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ADSORPTION OF Pb(II) USING NOVEL PLEUROTUS SAJOR-CAJU AND SUNFLOWER HYBRID BIOSORBENT

The present study was focused on the technical feasibility of using immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower for Pb(II) removal from the contaminated water. After preliminary evaluation, it was found that immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower effectively removed Pb(II) from wastewater at pH 4.5. The effect of various experimental parameters on Pb(II) uptake by hybrid biosorbent was systematically evaluated in a batch biosorption system. The optimized biosorbent dose, contact time, initial metal concentration and temperature were 0.05 g/100 cm³, 180 min, 800 mg/dm³ and 60 °C. Dynamics of the adsorption process were studied, and the values of rate constants of pseudo first order and pseudo second order kinetic models were calculated. Equilibrium isotherms for the adsorption of Pb(II) were analyzed by the Langmuir and Freundlich isotherm models. The sorption of Pb(II) followed the pseudo second order kinetic model. The Langmuir sorption isotherm fitted well to Pb(II) concentration data. The results revealed that this new hybrid biosorbent system was a promising candidate for eliminating Pb(II) from contaminated aquatic environment.

1. INTRODUCTION

As today's technology progresses, the natural environment suffers from the detrimental effects of pollution. The natural process of transportation of metal ions between soil and water consolidates metal contamination in high concentrations that affect the areas of natural ecosystems. The majority of toxic metal pollutants are waste products of industrial and metallurgical processes [1]. The majority of Pb(II) discharge into environment is generated by Pb-acid battery industry, printed wiring and paper mills. Excessive amount of Pb(II) in human can cause anemia, hypertension and brain

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damage [2]. Pb(II) is a potent neurotoxic metal when present above 0.05 mg/dm³ in drinking water [3]. Because of size and charge similarities, Pb(II) can replace Ca(II) in bone cells. Most recently, plant based biomaterials have been of interest for toxic metals removal [4]. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they present unused resources, widely available and are environmental friendly. The use of microbial cells as biosorbents for heavy metals is potential alternative to conventional methods of heavy metal decontamination from a variety of industrial aqueous process streams [5]. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physicochemical pathways of uptake [6]. Biosorption is a good alternative to the existing methods since it does not produce chemical sludges, it could be highly selective, more efficient, easy to operate and hence cost effective for the treatment of large volumes of wastewaters containing low pollutant concentrations [7].

Although freely suspended biomass may have better contact with adsorbates during biosorption process, the suspended biomass is normally not the practical form for the direct use in the removal of heavy metals. Since cell immobilization can enhance its stability, mechanical strength, reusability and the ease of treatment, the technique has been well used to remove toxic heavy metals [8]. Because the both microbial and agro-based materials have high biosorption potential as the biosorbents, a novel idea of producing a hybrid biosorbent (HB) was considered and an innovative HB matrix was produced by combining *Pleurotus sajor-caju* and sunflower waste biomass.

In this regard, the present study was carried out to assess the biosorption potential of the immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower for uptake of Pb(II) from aqueous solutions.

2. MATERIALS AND METHODS

The biosorption phenomenon was studied according to method described by Hanif et al. [9]. Sunflower waste biomass was collected from the Rose Laboratory and *Pleurotus sajor-caju* was collected from the Mushroom Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan.

Microorganism and culture medium. Pleurotus sajor-caju was maintained by subculturing on potato dextrose agar slants. Hyphal suspension for immobilization was prepared from 7 days old cultures grown on potato dextrose agar plates at 35 ± 2 °C. The liquid growth medium consisted of (gram per liter of distilled water); D-glucose, 5.0; KH₂PO₄, 5.0; NH₄NO₃, 2.0; (NH₄)₂SO₄, 4.0; MgSO₄·7H₂O, 0.2; peptone, 2.0; trisodium citrate, 2.5; yeast, 1.0. Preparation of hybrid matrix. The sieved samples of waste biomass were oven dried at 60 °C to constant weight, autoclaved for 15 min at 120 °C at 18 MPa and soaked in culture medium for 5–10 min under aseptic conditions. Six preweighed biomass samples were transferred to 100 cm³ of growth medium contained in 250 cm³ Erlenmeyer flasks. Each of these flasks was inoculated with 0.5 ± 0.024 cm³ of fungal mycelium suspension and incubated at 35 °C and shaken at 100 rpm for 6 days. The fungal mycelium suspension, optical density 0.5 ± 0.021 at 650 nm, was prepared from stationary phase culture of *Pleurotus sajor-caju*. After five days, *Pleurotus sajor-caju* was found entrapped within the fibrous network of waste biomass to form a hybrid biosorbent matrix.

Immobilization of biomass. 1 g of each live and dead hybrid biosorbent matrix of *Pleurotus sajor-caju* and sunflower waste biomass was dissolved in 100 cm³ of 2% sodium alginate. The mixtures were homogenized by high speed mixing. These mixtures were then reacted carefully with 0.1 M CaCl₂ to obtain the uniform sized beads of biomass. The immobilized hybrid biomass of live and dead fungus to be used in the optimization experimental parameters was prepared in a similar way.

Pb(II) solutions. Stock Pb(II) solutions (1000 mg/dm³) were prepared by dissolving Pb(NO₃)₂ in 1000 cm³ of deionized distilled water (DDW).

Batch biosorption studies. In all sets of experiments fixed volume of Pb(II) solutions (100 cm³) was taken in each 250 cm³ conical flask. The influence of experimental parameters such as pH (1–4.5), biosorbent dose (0.05–0.5 g/dm³), initial metal concentration (25–800 mg/dm³), contact time (15–1420 min) and temperature (30–60 °C) on sorption process was studied in a batch mode.

Determination of Pb(II) contents in the solutions. The Pb(II) concentration in the aqueous phase was determined using atomic absorption spectrophotometer and the metal uptake was calculated by the simple concentration difference method. Uptake of Pb(II) was calculated from the mass balance equation:

$$q = \frac{V(C_i - C_e)}{M} \tag{1}$$

where V is the volume of the solution (dm³), C_i is the initial concentration (mg/dm³), C_e is the final concentration in solution (mg/dm³) and M is the mass of the sorbent (g).

Statistical analysis. All data represent the mean of three independent measurements. The results are presented as mean±standard deviation values. All statistical analyses were done using Microsoft Excel 2007, Version Office Xp.

3. RESULTS AND DISCUSSION

3.1. INFLUENCE OF pH ON METAL ION BIOSORPTION

pH of the solution is a critical parameter as it strongly affects metal biosorption, surface charge of the adsorbent, degree of ionization and speciation of adsorbate species. It affects solution chemistry of metals, activity of functional groups in the biomass, and competition of metallic ions [10]. In order to evaluate the influence of pH on Pb(II) uptake, the batch equilibrium studies were carried out for a contact time of 1420 min with the initial pH range from 1 to 4.5 as high pHs promote precipitation of metals as hydroxides. The uptake capacities of *Pleurotus sajor-caju* of solutions play a vital role in the biosorption of Pb(II). The metal uptake by immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower waste biomass was 138.88 mg/g at pH 4.5. Whereas, the maximum equilibrium uptake of Pb(II) ion by dead *Pleurotus sajor-caju* and sunflower seed waste hybrid biosorbent was 155.82 mg/g, at pH 4.5 (Fig. 1). At high pH, the number of protons dissociated from functional groups on the cell wall increases and thus more negative groups for complexation of metal cations are provided [11].



Fig. 1. Effect of pH on uptake of Pb(II) by immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower; dose – 0.01g/dm³, initial metal concentration – 100 mg/dm³, volume – 100 cm³, temperature – 30 °C and contact time – 1420 min

In fact, it is known that at low pH most of carboxylic groups are not dissociated and cannot bond metal ions in solution. The increased biosorption is due to dissociation of carboxylic groups at higher pH [12]. Therefore, pH = 4.5 was selected for optimization of other experimental parameters. The most important aspect in biosorption study is to select a suitable biomass able to sequester the largest amount of metal of interest from its solution. Immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower waste have shown more uptake capacity for Pb(II) than the native biomass.

3.2. EFFECT OF BIOSORBENT DOSE

For metal uptake studies, biosorbent dose is an important factor to be considered. It determines the sorbent–sorbate equilibrium of the biosorption system [13]. The results obtained show that the optimum dose for maximum Pb(II) uptake using immobilized *Pleurotus sajor-caju* and sunflower hybrid biomass occurred at 0.5 g/dm³ (Fig. 2).



Fig. 2. Effect of dose on uptake of Pb(II) by immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower; pH – 4.5, initial metal concentration – 100 mg/dm³, volume – 100 cm³, temperature – 30 °C, and contact time – 1420 min

The maximum equilibrium uptake of Pb(II) ions by *Pleurotus sajor-caju* and sunflower hybrid biosorbent was at lower biosorbent dose. This shows that the maximum adsorption occurs at a minimum dose and hence the amount of ions bound to the adsorbent and amount of free ions remains constant. After that, the uptake capacity (mg/g) of biosorbent was gradually decreased with increase in the biosorbent dose. The result can be attributed to some kind of hindrance as due to aggregation /agglomeration of sorbent at higher concentration. Besides, the adsorption sites remain unsaturated during the sorption process due to lower adsorption capacity (mg/g) utilization of sorbent [14]. Higher uptake at low biosorbent concentration could be due to an increased metal to biosorbent ratio, which decreases upon an increase in immobilized biomass concentration [15]. Similar results have been reported elsewhere [13, 15].

3.3. EFFECT OF INITIAL METAL CONCENTRATION

Biosorption of metal by any biosorbent is highly dependent on initial concentration of metal ions [12]. The Pb(II) removal using immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower waste biomass corresponding to various initial metal concentrations (25, 50, 75, 100, 150, 200, 400 and 800 mg/dm³) is shown in Fig. 3.



Fig. 3. Effect of initial metal concentration on uptake of Pb(II) by immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower; pH – 4.5, dose – 0.01 g/dm³, volume – 100 cm³, temperature – 30 °C, and contact time – 1420 min

The maximum equilibrium uptake of Pb(II) ions by live *Pleurotus sajor-caju* and sunflower stem waste hybrid biosorbent was 275.36 mg/g and occurred at 800 mg/dm³. The sorption characteristics show that surface saturation was dependent on the metal ion initial concentration. On increasing metal ion concentration, the percentage of metal removed decreased due to diminishing loading capacity of biomass [16]. The observed enhancement of metal uptake could be due to an increase in electrostatic interactions (relative to covalent interaction) which involves site of progressively low affinity for metal ions. At low concentrations, biosorption sites took up available metal more quickly. However at higher concentrations, metal ions need to diffuse to biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [17]. Trend of a similar type for Pb(II) uptake by distillation of sludge biomass has also been reported [16].

3.4. ADSORPTION ISOTHERMS

To examine the relationship between sorbed (q_e) and aqueous concentration (C_e) of metals at equilibrium, Langmuir and Freundlich adsorption isotherms were tested. The Langmuir model [18] takes the form of:

$$\frac{C_e}{q_e} = \frac{1}{X_x K_L} + \frac{C_e}{X_x}$$
(2)

where q_e is the amount of metal ions sorbed (mg/g), C_e is the equilibrium concentration of metal ion solution (mg/dm³), X_m (mg/g) and K_L (dm³/mg) are the Langmuir constants. Freundlich mode [9] can be easily linearized by plotting it in a logarithmical (log–log) scale. The Freundlich equation is:

$$\log q_e = \frac{1}{n} \log C_e + \log K \tag{3}$$

where q_e is the amount of metal ions adsorbed (mg/g), C_e is the equilibrium concentration of solution of metal ions (mg/dm³), k (mg/g) and n are the Freundlich constants. R^2 values lower than 0.98 obtained by the Freundlich model indicated that model is not applicable (Table 1).

Table 1

Biosorbent	Langmuir isotherm parameters			Experimental	Freundlich isotherm parameters			
	$\begin{array}{c} X_m \\ (q_{\max}) \\ [mg/g] \end{array}$	K_L [dm ³ /g]	R^2	q [mg/g]	q [mg/g]	K [mg/g]	R^2	1/ <i>n</i>
DPSSWH	250.00	8.696×10 ⁻²	0.99	248.00	316.67	61.78	0.85	0.24
LPSSWH	270.27	3.60×10^{-2}	0.99	262.448	358.83	35.35	0.70	0.35
DPSStWH	277.77	7.5×10^{-1}	0.99	273.14	342.10	64.18	0.85	0.25
LPSStWH	285.71	1.792×10^{-2}	0.98	275.36	314.96	30.86	0.73	0.35

Langmuir and Freundlich isotherm parameters for Pb(II) biosorption

The results obtained from initial metal ion concentration studies tend to be in better correlation with the Langmuir isotherm model for Pb(II) (Table 1). If the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next ion, then the sorption process would follow the Langmuir adsorption isotherm. The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges. However, it is easier to handle mathematically in more complex calculations (e.g. in modeling the dynamic column behavior) where it may appear quite frequently.

3.5. EFFECT OF TEMPERATURE

The effect of temperature on the metal biosorption experiment was investigated at five different temperatures ranging from 30 to 60 °C at constant pH 4.5, initial metal concentration (100 mg/dm³), dose (0.05 g/100 cm³) and contact time of 1420 min (Fig. 4). Pb(II) capacity of immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower waste increase with temperature. The maximum sorption capacity of Pb(II) ion by live *Pleurotus sajor-caju* and sunflower stem waste hybrid biosorbent was 205.12 mg/g at 60 °C.



of *Pleurotus sajor-caju* and sunflower; $(pH - 4.5, dose - 0.01g/dm^3,$ initial metal concentration - 100 mg/dm³, volume - 100 cm³, and contact time - 1420 min

Similar results have been reported by Iqbal et al. [11]. The metal uptake capacity of Pb(II) sharply increases upon increasing temperature. A reasonable explanation might be that the actual attachment of metal ion on the cellular surface included not only chemisorption and ion exchange, but also physical adsorption and endothermic reaction [19]. These results are in accordance with earlier reported results [11, 13].

3.6. EFFECT OF TIME

The effect of the contact time was studied for 15–1420 min (Fig. 5). The results demonstrate that the metal uptake increases with increase in contact time. It is known that the rate of metal uptake is influenced by mass transfer from bulk solution to binding sites with various steps involved. First is the bulk transport of metal ions in solution phase, which is usually rapid because of mixing and adjective flow. Second, film transport involves diffusion of metal through a hydrodynamic boundary layer around

the biosorbent surface, and third, actual adsorption of metal ions by active sites of the biomass is considered to be rapid equivalent to an equilibrium reaction [6]. In the beginning biosorption was sharp probably due to decrease in pH of solution because of proton released by the biosorbent. The rapid initial sorption was likely due to extra cellular binding and slow sorption phase till equilibrium (360 min) likely resulted from intracellular binding [20].



Fig. 5. Effect of contact time on uptake of Pb(II) by immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower waste biomass; pH – 4.5, dose – 0.01 g/dm³, initial metal concentration – 100 mg/dm³, volume – 100 cm³, and temperature – 30 °C

These results are important as the equilibrium time is one of the important parameters for an economical wastewater treatment [5]. The similar explanation was proposed by several earlier workers [21–23].

3.7. BIOSORPTION KINETIC MODELS

Kinetics of absorption by any biological material has been widely tested by first order expression given by Lagergren and pseudo second order approach. The first order Lagergren [9] equation is:

$$\log(q_e - q) = \log q_e - \frac{k_{1, ads}t}{2.303}$$
(4)

The pseudo second order [9] equation is:

$$\frac{t}{q} = \frac{1}{k_{2, \text{ ads}} q_e^2} + \frac{t}{q_t}$$
(5)

where $q_e \text{ (mg/g)}$ is the mass of metal absorbed at equilibrium, $q_t \text{ (mg/g)}$ the mass of metal at time t (min), $k_{1,\text{ads}} \text{ (min}^{-1})$ the first order reaction rate constant of adsorption, $k_{2,\text{ads}} \text{ (g/(mg \cdot \text{min}))}$ the pseudo second order rate constant of adsorption.

Table 2

Biosorbent	Pseudo first order kinetic model			Experimental	Pseudo second orde kinetic model		ler	
	q_e [mg/g]	$k_{1,\text{ads}}$ $[\min^{-1}]$	R^2	q [mg/g]	q_e [mg/g]	k _{2,ads} [g/mg.min]	R^2	
DPSSWH	82.75	4.66×10^{-3}	0.97	169.56	172.41	1.59×10 ⁻⁴		
LPSSWH	92.49	4.37×10^{-3}	0.97	132.28	138.88	1.11×10^{-4}	0.00	
DPSStWH	82.28	2.99×10^{-3}	0.89	137.76	142.85	9.75×10^{-5}	0.99	
LPSStWH	77.49	2.07×10^{-3}	0.87	139.08	142.85	9.37×10 ⁻⁵		

Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Pb(II) biosorption

A comparison between Lagergren pseudo first order and pseudo second order kinetic models is shown in Table 2. The results obtained suggest that pseudo second order model fitted well to the kinetics data of Pb(II). The value of q_e obtained from pseudo second order kinetics model was in close agreement with that of experimental value and the correlation coefficient R^2 was also close to one.

4. CONCLUSIONS

• Hybrid biomass composed of microbial and plant waste biomass was found to be very useful in effective removal of Pb(II) from wastewater.

•The optimized pH, biosorbent dose and contact time were 4.5, 0.05 g/100 cm³ and 360 min, respectively, at 60 °C for Pb(II) uptake by immobilized hybrid biomass of *Pleurotus sajor-caju* and sunflower.

• The sorption of Pb(II) followed the pseudo second order kinetic model.

• The Langmuir sorption isotherm model fitted well to the Pb(II) concentration data.

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