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Treatment of metal wastewater in pilot-scale packed bed systems: Efficiency of single- vs. mixed-mushrooms

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Abstract: This study investigated the biosorption of heavy metals from industrial wastewater using mushrooms at small-sized pilot-scale. Mushrooms (*Agaricus bisporus* and *Pleurotus cornucopiae*) were modified with sodium hydroxide prior to packed bed experiments. Packed bed experiments were carried out in a two-stage continuous system to investigate the effects of different mushrooms, including *A. bisporus*, *P. cornucopiae*, and mixed sorbents. *A. bisporus* and *P. cornucopiae* showed each merits during each runs, and resulted in good-quality effluents. Nevertheless, the system packed with the two mushrooms demonstrated the best performance with a treated volume of 156L and a total metal uptake of 13.64 mg g^{-1}; the removal efficiencies were over 95.1% for all metals in the outlet effluent, and the treated effluent met the regulatory discharge standards. Models were applied to fit with some experimental data. Desorption studies were carried out for three cycles. The present study showed that the two-stage continuous system packed with different biosorbents could effectively remove various heavy metals from industrial wastewater.

Key words: Biosorption; Packed bed column; Pilot scale; Industrial wastewater; Heavy metal.

1. Introduction

With the rapid development of industries, large quantities of wastewater containing heavy metals are discharged into the environment, which caused serious ecological, environmental and healthy problems.[1, 2] Various methods, such as chemical precipitation, ion exchange, adsorption, membrane filtration, and electrochemical treatment, are adopted to deal with the heavy metal pollutions.[3] Compared with conventional technology, biosorption using industrial and agricultural materials has the advantages of low cost, high efficiency, minimization of secondary wastes, and regeneration ability.[4, 5] Thus, biosorption has been proposed as an effective and economic method for low concentration of heavy metal wastewater treatment.[3]

Packed bed column is considered to be the most widely used adsorption process in large-scale wastewater treatment due to its simple configurations, the relative ease of scaling up the procedures, economic and convenient operations.[6, 7] These potential industrial roles made the bed column process in biosorption receive increasing attention from researchers during recent years;[4] however, most of these studies are still restricted to the stage of laboratory.[8, 9] Besides, most adsorption studies on a continuous column process have focused mainly on the solution containing only single metal.[8, 10-13] These studies have limited industrial application, as the industrial effluents often contain several heavy metals, and other contaminants concomitantly.[13] Therefore, it is necessary to use actual industrial wastewater at the stage of pilot scale for demonstrating the applicability of biosorbents. Considering industrial effluents contain various pollutants (various metals, organics and other impurities), two-stage bed system packed with more than one type of biomass might be a meaningful way.

Mushrooms have been proved to be an effective biosorbent for the removal of heavy metals.[14-16] Compared with plants, mushrooms grow rapidly and have high biosorption capacity; nevertheless, as in the case of microorganisms, mushrooms are macro in size and tough in texture, which conduce to their development as biosorbents without the need for immobilization or deployment of sophisticated reactor configuration.[15, 17] Our previous work has exhibited the ability of *Agaricus bisporus* to adsorb Pb(II) and other metals in a continuous column process;[18] Whereas, *Pleurotus cornucopiae* showed a better ability of copper.[19] On the other hand, *A. bisporus* has better mechanical property; where *P. cornucopiae* are cheaper and more easily available, as Jintang County, known as “the hometown of Chinese *P. cornucopiae*”, is located in the suburbs of Chengdu, Sichuan Province. So the mixed mushrooms might achieve a better overall performance during the treatment of multi-metal wastewater in packed bed column.

To the best of our knowledge, no similar report about mushrooms applied to pilot-scale wastewater treatment is available up to now. The present study examines the biosorption capacities of *A. bisporus* and *P. cornucopiae* for heavy metal removal from industrial effluent in a two-stage continuous system at small-sized pilot-scale, respectively. Then, the application of the mixed biosorbents on metal removal in the two-stage system was also tested. Prior to the packed bed experiments, the biomass was pretreated with three modifiers. Bohart–Adams and Thomas models were utilized to analyze the breakthrough curves obtained from column I. The reusability of the system was performed by carrying out three cycles of biosorption and desorption. The industrial application was also discussed.

2. Methods

2.1. Biosorbent materials and chemicals

A. bisporus and *P. cornucopiae*, collected from mushroom production bases in the suburbs of Chengdu (Sichuan), were washed with ultrapure water, followed by being dried at 50℃ for two days. After being ground with a pulverizing mill (Xulang, HK-230), *A. bisporus* was sieved to pass through 10/40 mesh screen to obtain 0.45-2.0 mm granules; while *P. cornucopiae* passed through 5/10/40 mesh screen to obtain granules with particle sizes between 0.45 and 4.0 mm, among which around 70% were in a particle size between 0.45 to 2.0 mm.

All chemicals and reagents (Kelong Chemical Reagent Factory, Sichuan) utilized throughout this study were of analytical grade.

2.2 Industrial wastewater

The industrial wastewater was taken from a metal manufacturing factory located in the suburbs of Chengdu, China. The concentration of heavy metals (copper, nickel, zinc, lead, and cadmium) was analyzed using a flame Atomic Absorption Spectrometer (AAS; VARIAN, SpectrAA-220Fs). The pH value was measured by a pH meter (pHS-25), calibrated with buffers of pH 4.00, 6.86 and 9.18. The pH of wastewater was adjusted around 6.0 before the experiments. The characteristics of industrial wastewater and their discharge standard according to GB 21900-2008 are given in Table 1.

2.3. Preparation of modified biosorbents

Three modifiers (sodium hydroxide (NaOH), acetic acid, ethylene diamine tetraacetic acid (EDTA)) were applied to find out the optimal one. The modifications were carried out following the method in our previous research,[18] and the resulting biomass was filtered, washed, and dried. 0.1 g raw or modified biomass was put into 250 mL Erlenmeyer flasks with 100 mL industrial wastewater in a shaker incubator (SUKUN, SKY211B) at 120 rpm for 5h. The biosorption capacity (mg g^{-1}), was calculated by the concentration before and after biosorption.

A Scanning Electron Microscopy (SEM) (JSM-5900LV, Japan) was introduced to observe the surface morphology features of raw and modified biomass. A Fourier Transform Infrared (FT-IR) spectrometer (NEXUS-650, America) was used to analyze the main functional groups on the surface. The surface area of the biosorbent was measured by Brunauer–Emmett–Teller (BET) method (Micromeritics ASAP-2020, America) using nitrogen as the adsorbate.

2.4. Experimental setup

The small-sized pilot system was made up of two biosorbent columns, pump, flowmeter and PVC pipes. The two PP plastic columns (8.0 cm diameter and 80 cm length for each) packed with biosorbent giving a bed depth of 45 cm were employed in series. Fig. 1 shows the schematic of the two-stage continuous system. Table 2 lists the operational parameters of pilot plant. The bed system was packed with *A. bisporus* (defined as Run 1); *P. cornucopiae* (defined as Run 2); *A. bisporus* and *P. cornucopiae* (defined as Run 3), respectively. The column I, and column II were defined as the column of the two-stage bed columns closing to the inlet and outlet, respectively.

Before being packed in bed column, the modified biomass should be soaked and swelled. Considering the requirement of industrial production, the modification was merged into the procedure of soak. The biomass was soaked in 0.5% optimal modifier solution for 12 h in a basin, stirring several times during the period, followed by being packed in the biosorbent columns between a lay of a sieve at the bottom, and a lay of glass wool at the top. Besides, a layer of glass beads was placed at the top to provide a uniform inlet flow. 2.4L ultrapure water was passed through the column system at the flow rate of 40mL min^{-1} to remove modifier, color and trapped air from the beds.

2.5. Experimental procedure

At room temperature (298 K), continuous operations were conducted by pumping the industrial wastewater in a down-flow mode using a peristaltic pump at a desired flow rate of 40 mL min^{-1} . The flow rate was monitored regularly and adjusted when required. The effluent samples were collected at definite time intervals for all the experiments. The operation of the packed bed system was stopped when the outflowing concentration in column II consecutively exceeded the maximum permissible concentration according to the National Standards. The metal concentrations were measured using AAS after biosorption. All experiments were carried out in duplicate, and the results reported were the mean values.

After the biosorption stopped, the metal-loaded columns were regenerated with 3 L of 0.1M HNO_3 at a flow rate of 30 mL min^{-1}. Then the biosorbent-bed was washed with ultrapure water, and the regenerated bed was reused in another cycle.

2.6 Calculations

The Removal efficiency(%) can be calculated based on the inlet and the outlet effluent concentrations as follows:[20]

$$\text{Removal}(\%) = \frac{(C_{in} - C_{out})}{C_{in}} \cdot 100 \quad (1)$$

where C_{in} (mg/L) and C_{out} (mg/L) are the influent and outlet effluent metal concentrations, respectively.

The biosorption capacity of the target metal species was determined by the concentration before and after absorption:

$$\text{q} = \frac{t \cdot Q \cdot (C_{in} - C_{out})}{m} \quad (2)$$

where t is the treatment time (h), Q is the flow rate (L h^{-1}), m is the total mass of the biosorbent in the column (g).

2.7 Theoretical models

The Bohart-Adams model was frequently applied for modeling the breakthrough curves for metal ions' sorption.[21, 22] This model is used for the interpretation of the initial part of the breakthrough curve, and the mathematical expression of the model is as follows:

$$\ln\frac{C_t}{C_i} = K_{BA}C_i t - K_{BA}N_0\frac{Z}{\upsilon} \quad (3)$$

Where K_{BA}, N_0, υ, Z were kinetic constant(L mg-1 h-1), biosorption capacity(mg L-1), linear flow velocity (cm h-1), bed height (cm), respectively.

The Thomas model [23] was frequently applied for describing the column performance and predicting the breakthrough curve of metal sorption. This model assumes that the adsorption process follows Langmuir kinetics of adsorption–

desorption, and obeys second-order reversible reaction kinetics.[2, 24] The expression is as follows:[25]

$$\ln\left(\frac{C_i}{C_t}-1\right)=\frac{K_T\cdot q_0\cdot m}{F}-\frac{K_T\cdot C_i\cdot V_{eff}}{F} \quad (4)$$

where K_T, q_0, F were rate constant (L mg^{-1} h^{-1}), metal uptake capacity (mg g^{-1}), flow rate (L h^{-1}), respectively.

3. Results and discussion

3.1 Effect of modification

Biosorption of heavy metals (copper, cadmium, lead, nickel and zinc) by raw and modified mushrooms (*A. bisporus* and *P. cornucopiae*) is presented in Table 3. Modified *A. bisporus* enhanced 28.22% - 43.55% compared to raw biomass for total metal uptake. NaOH-modified *A. bisporus* showed the best performance with a total sorption capacity of 76.8 mg g^{-1}. NaOH increased swelling, simultaneously dissolved some components and exposed active sites, to facilitate the sorption of metal.[2] Modified *P. cornucopiae* obtained the same observations as above, which increased 41.44% - 68.17% for total metal uptake. *P. cornucopiae* modified with acetic acid, and NaOH performed similarly with the capacity of around 56 mg g^{-1}. NaOH or acetic acid modified *P. cornucopiae* showed the higher biosorption capacity on nickel and zinc uptake than NaOH-modified *A. bisporus*, despite the lower total metal uptake. These results suggested the preferences of the sorption on different metals among the two biosorbents. Relative research manifested that treatment with acetic acid resulted in the exposure of buried amino groups on the surface of biosorbent, forming ester carbonyl and acylamino.[26] Considering the operability, NaOH was chosen to be the modifier for the two biomass in the later experiments.

Besides, the mass loss of biosorbents was also invested. The weight loss of *A. bisporus* was 15.1% - 16.8% during NaOH modification; *P. cornucopiae* obtained the same observations as above with the weight loss of 30.5% - 34.2%. Generally speaking, the mass loss of *P. cornucopiae* was higher than that of *A. bisporus* during modification. Taking into account of the weight loss of biomass, chemical pretreatment could still improve the biosorption capacity. Furthermore, modifiers were able to reduce the organic substances discharge. In consequence, the low-cost chemical pretreatment on biomass had great significance to biosorbent.

Our previous study[18] has revealed the characterization information of raw and NaOH modified *A. bisporus* (SEM, FT-IR, specific surface area). The surface morphology of unmodified and NaOH modified *P. cornucopiae* revealed by SEM are shown in Fig. 2. After modification, the biosorbent was characterized by irregular and porous surface. The FT-IR spectra was depicted in Fig. 3. The peak at 3358 cm^{-1}, 2929 cm^{-1}, 1653 cm^{-1}, 618 cm^{-1} represented -OH group, C-H stretching, $-NH_2$ group, C-N-C scissoring, respectively.[10,16] The changes of peaks suggested those functional groups were involved throughout the process in modification. NaOH modified *P. cornucopiae* had a specific surface area of 1.43 $m^2\ g^{-1}$, according to the BET analysis.

3.2 Metal removal in *A. bisporus* columns

In Run 1, after the operation of about 15h, the amount of nickel was detected firstly in the effluent from column I, and then appeared a gradual increase. At about 45h of systems running, a significant increase in the nickel concentration in the treated effluent from column II was observed, and was 1.582 mg L^{-1}; at the next effluent sample, the concentration was up to 4.36 mg L^{-1}. Thus, the operation was stopped at the operation time of 50h. The outlet heavy metal (copper, nickel, zinc) concentration in the effluent from column I was plotted against the operation time, and the profile is shown in Fig. 4. The amount of lead and cadmium in effluent were very low, the concentration of lead in effluent from column I was around 0.1 mg L^{-1} at the operation time of 50h, while the cadmium was around 0.06 mg L^{-1}. At previously operation time, the concentration of lead and cadmium in effluent was much lower, thus, so the data of lead and cadmium were not shown in the figure. Approximately 120L wastewater was treated within the bed system packed with *A. bisporus*, after 50h of operation. The average concentration of copper, nickel, zinc, lead, and cadmium in effluent for this period from column II was 0.092, 0.48, 0.164, 0.06, and 0.031 mg L^{-1} respectively, which were all under the maximum permissible concentration. The performance of Run 1 listed in Table 4 showed that the removal efficiencies were over 92.4% for all heavy metals, and the total uptake of all the metals was 11.6 mg g^{-1}. The trace heavy metals remained in the resulting effluent indicated the superior performance of this packed bed system.

To make sure the amount of all heavy metals remaining in the treated effluent were limited in the maximum permissible concentration, the packed bed biosorption experiments were carried out until any metal reached a breakthrough concentration.[20, 27, 28] However, considering the potential problem or error, for example, caused by operation, in this study, the operation time was determined when this metal was detected exceeding the emission limit values succession twice.

In this study, the traces of heavy metal in the effluent from column I was always detected, especially nickel, zinc, and copper, although the concentrations were very low. The difficulty in the sorption of metals of combined state from industrial wastewater might lead to incomplete removal of metals.[29] The competition of various metals between themselves and with organics and other impurities existed in industrial effluent might also be expected to result in the inadequacy of heavy metal removal by the packed bed system.[30, 31] Similar observation was also reported by Cyr et al. [27] It seemed that biosorption in packed bed column could not remove all metals absolutely. However, compared with other methods in treating metal wastewater, biosorption is one of the most effective and economic one.[3]

3.3 Metal removal in *P. cornucopiae* columns

The effluent concentration profiles from column I in the two-stage system packed with *P. cornucopiae* are given in Fig. 5. The performances of this run are summarized at Table 4. At the operation of 45h and 50h, it was detected that the amount of cadmium remaining in the outlet effluent was 0.113, and 0.264 mg L^{-1}, respectively, which continuously exceeded the emission limit values. Meanwhile, the concentrations of other heavy metals in the effluent from column II were all below their discharge standard. So the operation was stopped at the time of 50h. In this run, approximately 120L industrial wastewater was treated, and the treated effluent reached the discharge standard (the average concentration of copper, nickel, zinc, lead, and cadmium was 0.035, 0.134, 0.112, 0.03, and 0.047 mg L^{-1}, respectively). At the 50th hour, i.e., the time the systems stopped running, the copper concentration in effluent from column I was barely detectable, and the amount of lead in the effluent from column I was roughly 0.01 mg L^{-1}. Considering the sensitivity and accuracy of the AAS, the data of copper and lead in effluent from column I was not presented in Fig. 5. The performance of Run 2 listed in Table 4 showed that the total metal uptake (9.60 mg g^{-1}) was lower than that from Run 1; nevertheless, the removal efficiencies from Run 2 were over 97.2% for all heavy metals, which was superior to Run 1. Besides, *P. cornucopiae* had another advantage of lower cost than *A. bisporus.* In total, these two biosorbents showed each merits during each runs.

In general, the uptake of metals by biosorbent (*A. bisporus* and *P. cornucopiae*) from industrial effluents seemed much lower than in batch experiment or that from synthetic water.[15, 18] Particle size played a crucial role, since when the particle size increased, the vacant sites and the surface area available decreased, resulting in the decrease in the time for saturation.[31] However, in large-scale wastewater treatment, the larger particle size of biosorbent at packed bed column was inevitable to guarantee the maneuverability of biosorbent. The complicated composition of industrial wastewater might be another important factor. Organics and other impurities existed in industrial effluent competed with metals on the adsorption site, leading to the lower uptake by biosorbent.[13] The limitation in adsorption selectivity of biomass might be the third cause.[3] Some hard metals, such as K^+, Na^+, are usually nontoxic, and could compete for sites with metals.[1]

3.4 Packed bed column modelling

In this study, Bohart-Adams and Thomas models were applied to test the accuracy and reliability of experimental data, as well as to calculate kinetic constants of the adsorption process. The values of characteristic parameters are summarized in Table 5. Generally speaking, Thomas model could provide better fits for the experimental data obtained from column I, compared with Bohart-Adams model. Nevertheless, two correlation coeffcients (R^2) of Bohart-Adams and Thomas models (copper in Run 1 and Cadmium in Run 2) were all a bit low. Relatively coarse operational procedure at the stage of pilot-scale and the complexity of the component in the industrial effluent might be the principal cause of the relatively low R^2.

Despite some researchers have developed mathematical models to study competitive adsorption of multi-component mixtures in packed bed.[32] Most studies modeling of the breakthrough curve mainly focused on the experimental data obtained from single metal solution.[10, 22, 24] The traditional models seemed unfit for multi-component competition adsorption for the reason of the low correlation coefficients; these new models were complex, and the application scope might be narrow. Thus, little study reported on the modeling of the breakthrough curve of multi-metal system or pilot-scale system. Based on current data, a negative correlation between the Thomas rate constant (K_T) and uptake capacity (q_0) was observed. Similar observation was reported by Bulgariu and Bulgariu.[21]

3.5 Metal removal in *A. bisporus* and *P. cornucopiae* columns

Based on the two-stage continuous system study of packing the same biosorbent, the column I of the small-sized pilot plant was packed with *A. bisporus*, while column II was packed with *P. cornucopiae* (Run 3). The performances of Run 3 are presented in Table 6. At about 60-65h of operation, nickel existing in the effluent from column II was found upto breakthrough concentration of 0.5 mg L^{-1}, approximately 156L of water was treated by this mixed-biosorbent packed bed system. The heavy metals in the treated effluents were all in the emission standard (the outlet effluent concentration of copper, nickel, zinc, lead, and cadmium were 0.062, 0.308, 0.186, 0.05, and 0.039 mg L^{-1} respectively), and the removal efficiencies were above 95.1% for all metals. Much more wastewater was treated by this system, compared with Run 1 (120L) and Run 2 (120L). The total metal uptake was 13.64 mg g^{-1}, which was taller than Run 1 (11.62 mg g^{-1}) and Run 2 (9.60 mg g^{-1}).

It was a novel finding that the total metal uptake increased when the mixture of biosorbents was applied to the treatment of multi-metal effluent. The criteria selected for stopping the experiments might be the main incentive. The Preferences of the sorption on various metals among different sorbents might be the major reason. Our previous study and many other reports also mentioned the preference of mushroom for metals.[14, 17] The profile of breakthrough curves obtained from packed bed column studies was the shape of an "S".[5, 12, 21, 31] The low concentration of metals in the outlet effluent when the operation stopped indicated the vacant of some adsorption sites. Once the mixed biosorbents were applied, the metals could make full use of those adsorption sites, thus the total metal uptake of biosorbents increased.

3.6 Desorption and regeneration

The usefulness of a biosorbent depends not only on its biosorption capacity, but also on the efficient regeneration and reuse.[4] The Sorption – Desorption parameters listed in Table 7 showed that the desorption of *A. bisporus* was 85.29% after three cycles, while *P. cornucopiae* was approximately 80%. The biomass in the packed bed system can undergo cyclic biosorption-desorption cycles without additional operations, such as, centrifugation, filtration, and packing. In addition, the biomass utilized in this study has been proved to have high efficiencies of desorption.[18, 33] Therefore, the requirement of fresh biosorbent is reduced, making the biosorption process more sustainable and cost effective. The exhausted biosorbents for the present system were put into a biogas digester for fermentation after being exhausted, and then the biogas residues were disposed of via landfill, while the biogas slurry was disposed of precipitation and flocculation for metal's extraction.

3.7 Implication for industrial application

The present study showed a good biosorption performance in a packed bed system containing multiple biosorbents. Thus, for making the utmost use of biosorbents and removing metals more effectively; it is vital to use multiple columns consisting more than one type of biomass to treat industrial wastewater containing various pollutants.[4, 34] Numerous studies indicate that a longer bed height may lead to a better performance and larger treated volume.[35, 36] Therefore, batteries of multiple columns can be introduced to optimize the performance during the process. Scale-up of the biosorption process can be also accomplished by using larger diameter columns or using multiple columns that work in parallel.

4. Conclusions

NaOH was introduced to modify *A. bisporus* and *P. cornucopiae*, and SEM and FT-IR have been used to analyze the surface characterization of the biosorbents. *A. bisporus* and *P. cornucopiae* showed each merits during each runs, and resulted in good quality effluents. Run 1 showed higher metal uptake (11.6 mg g^{-1}), whereas, Run 2 showed superior removal efficiency (over 97.2% for all metals). Run 3 which packed different biosorbent demonstrated best performance with a treated volume of 156 L. More than 95.1% heavy metals were removed, and the treated effluent met the regulatory discharge standards. The present study indicated that the two-stage continuous system packed with different biosorbents could effectively remove various metals from industrial wastewater.

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Figure Captions

Fig. 1 Schematic of the two-stage continuous system.

Fig. 2 SEM of *P. cornucopiae* (A) and modified *P. cornucopiae* (B)

Fig. 3 FTIR spectrums of *P. cornucopiae* (A) and modified *P. cornucopiae* (B)

Fig. 4 Breakthrough profile of nickel, zinc and copper in the effluent from column Ⅰ in the system packing with *A. bisporus.*

Fig. 5 Breakthrough profile of cadmium, nickel, zinc in the effluent from column Ⅰ in the system packing with *P. cornucopiae.*

Table 1
Characteristics of industrial wastewater.

Parameters	Values	Standard
Lead (mg L^{-1})	27.75	0.2
Cadmium (mg L^{-1})	21.125	0.05
Nickel (mg L^{-1})	6.300	0.5
Copper (mg L^{-1})	2.800	0.5
Zinc (mg L^{-1})	3.933	1.5
pH	4.9	6.0-9.0
Conductivity (μS cm^{-1})	727	-
COD	682	500
BOD	538	300

Table 2

Small-sized pilot plant operational parameters.

Parameter	Column-*A*	Column-*P*
Column diameter (cm)	8.0	8.0
Bed height (cm)	45	45
Biosorbent particle size(mm)	0.45-2.0	0.45-4.0
Biosorbent mass(g)	316	385
Flow rate (mL min^{-1})	40	40
Column Volume(cm^3)	2262	2262

Notations: Column-*A*: the bed column packed with *A. bisporus*; Column-*P*: the bed column packed with *P. cornucopiae.*

Table 3
Effect of different modifiers on heavy metals biosorption capacity (mg g^{-1}) by mushrooms.

		Copper	Cadmium	Lead	Nickel	Zinc	Total
A. bisporus	Native	6.0	18.8	26.1	1.5	1.1	53.5
	Acetic acid	7.9	24.6	33.2	1.7	1.2	68.6
	NaOH	9.2	26.3	37.7	2.1	1.5	76.8
	EDTA	8.5	24.3	33.7	1.8	1.6	69.9
P. cornucopiae	Native	3.9	7.6	18.6	1.9	1.3	33.3
	Acetic acid	6.4	13.2	30.5	3.0	2.7	55.8
	NaOH	6.9	11.4	32.0	3.4	2.3	56
	EDTA	5.0	10.3	27.2	2.7	1.9	47.1

Table 4

The performance of different runs.

	Run 1				Run2			
	Time (h)	Volume (L)	Uptake (mg g^{-1})	Removal (%)	Time (h)	Volume (L)	Uptake (mg g^{-1})	Removal (%)
Copper	50	120	0.51	96.7	50	120	0.43	98.8
Nickel	50	120	1.11	92.4	50	120	0.96	97.9
Zinc	50	120	0.728	95.9	50	120	0.61	97.2
Lead	50	120	5.26	99.8	50	120	4.32	99.9
Cadmium	50	120	4.01	99.9	50	120	3.28	99.8

Table 5

Parameters of Bohart-Adams and Thomas models for the sorption of metal ions by pilot-scale system.

	Metal	Bohart-Adams			Thomas		
		K_{BA}	N_0	R^2	K_T	q_0	R^2
Run1	Ni	0.0753	159.69	0.993	0.0764	1.13	0.990
	Zn	0.0984	141.44	0.988	0.1002	1.00	0.992
	Cu	0.0039	762.67	0.788	0.0042	4.9	0.818
Run2	Cd	0.0075	899.77	0.735	0.008	6.09	0.754
	Ni	0.0694	257.07	0.966	0.070	1.83	0.998
	Zn	0.0974	173.46	0.976	0.101	1.22	0.982

Notations: K_{BA}, Bohart-Adams rate constant (L mg^{-1} h^{-1}); N_0, saturation concentration (mg l^{-1}); K_T, Thomas rate constant (L mg^{-1} h^{-1}); q_0, equilibrium metal sorption (mg g^{-1});R^2, correlation coefficient.

Table 6
The performance of the bed column system packed with *A. bisporus* and *P. cornucopiae.*

Metal	Outlet effluent concentration ($mg\ L^{-1}$)	Uptake ($mg\ g^{-1}$)	Removal (%)
Copper	0.062	0.61	97.8
Nickel	0.308	1.33	95.1
Zinc	0.186	0.85	95.4
Lead	0.05	6.16	99.8
Cadmium	0.039	4.69	99.8

Table 7

Sorption – Desorption parameters.

Cycle No.	*A. bisporus* (mg g^{-1})				*P. cornucopiae* (mg g^{-1})			
	Cd		Pb		Cd		Pb	
	Sorption	Desorption	Sorption	Desorption	Sorption	Desorption	Sorption	Desorption
1	4.01	3.89	5.26	5.04	3.28	3.07	4.32	4.05
2	3.75	3.59	4.99	4.61	3.03	2.79	3.97	3.53
3	3.42	3.33	4.58	4.36	2.61	2.45	3.44	3.28

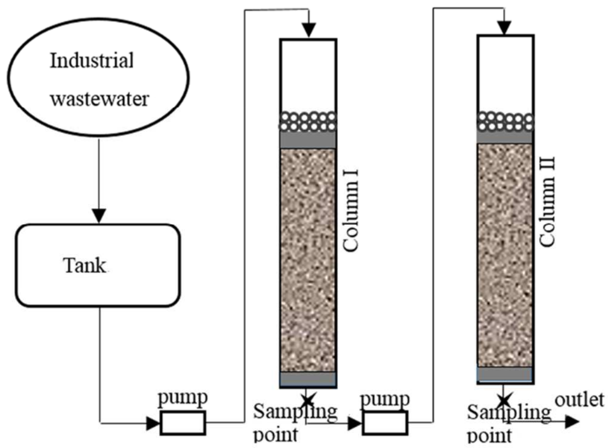
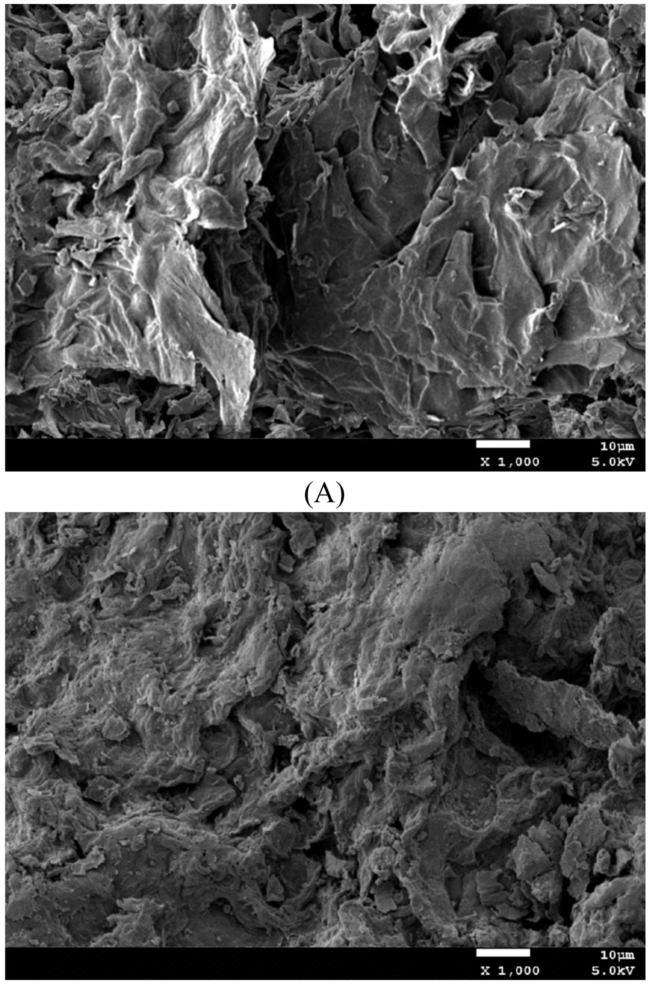


Fig. 1 Schematic of the two-stage continuous system.



(A)

(B)

Fig. 2 SEM of *P. cornucopiae* (A) and modified *P. cornucopiae* (B)

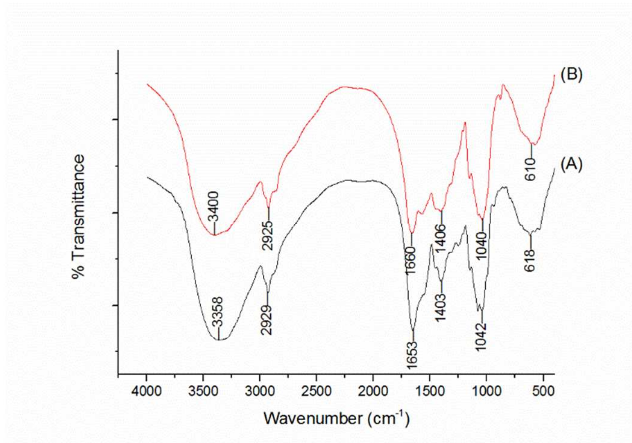


Fig. 3 FTIR spectrums of *P. cornucopiae* (A) and modified *P. cornucopiae* (B)

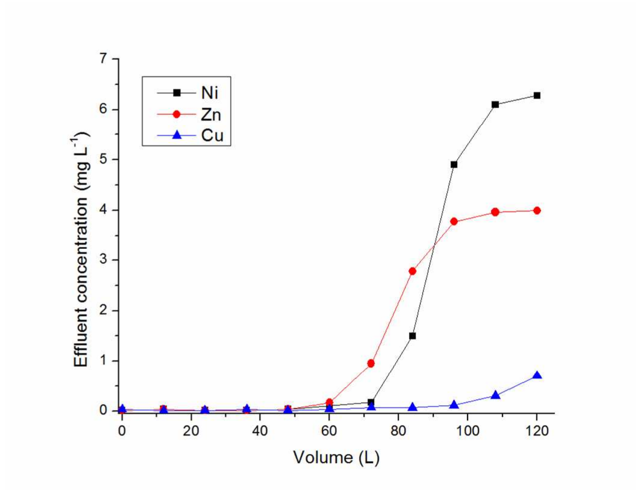


Fig. 4 Breakthrough profile of nickel, zinc and copper in the effluent from column Ⅰ in the system packing with *A. bisporus.*

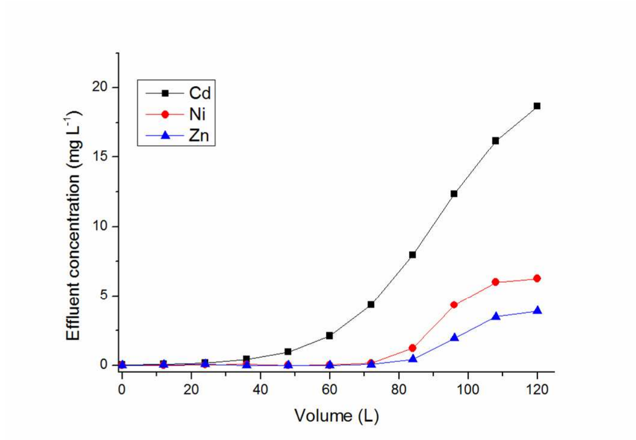


Fig. 5 Breakthrough profile of cadmium, nickel, zinc in the effluent from column Ⅰ in the system packing with *P. cornucopiae.*