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Lead (II) Removal from Aqueous Solution by Spent *Agaricus bisporus*: Determination of Optimum Process Condition Using Taguchi Method

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Abstract In this paper, Taguchi method was applied to determine the optimum condition for Pb (II) removal from aqueous solution by spent *Agaricus bisporus*. An orthogonal array experiment design ($L_9(3^4)$ which is of four control factors (pH, t (contact time), m (sorbent mass), and C_0 (initial Pb (II) concentration)) having three levels was employed. Biosorption capacity (mg metal/g biosorbent) and percent removal (%) were investigated as the quality characteristics to be optimized. In order to determine the optimum levels of the control factors precisely, range analysis and analysis of variance were performed. The optimum condition for biosorption capacity was found to be pH=5.00, t=5.0 h, m=0.010 g, and C_0=50 mg/L. And for percent removal, the optimum condition was found to be pH=4.00, t=4.0 h, m=0.100 g, and C_0=50 mg/L. Under these optimum conditions, biosorption capacity and percent removal can reach 60.76 mg/g and 80.50%, respectively.

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1 Introduction

Heavy metals are not biodegradable and tend to accumulate in biological systems, posing health hazards if their concentrations exceed allowable limits (Volesky 2001). Among the heavy metals, Pb is one of the three most toxic heavy metals (Jalali et al. 2002). Many important industrial applications, such as storage battery, manufacturing, printing pigments, fuels, photographic materials, explosive manufacturing, metal plating, mining, painting, car manufacturing, smelters, and metal refineries (Kansanen and Venetvaara 1991; Pip 1991) are major sources of Pb (II) pollution. Continuous absorption of Pb (II) may cause serious injuries to human health such as kidney damage and several others (Clarkson et al. 1998; dos Santos et al. 2004). Therefore, the removal of Pb (II) from wastewater is very important for the environmental protection and human health. Traditional methods for removal of Pb (II) such as ion exchange, chemical precipitation, ultra filtration, and chemical deposition do not seem to be economically feasible because of their relative high costs, particularly when used for the removal of heavy metals at low concentrations (<100 mg/L; Wilde and Benemann 1993). Furthermore, most of these methods generate toxic sludge, the disposal of which is an additional burden on the economic (Saeedet al. 2005a, b). Therefore, there is a dire need to find alternative methods which are environmental friendly, effective, and economic.

The biosorption process has become one of the most efficient methods for pollutant removal from water effluents and can be used in many industrial applications in order to promote efficiency and make it more economic (Cabuk et al. 2006). Among all the biosorbents, the ones which are made from waste materials from agriculture and food industry have gained important credibility during recent years because of their ecofriendly nature, excellent performance, and low cost domestic technique for remediation even for heavily metal-loaded waste water (Kumari et al. 2006). Besides, using these waste materials as biosorbents has the dual advantage of waste reuse and low sorbent cost. Therefore, a series of waste materials have been explored recently. Agricultural by products such as papaya wood (Saeed et al. 2005a, b), grape stalk (Martínez a et al. 2006), rice husks (Babel and Kurniawan 2003), yellow passion fruit (Jacquesb, et al. 2007), Nile rose plant powder (Abdel-Halim et al. 2003), and pine-fruit Brazilian coats (Brasila et al. 2006; Lima et al. 2007) and some other mushrooms such as *Agaricus macrosporus* (Melgar et al. 2007), *Amanita rubescens* (Sarı and Tuzen 2008), and *Lentinus edodes* (Chen et al. 2008) have been successfully employed as biosorbents for toxic metal removal. What is more, *Agaricus bisporus* has been used as biosorbent to remove Cr (VI) from aqueous solutions (Ertugay and Bayhan 2007).

In this study, spent *A. bisporus* was chosen as biosorbent and Pb (II) contaminated solutions as wastewater. Pb (II) has been selected for biosorption studies by many researchers employing algal biomass (Gupta and Rastogi 2008a, b), Robinia tree leaves (Zolgharnein et al. 2008), Ponkan peel (Pavana et al. 2008), lichen biomass (Uluozlu a et al. 2008), green algae (Gupta and Rastogi 2008a, b), grape stalk (Martínez a et al. 2006), rice husk (Wong et al. 2003), etc. However, no study has been carried out using spent *A. bisporus* which is the waste of mushroom product of *A. bisporus*. Furthermore, *A. bisporus* is widely grown in China, and the spent *A. bisporus* has no commercial value and will exert environmental burden because it will decay and, thus, contaminate the environment. Therefore, it is a good, eco-friendly, and inexpensive source of readily available biosorbent.

The objective of this study was to investigate the potential of spent *A. bisporus* in treating wastewater contaminated with Pb (II) and to find out the optimum biosorption condition to achieve the maximum removal capability. Factors affecting metal ion uptake by a sorbent in a batch system include pH, contact time, sorbent mass, initial metal ion concentration, etc. (Lima et al. 2007). Thus, these factors should be optimized. For this purpose, batch experiments were designed to study the influence of the four factors. To determine the optimum biosorption condition, Taguchi method was applied. An orthogonal array experiment design (L_9 (3^4)) that allows to investigate the biosorption capacity and percent removal of the four single factors having three levels was employed.

2 Materials and Methods

2.1 Preparation of the Biosorbent

Fresh spent *A. bisporus* which was purchased from Huike, a mushroom production site in Chengdu of China, was used in this study as the biosorbent. Before use, the mud on it was removed by a knife. Then, it was washed with deionized water 3–5 times to remove dirt. After these steps, it was dried at 50°C for 24 h and then was ground into fine powder by a pulverizing machine (XIBEILE, SQ2119N). Finally, it was sieved through a 24-mesh stainless steel sieve.

2.2 Preparation of Pb (II) Solutions

All chemicals used in this study were of analytical grade, and the solutions were prepared using deionized water. Stock solution of Pb (II) (1,000 mg/L) was prepared by dissolving Pb $(NO_3)_2$ into 10% HNO_3 solution. Pb (II) solutions of different concentrations were obtained by diluting the stock solution. Standard solution of Pb (II) (1,000 mg/L) for flame atomic adsorption spectrometry (VARIAN, SpectrAA-220Fs) and graphite furnace for AAS (VARIAN, SpectrAA-220Z) adjusting was obtained from China Iron and Steel Research Institute of NACIS. To adjust the pH, 0.1 mol/L HCl and NaOH solutions were used, and the pH value measurement was conducted utilizing a pH/mV handheld meter (PHB-8).

2.3 Metal Analysis Method

After the biosorption process, the samples were filtered immediately to remove the biosorbent by vacuum filtration using filter paper (Whatman 42). The filter residue and filtrate were digested using microwave-digestion method, respectively (5 ml HNO_3+1 ml H_2O_2 for each sample). The analysis of Pb (II) in the digest was performed by the flame atomic absorption spectrophotometer (VARIAN, SpectrAA-220Fs) with an oxidizing air acetylene flame and background correction of the deuterium lamp. For some digest samples, the Pb (II) concentrations were too low (<1,000 mg/L). In order to assure the accuracy of the result, these samples were analyzed using a graphite furnace for AAS (VARIAN, SpectrAA-220Z), with argon as inert gas.

In order to check out whether the digestion and analysis process were credible, standard reference material of Theae folium (GBW08505, bought from National CRM/RM Center) was digested and analyzed in the same method that was carried out in this study. Then, we compared the analysis results to the standard values of the Theae folium to check whether the digestion and analysis process were credible. Besides, two controls were also performed. The control without sorbent shown whether the metal ions were adsorbed onto the walls of the Erlenmeyer flasks or not. The control without metal ions (deionized water instead of metal solution) was used to estimate any leaching from the sorbent during the study period.

2.4 Single Factor Experiment

In order to determine reasonable levels of the four single factors in the Taguchi method experiments, single-factor experiments were carried out in 150-ml Erlenmeyer flasks containing 100 ml Pb (II) solutions. For each single factor, five different levels were designed, and other factors were kept constant. Each level of each single factor was conducted of ten parallel experiments. The final result was the mean of the ten. The experimental design is shown in Table 1.

2.5 Taguchi Method

2.5.1 Introduction

The Taguchi method is a powerful problem-solving technique for improving process performance, yield, and productivity. It reduces scrap rates, rework costs, and manufacturing costs due to its excessive variability in processes (Kaminari et al. 2007).

The techniques for laying out experiments in which multiple factors are involved are popularly known as the factorial design of experiments. This method helps researchers to determine the possible combinations of factors and to identify the best combination. It develops rules to carry out the experiments, which further simplifies and standardizes the design of experiments, along with minimizing the number of factor combinations that would be

Table 1 Single factor experiment design

Factors	Conditions	Levels				
		1	2	3	4	5
PH:	Contact time 3 h Sorbent mass 1.000 g Initial Pb (II) conc. 20 mg/L	2.00	4.00	6.00	8.00	10.00
Contact time(h):	pH 4.00 Sorbent mass 1.000 g Initial Pb (II) conc. 20 mg/L	0.5	1.0	3.0	5.0	7.0
Sorbent mass (g):	pH 4.00 Contact time 5 h Initial Pb (II) conc. 20 mg/L	0.100	0.500	1.000	2.000	3.000
Initial Pb (II) conc. (mg/L):	pH 4.00 Contact time 5 h Sorbent mass 0.100 g	5	10	20	50	100

required to test the factor effects. Based on these, Taguchi method was chosen for laying out this study.

2.5.2 Taguchi Method Design

Different steps of Taguchi method experiment design are as follows:

1. Determine percent removal and biosorption capacity as the quality characteristics to be optimized.
2. Identify the control factors and their alternative levels. Control factors are those design factors that can be set and maintained. The control factors and their levels for this study are represented in Table 2.
3. Design the orthogonal experiment. For this study, an L_9 (3^4) orthogonal array experiment was chosen. Based on the results of the single factor experiments, the orthogonal experiment was designed as is shown in Table 3.
4. Conducting the orthogonal experiment.

2.6 Calculation and Data Analysis Method

2.6.1 Calculation of the Biosorption Capacity and the Percent Removal

The biosorption capacity and the percent removal of removing Pb (II) from aqueous solutions by *A. bisporus* were calculated by the following equation:

$$q_{\mathrm{eq}} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$n = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

Table 2 Taguchi method experimental parameters and their levels

Process parameter	Designation	Level 1	Level 2	Level 3
PH	A	3.00	4.00	5.00
Contact time (h)	B	4.0	5.0	6.0
Sorbent mass (g)	C	0.010	0.100	0.300
Initial Pb (II) conc. (mg/L)	D	20	30	50

Table 3 Matrix experiment design

Trial No.	Operating factors and their levels			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

The levels are shown in Table 2

A pH, *B* contact time, *C* sorbent mass, *D* initial Pb (II) conc.

Where q_{eq} is the biosorption capacity (mg metal/g biosorbent); n is the percent removal (%); C_0 is the initial Pb (II) concentration (mg/L), C_e is the equilibrium Pb (II) concentration (mg/L), m is the sorbent mass (g) and V is the volume of metal solution put in contact with the adsorbent.

2.6.2 Data Analysis Method

The collected data were analyzed by using Statistical Package for the Social Sciences (SPSS) 16 statistical software for the evaluation of the effect of each factor on the biosorption process. And for the range analysis and the analysis of variance (ANOVA) of the data in the Taguchi method experimental design, SPSS statistical software was also used.

3 Results

3.1 Effect of pH on Pb (II) Uptake

The pH must be an important factor affecting the uptake of heavy metal ions from aqueous solutions by the sorbent. The cell wall of macrofungus such as *A. bisporus* is mainly consisted of polysaccharides, proteins, and lipids. They offer many functional groups such as carboxyl, carbonyl, hydroxyl, and amino which are involved in metal binding (Sangi et al. 2008; Akar et al. 2005). At low pH, the surfaces of these functional groups are closely associated with the hydronium ions (H_3O^+) and restrict the approach of metal cations as a result of the repulsive force (Aksu 2001; Sheng et al. 2004). Besides, most of the carboxylic groups are not dissociated and cannot bind the metal ions in solution at low pH, although they take part in complexation reactions (Chubara et al. 2004).

As can be seen in Fig. 1, percent removal increased with increasing solution pH and a maximum value was reached at around Ph 4.00. Increasing pH from 6.00 to 10.00 resulted in lower percent removal. This may be attributed to the decreased solubility of Pb (II) at high pH values. For this reason, the experiments were not conducted beyond pH 10.00. Taking these theories and results into account, pH 4.00 was chosen as the best level for further experiments.

3.2 Effect of Contact Time on Pb (II) Uptake

As is shown in Fig. 2, during the first 3 h, there was a fast rate of adsorption, and the biosorption amount can reach about 90% of the maximum biosorption capacity. This fast metal uptake by the sorbents may be attributed to the abundant availability of active sites on the biosorbent and its highly porous and mesh structure, which provides ready access and large surface area for the sorption of metals on the binding sites (Saeed et al. 2005a, b). After the initial rapid uptake, there was an ongoing slow adsorption appearing to reach the equilibrium at about 5.0 h, where the removal rate reaches the highest level of 63.30%. We can explain this phenomenon as follow: with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage. This two-stage biosorption, the first rapid initial uptake followed by a slow stage reaching equilibrium, is similar to previous reports on the biosorption of heavy metals with different sorbents (Saeed et al. 2005a, b; Akhtar et al. 2004; Saeed and Iqbal 2003). After 5.0 h, the biosorption rate degraded. Based on these, 5.0 h was fixed as the optimum contact time for further experiments.

3.3 Effect of Sorbent Mass on Pb (II) Uptake

The maximum metal ion percent removal was observed at 0.100 g sorbent mass per 100 ml Pb (II) solution. As it shows in Fig. 3, increase in the sorbent biomass strongly affected the removal of Pb (II) from aqueous solutions. This indicates that as the sorbent biomass increased, the unoccupied sorption sites became more surplus with every increase of the biomass. Saeed et al (2005a, b) obtained similar results.

However, as it shows in Fig. 4, the biosorption capacity degrades as the sorbent mass increases. This indicates that as the sorbent mass increases, the average utilization rate of the sorbent degrades. Therefore, 0.100 g was chosen as the best level for further experiments.

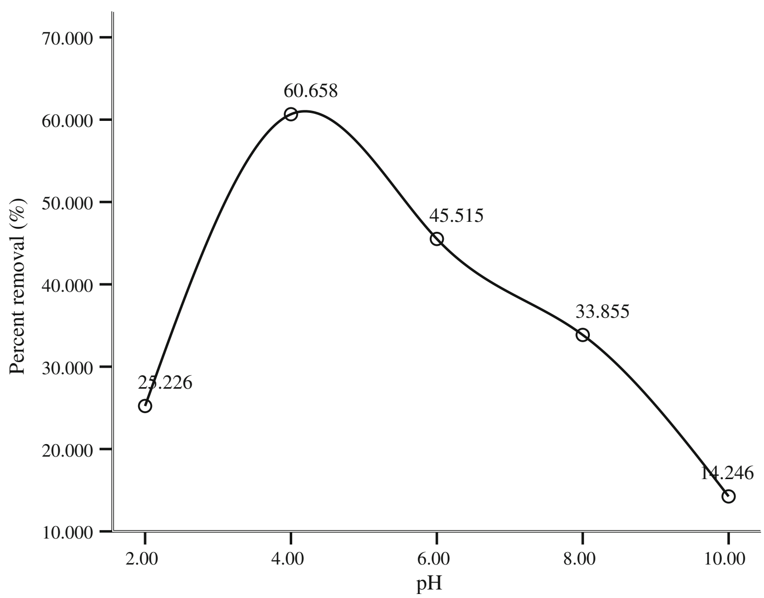

Fig. 1 Effect of PH on percent removal of Pb (II). (contact time=3.0 h, sorbent mass=1.000 g, initial Pb (II) conc.=20 mg/L)

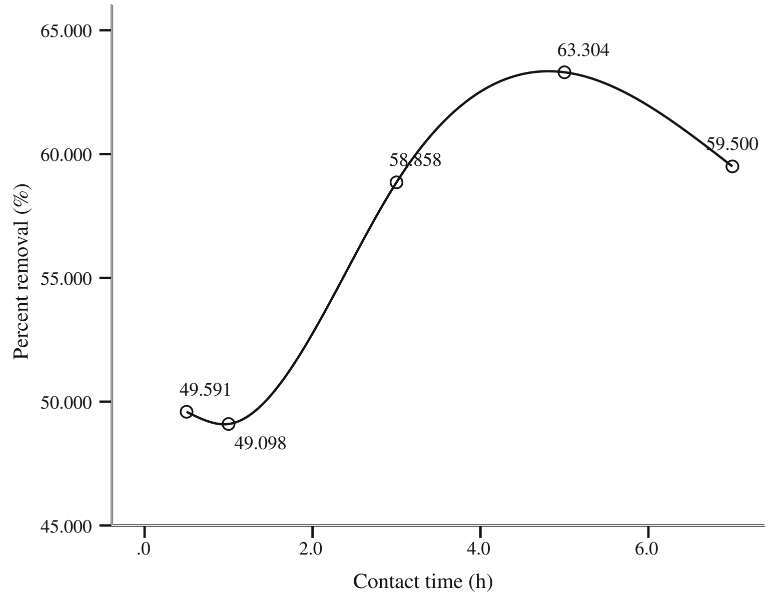

Fig. 2 Effect of contact time on percent removal of Pb (II). (pH=4.00, sorbent mass=1.000 g, initial Pb (II) conc.=20 mg/L)

3.4 Effect of Initial Pb (II) Concentration on Pb (II) Uptake

The heavy metal uptake mechanism is particularly dependent on the initial concentration of the Pb (II). Biosorption capacities of the sorbent increased with increasing metal ion concentration in the medium. This effect may be due to an increase in electrostatic interactions (relative to covalent interactions) which involve sites of progressively lower affinity for metal ions(Saeed 2005a, b; Al-Asheh and Duvnjak 1995).

The sorbent exhibited very high metal removal capacities for Pb (II). The result in Fig. 5 shows that as the initial concentration increases, the percent removal of Pb (II) increased as is generally expected due to equilibrium process. The maximum percent

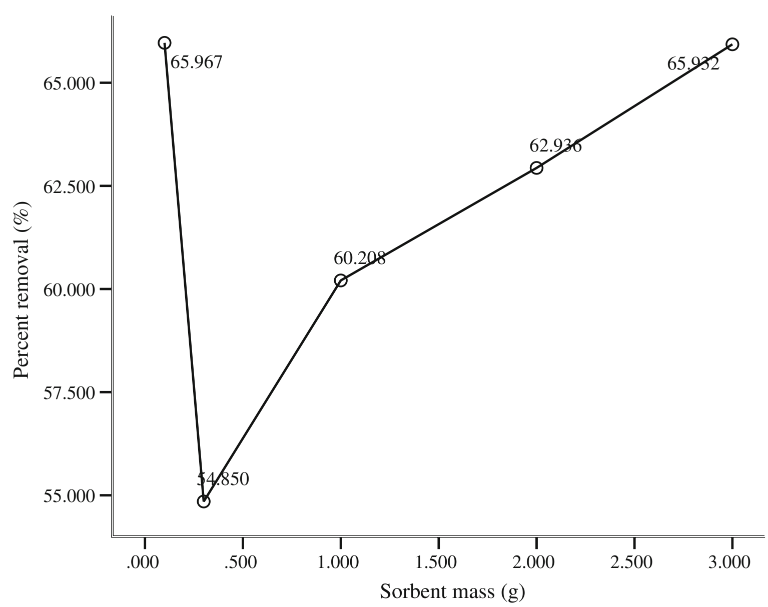

Fig. 3 Effect of sorbent mass on percent removal of Pb (II). (pH=4.00, contact time=5.0 h, initial Pb (II) conc.=20 mg/L)

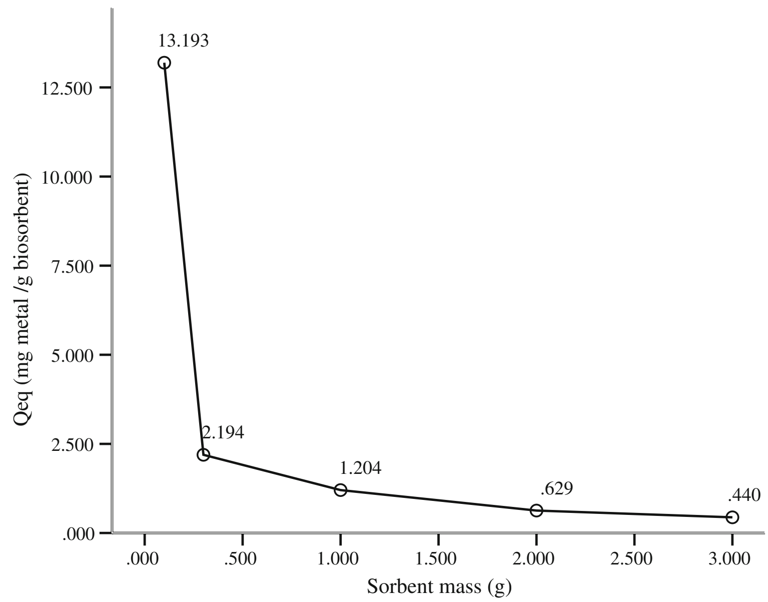

Fig. 4 Effect of sorbent mass on biosorption capacity of Pb (II). (pH=4.00, contact time=5.0 h, initial Pb (II) conc.=20 mg/L)

removal can achieve 81.84% under initial concentration of 50 mg/L. This value is higher than many corresponding biosorbents reported in the literatures (Chin-pin et al. 1990; Pagnanelli et al. 2003; Akhtara et al. 2003; Saeed et al. 2005a, b; Chakravarty et al. 2002). However, as is shown in Fig. 6, when the initial concentration increases to 100 mg/L, the biosorption capacity did not increase markedly. Based on both results, 50 mg/L was chosen as the best initial concentration for further experiments.

3.5 Taguchi Method Experiment

3.5.1 The Results and Its Range Analysis of Taguchi Method Experiment

The results of Taguchi method experiment are shown in Table 4. From the results presented in Table 4, we can find out that for the combination of the four factors, the optimum is the condition combination in experiment 4, that is, pH 4.00, contact time 4.0 h,

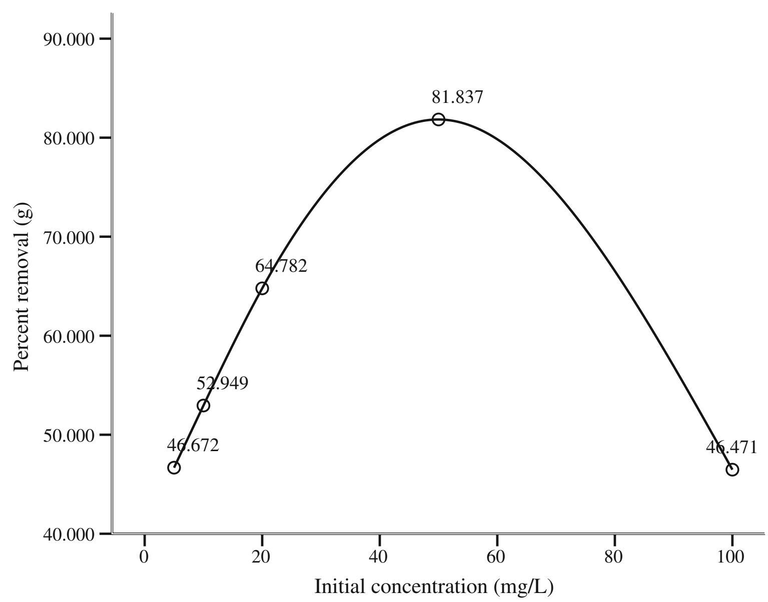

Fig. 5 Effect of initial Pb (II) concentration on percent removal of Pb (II). (pH= 4.00, contact time=5.0 h, sorbent mass=0.100 g)

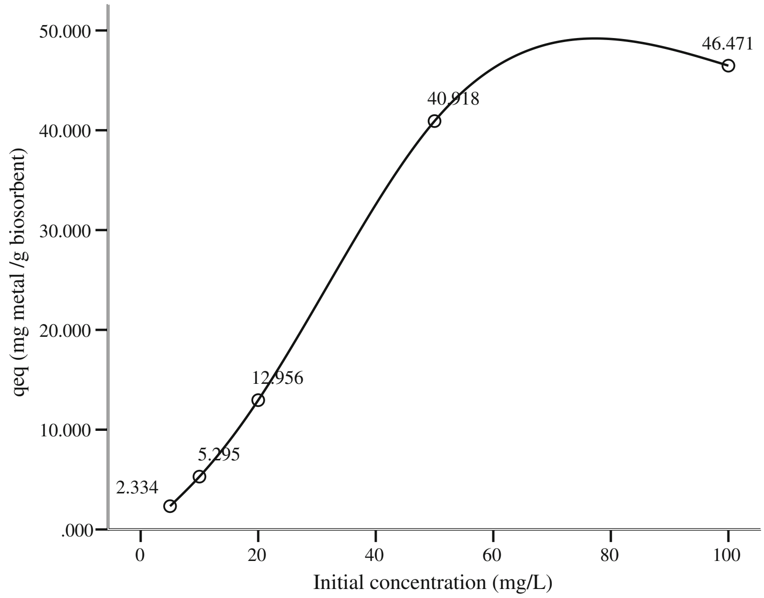

Fig. 6 Effect of initial Pb (II) concentration on biosorption capacity of Pb (II). (pH=4.00, contact time=5.0 h, sorbent mass=0.100 g)

biosorbent mass 0.1 g, and initial Pb (II) concentration 50 mg/L. Under this condition, the percent removal can reach 80.50%. And for all the experiment conditions, experiment 8 can reach the highest biosorption capacity of about 60.76 mg/g. The results of range analysis are shown in Table 5. K1, K2, and K3 are the average values of the results of each level in Taguchi method experiment. Range values are the average values of K1, K2, and K3. Based on the principle of "The larger the better," range analysis indicates the best levels for each single factors and shows which factor is the most important in the biosorption process. The results are concluded in Table 6.

3.5.2 Analysis of Variance

The results of ANOVA for the Taguchi method experiment are tabulated in Table 7. A statistical ANOVA was performed to see which process factors significantly affect the process responses. In the ANOVA, the Fischer ratio (or *F* test) was used to determine significant process factors. *F* test is a tool to see which process factor has a significant effect on biosorption capacity and percent removal. The *F* value for each process factor is simply a ratio of the mean of the squared deviations to the mean of the squared error. Minimum or critical values for the Fischer ratio (*F* critical values) can be found in most of the statistics

Table 4 Design matrix and the experimental results for the L^9 (3^4) orthogonal array experiment

Experiment no.	Operating factors and their levels				Results	
	A	B	C	D	Biosorption capacity (mg/g)	Percent removal (%)
1	1	1	1	1	1.1999	2.952
2	1	2	2	2	15.902	72.783
3	1	3	3	3	9.078	65.471
4	2	1	2	3	34.161	80.499
5	2	2	3	1	2.865	54.759
6	2	3	1	2	7.977	2.472
7	3	1	3	2	4.312	45.636
8	3	2	1	3	60.757	17.971
9	3	3	2	1	4.993	49.202

The levels are shown in Table 2. Each value in the results is the mean of ten parallel ones

A pH, *B* contact time, *C* sorbent mass, *D* initial Pb (II) conc.

Table 5 Range analysis for the L^9 (3^4) orthogonal array experiment

	A	B	C	D
Biosorption capacity				
K1	8.727	13.224	23.311	3.019
K2	15.001	26.508	18.352	9.397
K3	23.354	7.349	5.418	34.665
Range	14.627	19.159	17.893	31.646
Percent removal				
K1	47.069	43.029	7.798	35.638
K2	45.910	48.505	67.495	40.297
K3	37.603	39.048	55.289	54.647
Range	9.466	9.457	59.697	19.009

The levels are shown in Table 2

A pH, *B* contact time, *C* sorbent mass, *D* initial Pb (II) conc., *K* average value of each level, *Range* average value of K1, K2, and K3

and experimental design handbooks (Montgomery 2001). An *F* ratio is calculated from the experimental results and then compared to the critical value. If the *F* ratio calculated is larger than the *F*cr critical value, it is an indication that the statistical test is significant at the confidence level selected. If not, it indicates that the statistical test is not significant at the confidence level.

On the basis of the calculated *F* values, only biosorbent mass statistically inferred to have significant influences on percent removal. Other factors show no significance for both biosorption capacity and percent removal. The relative accuracy is 135.25 and 578.04 for percent removal and biosorption capacity, respectively. This is a very important finding since it indicates that the biosorption process was not influenced by the day and the environment, and it shows the stability and repeatability of the biosorption process.

Table 6 Optimum levels for each single factor in the L^9 (3^4) orthogonal array experiment

Factors	Levels	
	Biosorption capacity	Percent removal
A	3	1
B	2	2
C	1	2
D	3	3

The levels are shown in Table 2

A pH, *B* contact time, *C* sorbent mass, *D* initial Pb (II) conc.

Table 7 ANOVA for biosorption capacity and percent removal in the L^9 (3^4) orthogonal array experimental design

Operating factors	*dof*	SSD	*F* ratio	*F*cr critical value
Biosorption capacity				
A	2	323.082	1.000	19.000
B	2	578.038	1.789	19.000
C	2	512.021	1.585	19.000
D	2	1680.649	5.202	19.000
Error	2	323.08		
Total	10	3416.87		
Percent removal				
A	2	159.944	1.000	19.000
B	2	135.251	0.846	19.000
C	2	5967.942	37.313	19.000[a]
D	2	588.984	3.682	19.000
Error	2	159.94		
Total	10	7012.061		

The levels are shown in Table 2

[a] Significance level at a 95% confidence interval, $F0.05\ (2, 2)=19$, $F0.1\ (2, 2)=9$.

SSD sum of squares of deviations, *A* pH, *B* contact time, *C* sorbent mass, *D* initial Pb (II) conc.

4 Conclusions

In this study, spent *A. bisporus* was chosen as the biosorbent. The present results confirm that it is more effective for the removal of Pb (II) compared with those found in the literatures (Huang et al. 1990; Pagnanelli et al. 2003; Akhtar et al. 2003; Saeed et al. 2005a, b; Chakravarty et al. 2002), without any chemical or physical pre-treatment.

For the Taguchi method experiment, the optimum condition for biosorption capacity and percent removal was found out. Under these optimum conditions, biosorption capacity and percent removal can reach 60.76 mg/g and 80.50%, respectively. Besides, range analysis and ANOVA results indicate that only biosorbent mass statistically inferred to have significant influences on percent removal. Other factors show no significance for both biosorption capacity and percent removal.

Spent *A. bisporus* biosorbent is a low cost material that shows great potential to be applied in wastewater technology for remediation of toxic metal. Our findings may also have general industrial application in the field of treatment and disposal of liquid hazardous waste.

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