Pycnoporus sanguineus as Potential Biosorbent for Heavy Metal Removal from Aqueous Solution: A Review

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Abstract: *The development of a new treatment method to remove heavy metal ions from wastewater, which is cost effective and more efficient, is threatening to overcome conventional methods. The biosorption treatment technology has received much attention because it offers low-cost biosorbent and non-hazardous biomaterials. Biosorption of metal ions onto microorganisms involves a combination of the following metal-binding mechanisms: physical adsorption, ion exchange, complexation and precipitation. Previous works report that some microorganisms, such as bacteria, algae, yeast, fungi and cellulosic materials, are well known to be capable of adsorbing a large amount of metal ions. The purpose of this review paper is to provide information on the development of a biosorbent for heavy metal removal from white rot fungus, Pycnoporus sanguineus, which is less reported. Biosorption of metal ions onto this fungus largely depends on pH, initial metal concentration, temperature and biomass loading. Further, this fungus is an economical biosorbent because it can be reused several times and its applicability can be enhanced at an industrial scale.*

Keywords: Heavy metals, *Pycnoporus sanguineus*, biosorption of metal ions, biosorbent, thermodynamic

1.   INTRODUCTION

Rapid economic changes have resulted in elevated levels of toxic heavy metals and radionuclides entering the biosphere.[1] In earlier times, when there were still abundant natural resources and negligible development pressures, little attention was given to environmental issues, although some environment-related legislations pertaining to different sectors were authorised. Realising this, the Malaysian government, in as early as 1974, has taken concrete steps by introducing an enabling legislation called the Environmental Quality Act, 1974.[2] Heavy metal pollutants, such as copper (Cu), cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As) and chromium (Cr), were classified as priority pollutants by the Department of Environment of Malaysia. Heavy metals are those elements with specific densities at least five times the specific gravity of water, which includes Cd, Cu, Pb, zinc (Zn), Hg, As, silver (Ag), Cr, iron (Fe) and the platinum group elements.[3,4] Important heavy metals in water pollution include

Hg, Cd, Pb, Zn, Cu, nickel (Ni) and Cr.[5] Cu and Zn are essential trace elements for living organisms at lower concentrations (< 10 mg l^{-1}). However, they become toxic at higher concentrations (> 10 mg l^{-1}).[5] Strong heavy metals, such as Hg and Cd can be very toxic at concentrations as low as 0.001 mgl^{-1}–0.1 mg l^{-1}.[6–9] Industries such as electroplating, fertiliser, pesticide, surface finishing and aerospace contribute to heavy metal pollution when wastes or effluent-containing metals are discharged directly or indirectly into the environment.[6,7,9,10] Most of these metal ions (Cd, Cu, Zn, Hg, As, Ag, Cr and Fe, etc.) are released by these industries in simple cationic (+) forms.[11] Table 1 lists the uses of several heavy metals and their effects on human health.[12]

Table 1: Heavy metals uses and health effects on human.[12]

Heavy metals	Uses	Health effects	References
As	Metal processing plants, burning of fossil fuels, mining of arsenic containing ores and use of arsenical pesticides	Internal cancer, skin lesions and death	13–15
Cd	Electroplating, fertilisers, mineral processing and battery manufacturing	Cancer, lung insufficiency, disturbances in cardiovascular system, liver and kidney damage	16–22
Cu	Copper and brass plating, mining, metal industries and copper-ammonium rayon industries	Normocytic, hypochromic anemia, leukopenia, and osteoporosis; copper deficiency	23, 24
Cr	Metal plating, electroplating, leather, mining, galvanometry, dye production	Ulcer, skin irritation, liver and kidney damage	24–27
Pb	Metal plating, textile, battery manufacturer, automotive and petroleum industries	Spontaneous abortion, nervous system damage, kidney and brain damage	28, 29
Hg	Metallurgy industries, chemical manufacturing and metal finishing	Memory problems, increased heart rate, tremors, kidney and brain damage	29–31

1.1   Treatment Technologies for Heavy Metal Removal

Heavy metal contamination is becoming a great concern, in light of people's environmental awareness and of existing government policies. Several heavy metal removal technologies, including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration and phytoremediation, are commonly used in industries.[32] However, in removing heavy metals from industrial wastewaters, these technologies are uneconomical and unfavourable. A description of the processes and disadvantages of these treatment technologies is presented in Table 2. With increasing environmental attention and legal constraints on discharge effluents, there is a need for cost-effective technologies. There is a focus on the use of microbial biomass as a biosorbent to sequester metal ions from contaminated effluents and has received much attention from researchers.[33,34]

Table 2: Treatment methods used in heavy metals removal.[32,42,137,138]

Treatments	Process details	Disadvantages
Chemical precipitation	Precipitation of metal ions were achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers	Large amount of sludge produced during the process caused a disposal problem
Ion exchange	Metal ions from dilute solutions were exchanged with ions held by electrostatic forces on the exchange resin	High cost, partial removal for certain ions
Reverse osmosis	Metal ions were separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids	Expensive
Electrodialysis	Metal ions were separated through the use of semi-permeable ion selective membranes. An electrical potential between the two electrodes caused a separation of cations and anions, and cells of concentrated and dilute salts are formed	Metal hydroxides formed clogged the membrane
Ultrafiltration	Pressure driven membranes were used for the removal of metal ions	Generation of sludge caused disposal problem
Phytoremediation	Used certain plants to clean up soil, sediment and contaminated water with metal ions	The process took a long time to remove metal ions, regeneration of the plant is difficult

1.2   Biosorption Process - An Alternative Solution

Biosorption of metal ions using biological materials, such as algae, bacteria, fungi, yeast and industrial/agricultural wastes, has received greater attention because of its advantages over conventional methods.[35,36] It has been defined as the properties of such biomass that bind with metal ions from aqueous solutions.[9,11,37,38] As reported by some researchers, a biosorption process involves several mechanisms, such as ion exchange, physical adsorption, complexation and precipitation.[39,40] Ahalya et al.[32] and Sag et al.[41] stated that biosorption mechanisms can be divided into metabolism dependent and non-metabolism dependent.

Metabolism dependent is a slow process, which includes transportation across cell membranes and precipitation, whereas non-metabolism dependent is a rapid process, which includes precipitation, physical adsorption, ion exchange and complexation.[42] These processes are classified as: i) extracellular accumulation/precipitation; ii) cell surface sorption/precipitation; and iii) intracellular accumulation.[32,42] The major advantages of biosorption processes over conventional technologies include low cost, high efficiency, minimisation of sludge production, regeneration and metal recovery.[32,43] Table 3 summarises several factors that influence a biosorption process, as reported by some researchers.[12]

Table 3: Factors that influenced the biosorption process.[12]

Factors	Description	References
pH	Most important parameter in the biosorption process	44–45
Temperature	The biosorption performances was not influenced at a temperature range of 20°C–35°C	46
Biomass loading	Low biomass loading resulting in an increase of metals uptake. However, increase in biomass loading cause interference between active binding sites, thus decreasing the metals uptake	47
Presence of other metal ions	Existence of metals competition for the binding sites occurred by the presence of other metal ions	32

Both living and dead microorganisms, such as algae, bacteria, fungi and yeast are used as biosorbent materials for heavy metal biosorption.[9,44] Focus on the use of these microorganisms as biosorbent for metal removals are being studied widely as they are cheap and abundant.[45–48] Some literatures report that some microorganisms are capable of removing heavy metals in the range of

1 mg l^{-1}–100 mg l^{-1} even at low concentrations.[49,50] There are advantages in using living cells over the dead cells as biosorbents. Living cells work the same way as dead cells at lower metal concentrations and are able to generate new cells through growth, which allow more space for biosorption mechanisms to occur.[51] Dushenkov et al.[56] reported that living cells could adsorb metal ions rapidly and provide a higher degree of separation.

1.3　Mechanism of Biosorption Processes

Biosorption of metal ions onto microorganisms involves a combination of several metal-binding mechanisms, including physical adsorption, ion exchange, complexation and precipitation.[9,32] Each mechanism is described by Ahalya et al.[32] as follows:

Physical adsorption: Van der Waal's forces (electrostatic interaction) take place between metal ions in the solution and the cell wall of the microbes. These interactions are responsible in copper and lead biosorption, using *Zoogloea ramigera*, *Chlorella vulgaris* and *S. saprophyticus*.[46,57]

Complexation: Metal ion removal from an aqueous solution takes place by complex formation of metals on the cell surface after interaction between metal ions and active groups. Metal ions can be biosorbed or complexed by carboxyl groups found in microbial polysaccharides or other polymers. Aksu et al.[46] reported that copper biosorption onto *Zoogloea ramigera* and *Chlorella vulgaris* involves both adsorption and the formation of coordination bonds between metals and the carboxyl and amino groups of cell walls. Similar results in biosorption of electroplating heavy metals by some basidiomycetes fungi were also reported by Javaid and Bajwa.[58] The active groups responsible in metal biosorption are listed in Table 4.

Ion exchange: Polysaccharides that exist on cell walls of microorganisms consist of counter ions, such as K^+, Na^+, Ca^{2+} and Mg^{2+}. These ion exchange with metal ions, resulting in the metal ion uptake.[59,60]

Precipitation: This mechanism is dependent on or independent of cellular metabolism. Metal ion removal from aqueous solutions is often associated with the active defence system of microorganisms. This active system produces compounds that favour the precipitation process.[61]

Table 4: The functional groups that are responsible for metals biosorption.[72,139,140]

Formula	Basic groups	Formula	Acidic groups
$-NH_2$	Amino	$-COOH$	Carboxylic
$=NH$	Immino	$-SO_3H$	Sulphonic
$-N=$	Cyclic or non-cyclic nitrogen	$-PO(OH)_2$	Phosponic
$=CO$	Carbonyl	$-OH$	Enolic, phenolic
$-O-$	Ether	$=N-OH$	Oxime
$-OH$	Alcohol	$-SH$	Mercaptan

1.4   *Pycnoporus sanguineus*: Its Rationale as a Biosorbent in Wastewater Treatment

Pycnoporus sanguineus (*P. sanguineus*) is a filamentous fungus with dark red circular pores that belong to the family of Polyporaceae (Basidiomycetes).[62] This red fungus is hard and woody, and is found on rotting logs in tropical and subtropical areas.[63,64] Research on this white rot fungus has started as early as 1946, when Bose[65] successfully isolated polisporin, a compound that works actively against gram-positive and gram-negative bacteria and has no toxicity to experimental animals. Fidalgo[66] stated that some Brazilian indigenous people use the basidiomycetes of *P. sanguineus* to stop haemorrhages. In Australia, this fungus is used medicinally in a variety of ways by desert aborigines. It is "sucked to cure sore mouths," rubbed inside the mouths of babies with oral thrush, or rubbed on sore lips. It is also used as a teething ring.

For heavy metal removal, this fungus is able to adsorb metal ions effectively, either in batch or column studies.[16,67–72] In fact, it can be grown easily in low-cost growth media and more yields can be harvested when growing at optimum conditions.[28,71] Therefore, there should be an abundant supply of the fungus from local forests to make sure that there is a continuous supply of biosorbents for heavy metal removal. Wang and Chen[9] stated that the presence of heavy metals affects metabolic activities of fungal cultures, and can affect commercial fermentation processes, and is creating interest in the interaction between the behaviour of the fungus and the presence of heavy metals. Studies done by several researchers show that the fungus is more suitable in removing metals from wastewater than other microbes because of its tolerance toward heavy metals and other adverse conditions, such as low pH, high cell wall-binding capacity and high intracellular metal uptake capacity.[16,73]

This fungus is also reportedly able to decolorise dye as it produces laccase.[74] Laccase is an enzyme that catalyses the oxidation of a phenolic

substrate by coupling it with the reduction of O_2 to water, without any intermediate harm, making it the best tool for environmentally benign processes.[75,76] Lu et al.[77] reported that purified laccase from *P. sanguineus* is able to decolorise Remazol Brilliant Blue R (RBBR) by up to 89.6% after 10 min. Apart from an economic point of view, the fungus is also easy to grow. It can be manipulated genetically and morphologically, which makes it a good biosorbent for heavy metals and for dye removal.[6,9,77]

2.   METAL REMOVAL USING *P. SANGUINEUS*

2.1   Batch Studies

The ability of dead and living cells of *P. sanguineus* to adsorb heavy metal ions (Cd, Cu and Pb) from aqueous solutions, either in batches or columns, has been reported.[16,67,68,70–72] *P. Sanguineus* is able to adsorb copper at 13.6 mg g^{-1} when the dead cells are used (Figure 1). Mashitah et al.[67] reported that metal uptake can be increased when biosorbents are treated with boiling water and sodium bicarbonate, with an increase in copper uptake of up to 9.7 mg g^{-1}. Several factors have been found to affect metal uptake increments after pretreatment, such as cell membrane rupture, thus exposing available binding sites, releasing lipids and proteins that cover reactive sites, and releasing polymers, such as polysaccharides that have high affinity toward certain metal ions.[60,78–82] X-ray energy results by Mashitah et al.[68] showed that calcium ions present on cell walls are released and replaced by Pb^{2+} ions. This means that an ion exchange mechanism is involved in metal biosorption.[16,67,68]

Freely suspended live *P. sanguineus* cells (not immobilised) show the lowest metal biosorption.[71] However, after immobilisation with calcium alginate, the metal uptake increment is observed and more than 90% is removed.[72,83] Uses of immobilised biosorbents, compared with free cell biosorbents, are more realistic in industrial operations as they offer several advantages, such as easy separation after the biosorption process, minimal clogging in a continuous process and regeneration.[35,84,85] The natural polymers, which are mostly used as matrices for the immobilisation of microbial cells because they are non-toxic, low cost and efficient are alginate, chitosan, chitin and cellulose derivatives.[35,85,86]

Metal biosorption is influenced by many factors, such as pH, temperature, initial metal concentration and biomass loading. Some literatures have reported that pH affects the solubility of metal ions and the ionisation of functional groups on fungal cell walls.[17,35,72,87] Functional groups, such as

carboxyl, amine and phosphate, have been identified as responsible in the biosorption of heavy metals.[37,49]
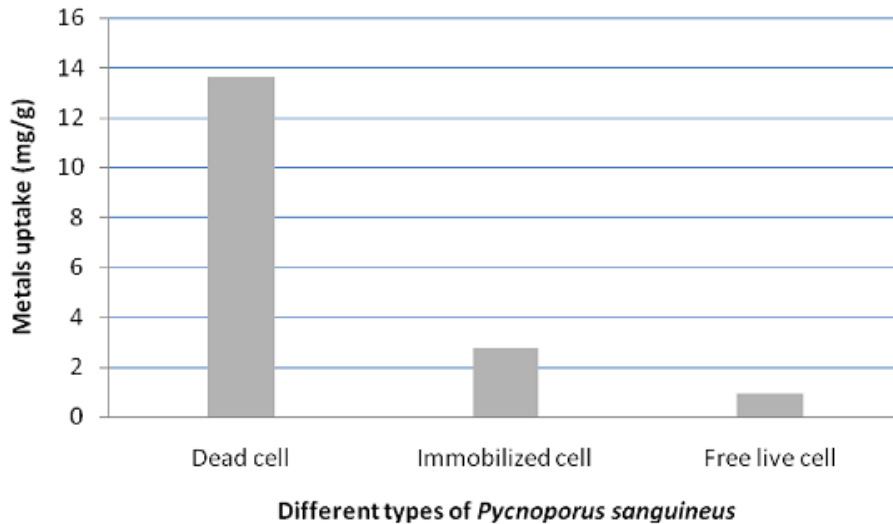

Figure 1: Cu(II) uptake using different forms of *P. sanguineus* biosorbents.

At a lower pH, H^+ ions compete with metal cations for the exchange site, which results in a lower uptake of metal ions.[16,18] However, a very high pH should be avoided during an experiment because when metal ions precipitate, the biosorption of metal ions is impossible.[19,72,88,89] The optimal pH for Cd, Cu, and Pb removal of dead and living cells of *P. sanguineus* has been reported in the range of 3.0–7.0.[16,67,71,72]

Temperature is another notable parameter identified as a major influence in metal ion uptake.[9,90] Mashitah et al.[67] reported that biosorption of Cu(II) by dead cells of *P. sanguineus* is not significantly affected when temperature increases from 30°C to 40°C. However, as temperature increases above 40°C, metal uptake decreases, indicating that the biosorption process is exothermic in nature.[67,91] This may be attributed to the damage in cell walls at higher temperatures, resulting in a decrease in metal uptake.[67,92] However, a reverse trend has been observed in the biosorption of Cd(II) and Cu(II) onto immobilised *P. sanguineus*, in which metal uptake is favourable at higher temperatures.[16,72] According to Sag and Kutsal,[93] biosorption is expected to increase when increasing the temperature when chemical adsorption mechanisms play a dominant role in the whole biosorption process.[94]

On the effect of initial metal concentration, Horsfall and Spiff[95] stated that biosorption capacity increases with an increase in metal ion concentration.

This is attributed to an increase in the mass transfer driving force of metal ions between the aqueous solution and the biosorbent phases, which leads to an increase in metal ion uptake.[16,18,94,96] However, the percentage of metal ion removal by immobilised *P. sanguineus* shows a reversed trend when the Cd(II) and Cu(II) are used, in which biosorption capacity decreases by more than 40% when metal concentration increases from 50 mg l^{-1} to 300 mg l^{-1}.[16,72] These results show that binding sites available for biosorption to occur are limited at higher metal concentrations, resulting in lower metal uptake.[16,18]

　　　　Biomass loading is also an important parameter that affects metal biosorption capacity. Cu(II) uptake by dead *P. sanguineus* decreases as biomass loading increases from 0.5 g to 3.0 g.[67] Itoh et al.[97] claimed that at a lower biomass loading, a larger quantity of metal ions is sorbed when the distance between cells increases. However, as biomass loading increases, a "screen effect" from the dense outer layer of the biomass shields the binding sites, resulting in lower metal uptake.[16,67,98] Similar results have been obtained for Cd(II) and Cu(II) on immobilised *P. sanguineus*.[16,72]

　　　　Equilibrium studies involving Langmuir, Freundlich, Redlich Peterson, Temkin and Dubinin-Radushkevich are among the equilibrium models used widely by researchers.[9,16,37,99] Isotherm equations for all models are listed in Table 5. To determine biosorption mechanisms, such as chemical reaction, diffusion control and mass transfer, several kinetic models (pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion) may be used. Non-linear and linear equations are described in Table 6. The utilisation of equilibrium and kinetic models, using algae, bacteria, fungi and yeast in metal biosorption are summarised in Table 7. Thermodynamic parameters, such as Gibbs free energy changes (ΔG^o), standard enthalpy (ΔH^o), and entropy change (ΔS^o), are also important in determining which processes occur spontaneously.[16,18] The equations for such parameters are listed in Table 8.

Table 5: Equilibrium isotherm models.

Models	Equation	Linear equation	References
Langmuir	$q_e = \dfrac{q_{max}K_c C_e}{1 + K_c C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}K_c} + \dfrac{C_e}{q_{max}}$	16,18,100
Freundlich	$q_e = K_f C_e^n$	$\ln q_e = \dfrac{1}{n}\ln C_e + \ln K_f$	35, 72, 101
Redlich-Peterson	$q_e = \dfrac{K_{rp}C_e}{1 + a_r C_e^{\beta^R}}$	$\ln\left(K_{rp}\dfrac{C_e}{q} - 1\right) = \beta^R \ln(C_e) + \ln a_r$ $B^R\ (0 < \beta^R < 1)$ For $\beta^R = 1$, the equation are converts to the Langmuir form.	16, 37
Temkin	$q_e = \dfrac{RT}{b_T}(\ln A_T C_e)$	$q_e = \dfrac{RT}{b_T}\ln A_T + \dfrac{RT}{b_T}\ln C_e$	99, 102
Dubinin-Radushkevich	$q_e = q_s \exp(-K_D \varepsilon^2)$	$\ln q_e = \ln q_s - K_D \varepsilon^2$ $\varepsilon = RT\ln(1 + \dfrac{1}{C_e})$ $E = \dfrac{1}{\sqrt{2K_D}}$	99, 102–103

Table 6: Kinetic equation models.

Models	Equation	Linear equation	References
Pseudo 1st	$\dfrac{dq_t}{dt} = k_1(q_{e-} q_t)$	$\log(q_e - q_t) = \log(q_e) - \dfrac{k_1}{2.303}t$	35, 72, 100
Pseudo 2nd	$\dfrac{dq_t}{dt} = k_2(q_{e-} q_t)^2$	$\dfrac{t}{q_t} = \dfrac{1}{q_e}t + \dfrac{1}{k_2 q_e^2}$	100
Elovich	$\dfrac{dq_t}{dt} = \alpha^E e^{\beta^E q_t}$	$q_t = \dfrac{1}{\beta^E \ln t} + \dfrac{1}{\beta^E}\ln(\alpha^E \beta^E)$	104
Intraparticle diffusion	$q_t = K_s t^{0.5}$	–	105, 106

Table 7:   Summary of work done using various microorganisms for metal removal (in batches).

Biosorbent	Metals	Maximum metals uptake ($q\,max$)	Desorption efficiency	Best fitted equilibrium model	Best fitted kinetic model	References
Treated alga[a] (*Undaria pinnatifida*)	Cu(II)	38.82 mg g^{-1}	–	Langmuir and Temkin	Pseudo 2nd order	107
	Ni(II)	24.71 mg g^{-1}				
Ulva fasciata sp.[a]	Cu(II)	26.88 mg g^{-1}	–	Langmuir	Pseudo 2nd order	108
Spirogyra neglecta (non-living)[a]	Cu(II)	115.3 mg g^{-1}	82% (0.1 M HCl)	Langmuir	–	109
	Pb(II)	116.1 mg g^{-1}	90% (0.1 M HCl)			
Spirogyra condensate[a] *Rhizoclonium hieroglyphicum*[a]	Cr(III)	14 mg g^{-1} 11.81 mg g^{-1}	> 75% (0.1 M H$_2$SO$_4$)	Freundlich	Pseudo 2nd order	110
Red algae (*Ceramium virgatum*)[a]	Cd(II)	39.7 mg g^{-1}	–	Langmuir	Pseudo 2nd order	111
Oedogonium sp.[a]	Cd(II)	88.2 mg g^{-1}	0.1 M HCl	Langmuir	Pseudo 2nd order	112
Microcystis novacekii[a]	Pb(II)	70.0 mg g^{-1}	–	Langmuir	–	113
Hypnea valentiae[a]	Cd(II)	17 mg g^{-1}	–	Langmuir	Pseudo 1st order	114
Gelidum[a]		33.0 mg g^{-1}		Langmuir and Langmuir-Freundlich	Pseudo 1st and 2nd order	115
Algal Waste[a]	Cu(II)	16.7 mg g^{-1}	–			
Composite material[a]		10.3 mg g^{-1}				

Table 7: (*continued*)

Biosorbent	Metals	Maximum metals uptake (*q max*)	Desorption efficiency	Best fitted equilibrium model	Best fitted kinetic model	References
Plain alginate beads		21.2 mg g^{-1}				
Dry biomass[a]		30.1 mg g^{-1}				
Immobilized live *Oscillatoria* sp. H1[a]	Cd(II)	32.2 mg g^{-1}	85% (0.1 mol l^{-1} HCl)	Langmuir and Freundlich	Pseudo 2nd order	116
Immobilised heat-inactivated *Oscillatoria* sp. H1[a]		27.5 mg g^{-1}				
Looge (LS) immobilised biomass of *Chlorella sorokiniana* (LSIBCS)[a]	Cr(III)	69.26 mg g^{-1}	98% (0.1 mol l^{-1} HNO$_3$)	Langmuir	Pseudo 2nd order	117
Free biomass of *C. sorokiniana* (FBCS)[a]		58.80 mg g^{-1}	–			
Codium vermilara[a]	Cd(II)	21.8 mg g^{-1}				
	Cu(II)	16.9 mg g^{-1}				
	Pb(II)	63.3 mg g^{-1}				
	Ni(II)	13.2 mg g^{-1}				
	Zn(II)	23.8 mg g^{-1}	–	Langmuir	–	118
Spirogyra insignis[a]	Cd(II)	22.9 mg g^{-1}				
	Cu(II)	19.3 mg g^{-1}				
	Pb(II)	51.5 mg g^{-1}				
	Ni(II)	17.5 mg g^{-1}				
	Zn(II)	21.1 mg g^{-1}				

Table 7: (*continued*)

Biosorbent	Metals	Maximum metals uptake ($q\ max$)	Desorption efficiency	Best fitted equilibrium model	Best fitted kinetic model	References
Asparagpsis armata[a]	Cd(II)	32.3 mg g^{-1}				
	Cu(II)	21.3 mg g^{-1}				
	Pb(II)	63.7 mg g^{-1}				
	Ni(II)	17.1 mg g^{-1}				
	Zn(II)	21.6 mg g^{-1}				
Chondrus crispus[a]	Cd(II)	75.2 mg g^{-1}				
	Cu(II)	40.5 mg g^{-1}				
	Pb(II)	204.1 mg g^{-1}				
	Ni(II)	37.2 mg g^{-1}				
	Zn(II)	45.7 mg g^{-1}				
			–	Langmuir	–	118
Ascophyllum nodosum[a]	Cd(II)	87.7 mg g^{-1}				
	Cu(II)	58.8 mg g^{-1}				
	Pb(II)	178.6 mg g^{-1}				
	Ni(II)	43.3 mg g^{-1}				
	Zn(II)	42.0 mg g^{-1}				
Fucus spiralis[a]	Cd(II)	114.9 mg g^{-1}				
	Cu(II)	70.9 mg g^{-1}				
	Pb(II)	204.1 mg g^{-1}				
	Ni(II)	50.0 mg g^{-1}				
	Zn(II)	53.2 mg g^{-1}				
Nonviable *Bacillus* sp[b]	Hg(II)	7.94 mg g^{-1}	–	Freundlich	–	119
Bacillus jeotgali U3[b]	Cd(II)	53.5 mg g^{-1}		Langmuir		
			–		–	120
	Zn(II)	128 mg g^{-1}		Freundlich		
Bacillus thuringiensis[b] (Vegetative)		35.46 mg g^{-1}				
	Ni(II)		–	Langmuir and Freundlich	–	121
Bacillus thuringiensis[b] (Mixture)		45.87 mg g^{-1}				

Table 7: (*continued*)

Biosorbent	Metals	Maximum metals uptake (*q max*)	Desorption efficiency	Best fitted equilibrium model	Best fitted kinetic model	References
Cyanobacterium *Gloeocapsa* sp.[b]	Pb(II)	232.56 mg g^{-1}	–	Langmuir	Pseudo 2nd order and intraparticle diffusion	122
Marine *Aspergillus niger*[f]	Cr(VI)	117.33 mg g^{-1}	–	Langmuir	Pseudo 2nd order	123
Botrytis cinerea[f]	Zn(II)	12.98 ± 0.9623 mg g^{-1}	98 % (10 mM HCl)	Langmuir	–	124
Aspergillus flavus[f]	Cu(II)	10.82 ± 1.46 mg g^{-1}	–	Freundlich	–	125
	Pb(II)	13.46 ± 0.99 mg g^{-1}				
Free biomass *A. niger*[f]	Cd(II)	69.44 mg g^{-1}	–	Langmuir	Pseudo 2nd order and intraparticle diffusion	126
	Cu(II)	17.60 mg g^{-1}				
Immobilised *A. niger*[f]	Cd(II)	60.24 mg g^{-1}				
	Cu(II)	34.13 mg g^{-1}				
Macrofungus (*Inonotus hispidus*) biomass[f]	As(III)	51.9 mg g^{-1}	11–28% (1 M HCl, 1 M HNO$_3$)	Langmuir	Pseudo 2nd order	127
	As(V)	59.6 mg g^{-1}	10–25% (1 M HCl, 1 M HNO$_3$)		Pseudo 2nd order	
Macrofungus *L. scrobiculatus*[f]	Cd(II)	53.1 mg g^{-1}	95% (1 M HNO$_3$)	Langmuir	Pseudo 2nd order	128
	Pb(II)	56.2 mg g^{-1}			Pseudo 2nd order	
Penicillium simplicissimum immobilised within loofa sponge (PSILS)[f]	Cu(II)	112.3 mg g^{-1}	98% (100 mM HCl)	Langmuir	Pseudo 2nd order	129
	Pb(II)	152.6 mg g^{-1}				
Rhizopus oligosporus[f]	Cu(II)	79.37 mg g^{-1}	–	Langmuir	Pseudo 2nd order	130

Table 7: (*continued*)

Biosorbent	Metals	Maximum metals uptake (*q max*)	Desorption efficiency	Best fitted equilibrium model	Best fitted kinetic model	References
Viable *Rhizopus oryzae*[f]	Cu(II)	19.4 mg g^{-1}	–	Langmuir	Pseudo 2nd order	131
Pretreated *Rhizopus oryzae*[f]		43.7 mg g^{-1}				
Cladosporium cladosporioides[f]	Cu(II)	9.43 mg g^{-1}	–	Langmuir	Pseudo 2nd order	132
Gliomastix murorum[f]		10.9 mg g^{-1}				
Bjerkandera sp[f]		13.2 mg g^{-1}				
P. sanguineus[f] (Dead)	Cu(II)	9.7 mg g^{-1}	–	–	–	67
P. sanguineus (Live immobilised)	Cd(II)	3.42 mg g^{-1}		Langmuir	Pseudo 1st order	16
	Cu(II)	2.96 mg g^{-1}		Langmuir	Pseudo 2nd order	72
Candida albicans biomass[y]	Pb(II)	833.33 mg g^{-1}	–	Langmuir	Pseudo 2nd order	133
Deactivated protonated yeast[y]	Ni(II)	9.01 mg g^{-1}	> 90 % (0.1 N HCl)	Freundlich and Redlich Peterson	Pseudo 2nd order	134
Waste beer yeast[y]	Cu(II)	0.0228 mmolg^{-1}	–	Langmuir and Freundlich	–	135
	Pb(II)	0.0277 mmolg^{-1}				
Waste baker's yeast biomass[y]	Cd(II)	31.75 mg g^{-1}	–	Langmuir	–	136
	Pb(II)	60.24 mg g^{-1}				

Notes: a = algae, b = bacteria, f = fungal, y = yeast.

Table 8: Thermodynamic parameters.

Thermodynamic parameters	Equation	Assumption	References
ΔG^0	$\Delta G^o = -RT \ln K_c$ (1) $\ln K_c = \dfrac{\Delta S^o}{R} - \dfrac{\Delta H^o}{RT}$ (2)	Negative value - Biosorption is spontaneous	16, 18
ΔH^0	Determined from slope of Equation (2)	Positive value - Endothermic process Negative value - Exothermic process	37, 72, 141, 142
ΔS^0	Determined from intercept of Equation (2)	Positive value - increased randomness at the solids/solution interface during the biosorption of metal ions onto the biosorbent Negative value - process is enthalpy driven	37, 141, 143

2.2   Column Studies

In as much as data obtained under batch conditions are generally not applicable to most wastewater treatment systems (such as column operations), removal of heavy metals using columns is applied.[70,144] The ability of macrofungi *P. sanguineus* (immobilised, dead and living) to remove Pb(II) ions in columns at different bed heights, flow rates and initial Pb(II) concentrations are shown in Figures 2–7.[69,70]
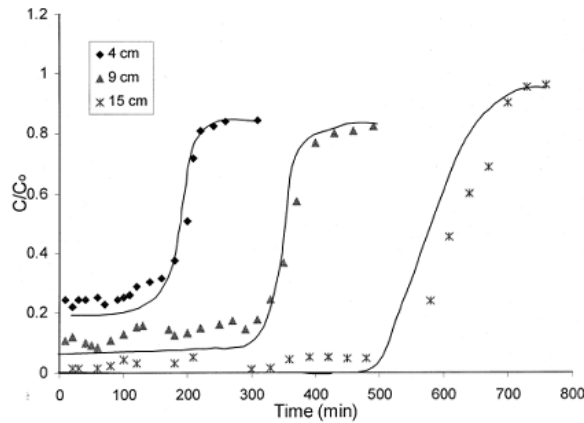

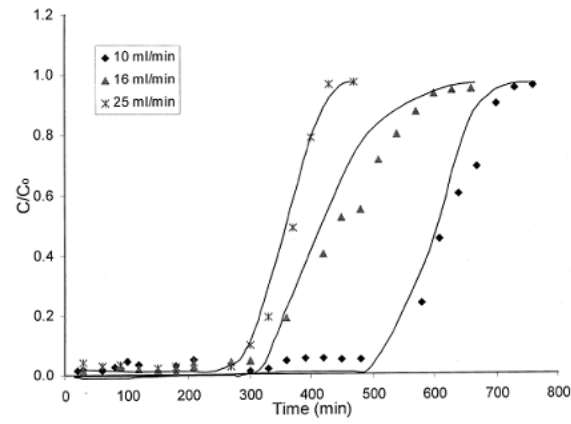Figure 2: Effect of bed height on Pb(II) ion removal on dead *P. sanguineus*.

Figure 3: Effect of flow rate on Pb(II) ion removal on dead *P. sanguineus*.
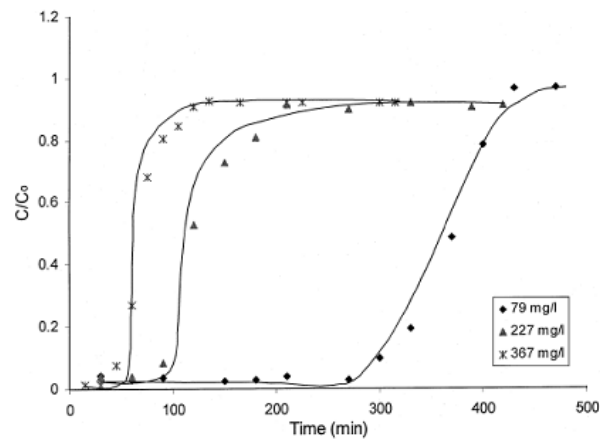

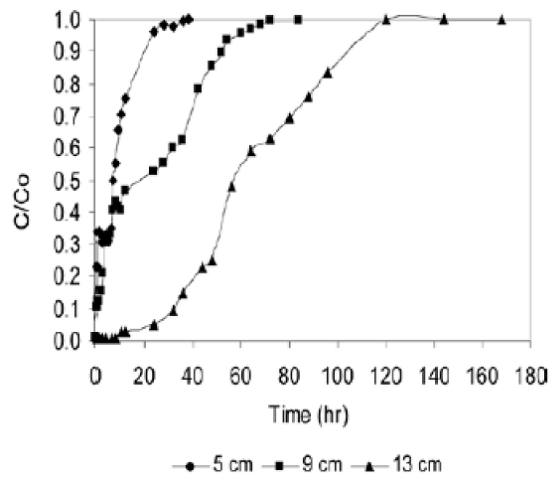Figure 4: Effect of initial Pb(II) concentration on dead *P. sanguineus*.

Figure 5: Effect of bed height on Pb(II) ion removal on immobilised live *P. sanguineus*.
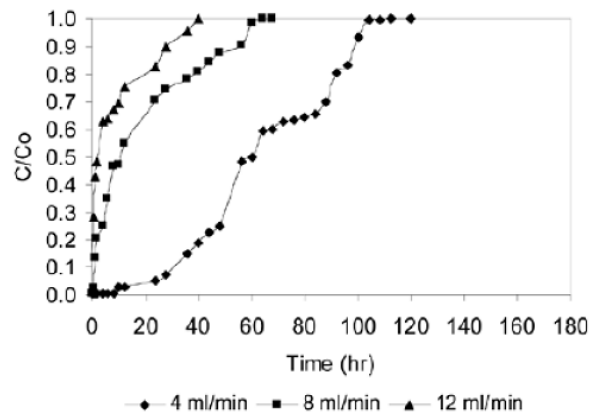

Figure 6: Effect of flow rate on Pb(II) ion removal on immobilised live *P. sanguineus*.
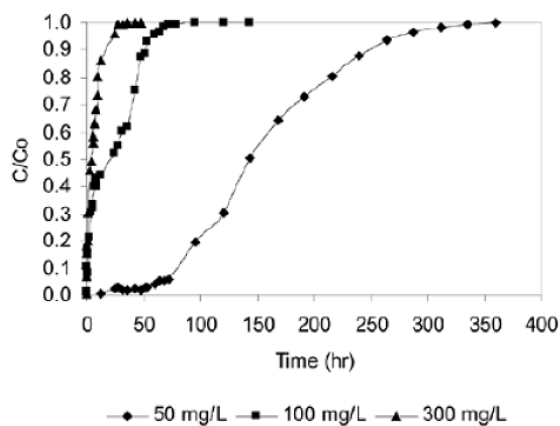
Figure 7: Effect of initial Pb(II) concentration on immobilised live *P. sanguineus*.

2.3   Effect of Bed Height

On the effect of bed height, Figure 2 and Figure 5 show that at a lower bed height, a biosorbent gets saturated early compared with the other two bed heights. For both biosorbents, more binding sites are available at higher bed heights for biosorption of metal ions to occur, thus increasing metal uptake capacities.[69,70,145] As bed height increases, exhaustion/saturation time also increases, resulting in a broad mass transfer zone.[69,146] A similar result has also been reported for metal ion removal using green coconut shells in fixed bed columns.[147]

2.4   Effect of Flow Rate

Figure 3 and Figure 6 show that flow rate plays an important factor in metal uptake. This behaviour shows that as flow rate increases, exhaustion/saturation time increases because of insufficient contact time between metal ions and biosorbents, resulting in lower metal ion uptake.[145] A steeper breakthrough curve can also be observed at a higher flow rate for both biosorbents. Therefore, it is important to determine the optimum flow rate to get the maximum metal ion removal.

2.5   Effect of Initial Metal Concentration

As the initial metal concentration increases, there are significant effects on breakthrough curves, as shown in Figure 4 and Figure 7. Malkoc and Nuhoglu[146] reported that at higher metal concentrations, the biosorbent becomes saturated quickly, causing a faster breakthrough curve. At lower Pb(II) concentrations, Mashitah et al.[69] reported that less driving force has been

observed between Pb(II) ions and biosorbents, resulting in longer (two weeks) exhaustion/saturation time.[146]

2.6   Regeneration

As reported previously, biosorption processes offer several advantages, one of which is its ability to regenerate and another is its reduced process costs in a continuous operation.[69,145,148] Regeneration processes also act as indicators on whether a biosorbent can be safely disposed of into the environment. Therefore, it is important to regenerate biosorbents after using the same process for metal biosorption. Table 9 shows the regeneration of metal ions in columns by various biosorbents.

Baral et al.[151] reported that a higher percentage of desorption efficiency (80%) indicates that ion exchange mechanisms play a significant effect on the biosorption process. Table 9 also shows that acid and alkaline are used as eluant agents by most researchers. However, Mashitah et al.[69] reported that a biosorbent, which is of immobilised *P. sanguineus,* that is exposed to an acidic eluant may cause physical-chemical damage to cell wall structures. This could result in weight loss and in the reduction of biosorption capacity in subsequent cycles.[145,152]

Table 9: Regeneration of metal ions in columns using various biosorbents.

Biosorbent	Metal ions	Elution agent	% Elution (first cycle)	Cycles	References
Dead *P. sanguineus*	Pb(II) Cu(II) Cd(II)	0.1 M HCl	100 95 100	4	70
Immobilised live *P. sanguineus*	Pb(II)	0.1 M HCl	85	2	69
Grape stalk wastes	Ni(II)	0.1M $HClO_4$	80–85		149
Treated rice husk	Cd(II)	0.01 N HCl	97	2	150
Thermally activated weed	Cr(VI)	0.1 N NaOH	80	3	151

3.   CONCLUSION

The development of a new treatment method to remove heavy metal ions from wastewater, which could be cost effective and more efficient, is threatening to overcome conventional methods. The biosorption treatment technology has received much attention as it offers low-cost biosorbent and non-hazardous

biomaterials. Biosorption of metal ions using dead and living cells of *P. sanguineus* has been studied because less work has been carried out using this species as a biosorbent. Both biosorbents have been found capable of adsorbing metal ions effectively. The white-rot fungi, *P. sanguineus,* is recommended as a biosorbent for Cd(II), Cu(II), and Pb(II) biosorption in batch and column systems because it is easily available in extensive quantities, easily grown in basic fermentation media and, is low cost. The biosorbent can also be regenerated and reused several times, making it more economical and viable at an industrial scale.

Nomenclature

a_{rp}	Redlich-Peterson isotherm constant	$(\mathrm{dm^3\ mg^{-1}})^\beta$
β	Redlich-Peterson isotherm constant	
ε	Polanyi potential constant	$(\mathrm{kJ^2\ kmol^{-2}})$
α^E	initial adsorption rate	$(\mathrm{mg\ g.min^{-1}})$
β^E	Extent of surface coverage and the activation energy involved in chemisorptions	$(\mathrm{g\ mg^{-1}})$
A_t	Temkin isotherm constant	$(\mathrm{dm^3\ mmol^{-1}})$
b_T	Temkin isotherm constant	
C_e	Equilibrium concentration	$(\mathrm{mg\ l^{-1}})$
E	Activation energy	$(\mathrm{kJ\ mol^{-1}})$
k_1	Rate constant of first-order biosorption	$(\mathrm{1\ min^{-1}})$
k_2	Rate constant of second-order biosorption	$(\mathrm{g\ mg.min^{-1}})$
K_c	Langmuir equilibrium constant	$(\mathrm{dm^3\ mg^{-1}})$
K_D	Dubinin-Radushkevich isotherm constant	
K_f	Freundlich constant	
K_{rp}	Redlich-Peterson isotherm constant	$(\mathrm{dm^3\ mg^{-1}})$
K_s	Intraparticle diffusion constant	
n	Freundlich constant	
q	Metal ions biosorbed per g of biomass	$(\mathrm{mg\ g^{-1}})$
q_{max}	Maximum specific uptake corresponding to the sites saturation	$(\mathrm{mg\ g^{-1}})$
q_e	Amount of metal ions uptake at equilibrium	$(\mathrm{mg\ g^{-1}})$
q_s	Dubinin-Radushkevich isotherm constant	$(\mathrm{mg\ g^{-1}})$
q_t	Amounts of adsorbed metal ions on the biosorbent at time t	$(\mathrm{mg\ g^{-1}})$

R	Universal gas constant	$(8.314 \text{ J mol.K}^{-1})$
T	Absolute temperature	(K)
t	Contact time	(min)

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