-mutagenic, anti-inflammatory, anti-carcinogenic, antioxidant properties and can be used for medicinal purposes. Therefore, mushroom cultivation for bioremediation of pollutants, heavy metals and dyes by adsorption is not encouraged in these countries.

Adsorption by mushroom biomass or fruit bodies is worthy to remove pollutants from the environment; nevertheless, there is a need of safe disposal practices. Another problem related to mushroom cultivation is the generation of spent mushroom substrate. After the harvesting of mushroom fruit bodies, mushroom substrate is discarded as solid waste which is called as spent mushroom substrate, mushroom soil, recycled mushroom compost, or spent mushroom compost (Fig. 1). This substrate is a by-product of the mushroom industry, which gives rise to the most significant environmental issues, and therefore needs a strategy for its proper disposal.

Spent mushroom substrate as adsorbent

In the earlier attempts, spent mushroom substrate was disposed by landfills or by burning in open fields. In the case of landfill, spent mushroom substrate is piled up on the land; however, release of leachates from the pile may adversely affect the ground water quality (Kamarudzaman et al. 2014) and adjacent land. Later, spent mushroom substrate was used for a variety of purposes like animal feed, production of enzymes, vermicomposting and soil quality improvement (Fig. 1). The use of spent mushroom substrate in laccase, xylanase, lignin peroxidase, cellulase and other enzymes production is suggested by Phan and Sabaratnam (2012). Spent mushroom substrate can be a good feedstuff for animals due to the presence of vitamins and microelements like iron, calcium, magnesium and zinc, and essential amino acids (Foluke et al. 2014). The spent mushroom substrate was also used for improving the soil quality and crop yield (Ribas et al. 2009).

Selection and preparation of spent mushroom substrate as adsorbent

During the mushroom cultivation, cellulosic, lignocellulosic and hemicellulosic fibers are utilized by the mushroom for the growth. This leads to the gradual degradation of the substrate and pore formation. The pore size is increased with increase in time due to the continued substrate degradation process, which further increase adsorption properties of spent mushroom substrate.

The choice of spent mushroom substrate may vary as per availability in the local area (García-Delgado et al. 2013). Selection of appropriate spent mushroom substrate and its application in adsorption of pollutants seems to be a sustainable technology that will not only remove the pollutants, but also solve the problem of waste disposal (Prasad et al. 2013). The popular mushroom species around the world are *Agaricus* species and *Pleurotus* species, and therefore, cultivation of these species generates huge amount of waste which accumulates in the environment and causes ill effects. Therefore, spent mushroom substrate needs proper disposal practices

(García-Delgado et al. 2013). The spent mushroom substrate of these mushrooms is readily available and inexpensive biomaterial with high capacity of pollutant adsorption.

Spent mushroom substrate for adsorption of pollutants, dyes, and heavy metals have been prepared by different methods and analyzed. According to the method proposed by Siasar and Sargazi (2015), 2 g of spent mushroom substrate was added with 20 ml of water and the resultant solution was filtered through filter paper AK-01 blue. Spent mushroom substrate was retained by the filter which was collected and dried; and further, used in the adsorption experiment. In the method developed by Tay et al. (2011), the sample of spent mushroom substrate was prepared at 121 °C, 18 psi for 15 min and then dried in an oven at 60 °C. This was followed by grinding and sieving to obtain particle size lesser than 710 µm. This adsorbent was stored in dry cabinet. In another method, all conditions of preparing spent mushroom substrate adsorbent from *Pleurotus* species were kept same, except particle size which was lesser than 150 µm. This adsorbent was stored in silica-filled desiccators and used in performing the experiment for lead and cadmium adsorption (Tay et al. 2011; Abdul-Talib et al. 2013).

Characterization of spent mushroom substrate adsorbent

The adsorbent must be sufficiently porous to adsorb pollutants from the surrounding. The spent mushroom substrate is composed of different types of polymers such as lignin, cellulose, and hemicellulose which are degraded by mushroom mycelia during its growth and utilized as carbon and energy sources. This degradation results in numerous pores in the spent mushroom substrate that makes it a suitable substrate for adsorption (Yan and Wang 2013). These pores can be classified as micropores if pore diameter is lesser than 2 nm, mesoporous if pore diameter is in between 2–50 nm, and macropores if pore diameter is greater than 50 nm. The macroporous material has a great potential for adsorbing large sized adsorbates as compared to mesoporous or microporous adsorbent material. The structure of cell wall, micropores, mesopores, and macropores must be evaluated in order to analyze the potential of adsorbent. The characterization of spent mushroom substrate for using it as adsorbent can be done by the following methods:

Brunauer–Emmett–Teller Analysis

The specific surface area and total pore volume of spent mushroom substrate can be measured by surface area analyzer, a fully automated analyzer which evaluates the material by nitrogen multilayer adsorption measured as a function of relative pressure. Nitrogen does not react chemically with the substrate and therefore used in the analyzer. This technique determines the surface area and pore area and helps in acquiring important information for performing adsorption studies. Further, adsorbent categories can be defined on the basis of Brunauer–Emmett–Teller analysis, such as dispersed, nonporous, macroporous materials. Macroporous material have pore diameter greater than 50 nm is well fitted to type II isotherm. Mesoporous materials have pore diameter between 2 and 50 nm is well fitted to type IV isotherm. Microporous material has diameter lesser than 2 nm and well fitted to type I isotherm.

Scanning electron microscopy/energy dispersive x-ray spectroscopy analysis

It is an analytical technique used for the elemental analysis or chemical characterization of spent mushroom substrate. It is based on the interaction of X-ray and spent mushroom substrate. When X-rays are focused on the spent mushroom substrate, unique set of peaks can be observed on its electromagnetic emission spectrum according to the atomic structure of materials present in spent mushroom substrate.

Fourier-transform infrared spectroscopy analysis

This analysis provides an insight of adsorption process. The functional groups, involved in the adsorption process, can be determined by analyzing the peaks obtained by Fourier-transform infrared spectroscopy. Differences in the peaks of spent mushroom substrate before and after adsorption can be investigated by Fourier-transform infrared spectroscopy. These peaks reveal the important groups involved in the adsorption process (Kamarudzaman et al. 2014).

Solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance

Solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance is used to investigate the structural changes and interactions of cellulose with the pollutant during adsorption. It is also used to detect the presence of β-D-glucan and trace compounds present in dried powder of mushroom samples. For this purpose, the high- resolution solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance spectra can be recorded at the resonance frequency of approximately 100 MHz with the use of 4 mm rotors and frequency of 12 kHz and pulse duration of 1.9 µs. A high-power proton-decoupling field of 92 kHz can be applied during data acquisition. The spectra can be obtained at room temperature averaging over 5000–33,000 scans. Hydration of mushroom polysaccharide give rise to conformational stabilization, which is reflected in spectra by narrowing and splitting of resonance line (Fričová and Koval'aková 2013).

To evaluate the strategies for potential implementation, adsorption isotherms, adsorption kinetics, intra-particle diffusion ability can be used to explain the feasibility of adsorption process.

Adsorption of heavy metals by spent mushroom substrate

Heavy metals are noxious products discharged by a number of industries after the completion of industrial processes and are major pollutants in the soil and water. These are discharged by electroplating and metal finishing and metallurgical industries, leather tanning, textile dyeing and printing-based industries, fertilizer industries, acid mine drainages, and landfill leachates. Besides, agricultural and domestic activities also discharge heavy metals in the environment.

These are recalcitrant and hence accumulate in the environment and enter the food chain (Igwe and Abia 2006). After intake, heavy metals accumulate in the living tissue and disrupt biological processes due to their toxicity. Conventional methods for removing metal ions include a number of processes such as filtration, chemical precipitation and electrochemical treatment, ion exchange, membrane technologies, and activated carbon. Many of these processes are ineffective, especially when metal ion concentration in aqueous solution is 1 to 100 mg/L. Moreover, they produce huge amounts of toxic sludge which is difficult to dispose. Further, these cannot be implemented at large scale due to financial constraints. Nowadays, microbial adsorption-based approaches are gaining much attention in removing the metals from the environment. The most popular microbial option for adsorbing metal is mushroom mycelium which can be obtained from mushroom industry or mushroom cultivation units. The spent mushroom substrate, as green adsorbent, presented as an alternative to traditional physico-chemical means for removing heavy metals from soil and water. Spent mushroom substrate makes complex with heavy metals and increases its stability, however, reduces its bioavailability, which in turn reduces the toxic effect of metal on living beings.

According to Wang and Chen (2009), there are two methods for the removal of heavy metals. The first method is related to the usage of living biomass of mushroom for metal adsorption and removal; while the other methods, rely on the immobilization technology and modification in the adsorbent for making a type of ion exchange resin to use in regeneration or reuse (Wang and Chen 2009). The use of spent mushroom substrate as green adsorbent is mentioned in Table 2.

Adsorption of dyes

Dyes are considered as one of the toxic pollutant, released from various industries. During the process of dyeing, about 10–20% of dyes is not utilized which releases with the effluent and reaches the water bodies. These discharges increase the biological oxygen demand and chemical oxygen demand of the water bodies and make them unsuitable for use. The dyes are complex molecules and therefore not efficiently degraded by bacteria (Singh et al. 2013). The partial degradation of dyes leads to the production of toxic and mutagenic compounds like aromatic amines (Lade et al. 2015). Fungi possess a variety of enzymes that helps them to grow in a variety of environmental conditions. Moreover, live or dead biomass of fungi can adsorb a variety of pollutants. Consider this fact, fungal culture bearing spent mushroom substrate is used as adsorbent for dyes by many researchers (Toptas et al. 2014; Yan et al. 2015) in its raw and modified form (Table 3).

Adsorption of pollutants

Industrial and agro-industrial activities lead to the release of effluent in the water bodies. This effluent is loaded with a variety of chemicals, dyes or pollutants which poses adverse effect on the environment and living beings. The natural remediation process is slow and depends on the presence of microbes in soil. The supplementation of soil and water with spent mushroom substrate can be useful in the remediation of pollutants. The remediation of different pollutants is shown in Table 3.

Factors affecting the process of adsorption

A number of factors influence the adsorption of metals from the effluents such as pH, temperature, concentration of adsorbent and adsorbate, and bioavailability of pollutants. The bioavailability of metal depends on various factors like buffering capacity, mineral content of the substrate, organic content of the substrate, and cation exchange capacity. Keeping all the factors in mind, an efficient method can be developed for the adsorption of heavy metals and pollutants to reduce the risk of exposure of living beings to heavy metals and pollutants (Ayangbenro and Babalola 2017). The factors affecting the adsorption process are discussed here.

5.1 pH

The pH is an important factor as it affects the selectivity of spent mushroom substrate. Therefore, it is necessary to maintain desired pH in order to induce the binding of spent mushroom substrate to a variety of pollutants and metals.

Table 2 Removal of heavy metals using spent mushroom substrate (SMS) in raw and modified form

S. no.	Spent mushroom substrate (SMS)	Raw or modified	Heavy metals	Pollutant removal	References
1	SMS *of Pleurotus*	Raw	Copper and nickel	Maximum uptakes of copper and nickel were 3.54 mg/g and 1.85 mg/g, respectively	Tay et al. (2016)
2	SMS	Modified to form activated carbon	Nickel	50% nickel was adsorbed at activated carbon have a great potential (51.35%) to adsorb nickel from the water as compared to Amberlite IRC86 resin (39.31%) and zeolite NK3 (34.35%)	Md-Desa et al. (2016)
3	SMS of *Pleurotus*	Raw	Copper	maximum adsorption of copper was reported to be 3.54 mg/g	Tay et al. (2016)
4	SMS of *Pleurotus*	Raw	Manganese	Optimum adsorption of manganese ions was achieved at pH 6, contact time 20 min	Kamarudzaman et al. (2015)
5	SMS of *Pleurotus ostreatus*	Raw	Iron	The optimum adsorption of iron was achieved at an initial pH ranging from 4 to 5, contact time 10 min., and initial iron concentration of 50 mg/L and 0.4 g adsorbent dosages	Kamarudzaman et al. (2013)
6	SMS of *Lentinus edodes*	Raw	Cadmium, lead and chromium	cadmium, lead, and chromium from solution	Tay et al. (2012)
7	SMS of *Pleurotus ostreatus*	Raw	Copper	Optimum adsorption parameters were initial pH 5, contact time 10 min, and initial copper concentration 50 mg/L	Tay et al. (2012)
8	SMS of *Pleurotus ostreatus*	Raw	Nickel	50% of nickel adsorption was obtained at half saturation constant of 0.7 g adsorbent concentration, initial pH in range of 4–8, contact time of 10 min., 50 mg/L concentration of nickel	Tay et al. (2011)

The selectivity of spent mushroom substrate depends on the functional groups, which may vary according to pH. The binding properties of metal in the solution are also dependent on pH (Dursun 2006) as it also affects the solubility of metal ions in the solution. In order to demonstrate the effect of pH on adsorption capacity, several experiments were conducted with different metals and spent mushroom substrate (Tay et al. 2012; Siasar and Sargazi 2015; Chen et al. 2016).

Bioavailability of pollutants in natural condition

In natural condition, bioavailability of pollutant is considered as an important factor in planning the adsorption strategy. For example, soil characteristics play an important role in the adsorption of pollutants from the soil by using spent mushroom substrate. Soil properties are affected by the presence of organic matter because organic matter has a strong impact on the cation exchange capacity, buffer capacity, and on the retention and bioavailability of heavy metals. Soil with low organic matter usually found to have a high content of heavy metals which is bioavailable to plants and microbes. In contrast to this, organic content of the soil binds with the heavy metals and makes them less mobile and less bioavailable to microbes and plants (Ayangbenro and Babalola 2017). Therefore, idea of using spent mushroom substrate is related to increase the organic content of the

Table 3 Removal of dyes and pollutants using spent mushroom substrate (SMS) in raw and modified form

S. no.	Spent mushroom substrate (SMS)	Raw or modified	Dyes	Pollutant removal	References
1	Spent mushroom substrate	Oxalic acid-treated spent mushroom substrate	Methylene blue adsorption	Adsorption capacity was reported to increase in pH range 2–4	Yan et al. (2015)
2	SMS of *Agaricus bisporus*	Raw	Levafix Braun E-RN and Acid red 111 or Basic red 18	With increasing the amount of spent mushroom substrate from 0.05 to 1.0 g to fixed dye concentration, i.e., 100 mg/L, rate of adsorption increased	Toptas et al. (2014)
3	SMS of *Agaricus*	Raw	Lead	the optimum condition for removal of lead was reported to be pH 4, time 4 h, sorbent mass 0.010 g, initial lead concentration 50 mg/L.	Huang et al. (2009)
4	Spent mushroom substrate	SMS co-pyrolyzed with *Saccharina japonica*, i.e., kelp seaweed biomass	Pollutant	Spent mushroom substrate co-pyrolyzed with 10% kelp extract was also reported to be a good adsorbent	Sewu et al. (2017)
5	Spent mushroom substrate	Raw SMS applied to the soil	Cymoxanil and pirimicarb, tebuconazole and triadimenol	SMS amended soil showed 90% adsorption of nonpolar pesticides	Álvarez-Martín et al. (2016a)
6	Spent mushroom substrate	Raw	Carbendazim	Adsorption of fungicides results in decrease bioavailability of pesticides	Álvarez-Martín et al. (2016b)
7	Spent mushroom substrate	Not reported	Sulfa antibiotics	Intra-particle diffusion study showed that film diffusion occurred during the adsorption of sulfa drugs on to SMS	Zhou et al. (2016)
8	Spent mushroom substrate	SMS biochar coated with aluminum hydroxide	Fluoride	The maximum fluoride adsorption capacity was 36.5 mg/g	Chen et al. (2016)
9	Spent mushroom substrate	Modified to form activated carbon	Not reported	Reported to be good adsorbent	Tay et al. (2015)
10	Spent mushroom substrate	Raw	Azoxystrobin fungicide	Fungicide adsorbed successfully. In laboratory conditions, the dissipation of fungicide much slower than that in field condition	Herrero-Hernández et al. (2015)
11	Spent mushroom substrate	Super adsorbent	Not reported	Super adsorbent has been produced successfully, however, not used in pollutant adsorption studies to till date	Ding and Gong (2013)
12	Spent mushroom substrate	Raw	Linuron, diazinon and myclobutanil	SMS was found to be more effective for myclobutanil pesticide adsorption	Rodríguez-Cruz et al. (2012)
13	Spent mushroom substrate	Raw	Eight different fungicides	Highest degradation of mancozeb was achieved	Marín-Benito et al. (2012)

Table 3 (continued)

S. no.	Spent mushroom substrate (SMS)	Raw or modified	Dyes	Pollutant removal	References
14	Spent mushroom substrate	Raw	Tebuconazole	SMS was reported to bind with the pesticide to immobilize it and further prevents its spreading in the soil	Herrero-Hernández et al. (2011)
15	Spent mushroom substrate		Penconazole and metalaxyl pesticides	Immobilization of metalaxyl and retention of penconazole	Marín-Benito et al. (2009)

SMS spent mushroom substrate

soil, which further immobilize metals in the soil due to their adsorption and make them unavailable to plants. Therefore, spent mushroom substrate-based amendments help in reducing the toxicity of heavy metals by reducing their bioavailability to the plants.

Temperature

Temperature also plays an important role in adsorption of heavy metals and pollutants. The raise of temperature increases the fluidity of liquid due to decrease in viscosity and hence increases the adsorption. Another reason of high adsorption due to increase in temperature is related to increase rate of diffusion of adsorbate particles into adsorbent. Temperature also affects the stability of metal ions present in the solution (Ayangbenro and Babalola 2017). Therefore, increase in temperature increases the metal adsorption capacity.

Contact time

Another important factor in the study of metal and pollutants removal by spent mushroom substrate is contact time. It is the time to which spent mushroom substrate is exposed to the metal or pollutant. The adsorption is a process in which attaining equilibrium is an important criterion. Adsorption of heavy metals, dyes, and pollutants occurs initially at faster speed; however, on increasing the contact time the process gradually decreases. After applying spent mushroom substrate to the solution, adsorption of heavy metals or pollutants gradually decreases with increase in the contact time. Initially, a large number of binding sites are available on the spent mushroom substrate to which metal or pollutant binds. However, on increasing the contact time, spent mushroom substrate covered with adsorbate and reduced vacant sites. The remaining vacant sites cannot be occupied further, due to repulsive forces between the molecules of adsorbate and pollutant or metal covered adsorbent (Siasar and Sargazi 2015).

Characteristics of biosorbent

The most important characteristic of biosorbent includes its porosity. The biosorbent must be porous in order to allow the uptake of metals and pollutants. Secondly, it must possess active functional groups bearing negative charge like alkyl, hydroxyl, or amino compound, aliphatic alcohol, carboxyl and carbonyl groups. The spent mushroom substrate is rich in calcium because calcium salts are used in the preparation of mushroom substrate. These calcium ions can be replaced by the metal ions by ion exchange process during adsorption. This replacement of calcium ions with metal ions can be observed by changing peaks in the Fourier-transform infrared spectroscopy analysis (Tay et al. 2011).

The binding of cations on the negatively charged surface of spent mushroom substrate may increase adsorption of anions. Occasionally, the binding of cations to spent mushroom substrate may enhance the adsorption of another cation due the pH-based buffering effects. This can be understood by the example of adsorption of zinc on the calcium-rich spent mushroom substrate. In the preparation of mushroom substrate, calcium carbonate is used which saturate the spent mushroom substrate with the calcium ions. It is reported that this calcium containing spent mushroom substrate has better efficiency for zinc adsorption (Fourest et al. 1994) because calcium ions are replaced by zinc during adsorption process.

Status of fungal biomass on spent mushroom substrate

As mentioned earlier, the spent mushroom substrate is an immobilized source of mushroom mycelium. During mushroom cultivation, mushroom mycelium is immobilized on agricultural or agro-industrial wastes. During the mushroom cultivation, ambient conditions are provided to cultivate mushrooms. Therefore, these substrates possess living biomass. This biomass remains viable in spent mushroom substrate even after the harvesting of fruiting bodies. However, mycelium loses its viability when stored for a longer time. After long-term storage, mushroom mycelium can be used as source of dead fungi. Besides long-term preservation of spent mushroom substrate, the viability of mycelium is also affected by its modification in any form. Initially, when it is applied immediately after collection, there is need to maintain the conditions in order to maintain its viability. After drying, chemical treatment, or using old/preserved spent mushroom substrate, better adsorption can be achieved without the need of maintaining the conditions like pH, temperature during adsorption process. Live mycelium bearing spent mushroom substrate, usually, adsorbs metal and pollutants on the basis of metabolism-dependent process. However, dead mycelium bearing spent mushroom substrate, treated spent mushroom substrate adsorbs the metals by the metabolism-independent process. The spent mushroom substrate can bind with positive charge metals and involved in metal chelation. In this way, spent mushroom substrate adsorbs metals which are present in the solution (Javanbakht et al. 2014).

Particle size of biosorbent

The particle size of biosorbent is an important property to consider for adsorption process. The fine particles have more surface area as compared to coarse particles. Therefore, fine particles can adsorb more compared to coarse particles. The adsorption is not a rate controlling process. It depends on intra-particle mass transfer, which controls the rate of adsorption and therefore considered as a constraint for the adsorption process (Javanbakht et al. 2014).

Influence of initial metal concentration

The initial concentration of pollutants, dyes, or metals poses a great influence on the adsorption process. Initially, adsorption increases with increase in the concentration of pollutant or metals due to their availability in high amount. There is interference of mass transfer resistance in the adsorption process. However, higher initial concentration of pollutant exerts high driving force to overwhelm the mass transfer resistance between pollutant/metal ions and adsorbents (Gadd 2009). This type of phenomenon for copper ions adsorption was reported by Tay et al. (2012).

Advantages of spent mushroom substrate as biosorbent

The spent mushroom substrate is waste from mushroom industry, and therefore, it is beneficial to use for adsorption of metals and pollutants. Moreover, it is economic technique to implement in the field. A few studies conducted in the field shed the light on the suitability of spent mushroom substrate for adsorption of pollutants (Herrero-Hernández et al. 2011).

The spent mushroom substrate can be reused, recycled for the adsorption of pollutants (Javanbakht et al. 2014). The adsorption capacity of spent mushroom substrate may be increased by using different chemical treatments and by modifying it in activated carbon form (Tay et al. 2015; Md-Desa et al. 2016). There is also possibility of metal recovery after adsorption of metals on spent mushroom substrate. A detailed study on the metal recovery options will make the use and disposal of spent mushroom substrate, a safer option. Proper utilization of spent mushroom substrate will also reduce the generation of waste from mushroom industry. The spent mushroom substrate can be composted and stored for a longer time with maintaining its sorption capacity. It will not release any toxin which adversely affects the growth of soil microbes and living beings.

Limitations of spent mushroom substrate as biosorbent

As mentioned earlier, spent mushroom substrate is generated as waste from mushroom production units. Therefore, it is economic option, if used in natural form, to adsorb the pollutants from the environment. The cost is slightly higher in the cases where a special treatment is given to spent mushroom substrate to modify its properties. The major limitation with spent mushroom substrate is its disposal after adsorption. The current options of disposing spent mushroom substrate like incineration and landfill are not feasible option (Javanbakht et al. 2014). Heavy metals loaded spent mushroom substrate may be used for the recovery of metals. The detailed methodology is required to be developed for the extraction of metals and reuse of spent mushroom substrate (Siasar and Sargazi 2015). Another limitation of using spent mushroom substrate for adsorption lies in the differences in the adsorption capacity of different species of mushroom. As mentioned in the aforesaid paragraph, a single species of mushroom do not possess the capacity to adsorb all types of pollutants from the environment. Moreover, there is scarcity of reports on the field scale studies. Therefore, a detailed investigation is required for the adsorption of pollutant by spent mushroom substrate in field conditions. There is need of many efforts to improve biosorption process like optimization of process at pilot scale to implement technology.

Conclusion

In this paper, the possibility of using mushroom and spent mushroom substrate as green adsorbent has been discussed along with their pros and cons. A detailed review of the adsorption of pollutants using spent mushroom substrate and mushroom revealed their suitability in the adsorption of pollutants. Mushroom and spent mushroom substrate can be modified for enhancing their adsorption capacities. This technology provides a good option for adsorption of pollutants. However, the main problem of using mushroom or spent mushroom substrate is the generation of toxic sludge after adsorption. It is necessary to address and solve the problem of toxic sludge generation and utilization by doing research in this area. The utilization of spent mushroom substrate has high potential to be developed into a sustainable technology. It is an environmental friendly approach for adsorbing pollutants from industrial effluents and soil. Moreover, the utilization of spent mushroom substrate will not only reduce the waste of mushroom farm, but also remove pollutants from the effluent and soil. Therefore, efforts need to be done to implement the technology in the field.

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