



Column Studies on Removal of Ag(I) from Electroplating Wastewater by Macrofungus *Pleurotus platypus*: Use of Modelling and Response Surface Methodology

Devlina Das, Vimala R. and Nilanjana Das

Environmental Biotechnology Division, School of Biosciences and Technology, VIT University, Vellore-632 014, T.N., India

Nat. Env. & Poll. Tech.

Website: www.neptjournal.com

Received: 28-1-2013

Accepted: 19-2-2013

Key Words:

Ag(I)

Biosorption

Pleurotus platypus

Electroplating wastewater

Packed bed column

ABSTRACT

This study described the removal of Ag(I) from wastewater using macrofungus *Pleurotus platypus* in a packed bed column. The effect of operating parameters such as bed height, flow rate and initial metal concentration were investigated on removal of Ag(I) under optimized condition. The breakthrough curve profile signified that the breakthrough time and exhaustion time increased with an increase in bed height and a decrease in flow rate and initial metal concentration. The data were supported by 3D mesh diagrams and perturbation plots obtained from 2D factorial design. The column data were analysed using four models viz., BDST model, Empirical model, Thomas model and Yan model. The BDST model was found to be the best to fit the breakthrough curves at experimental conditions. The column was regenerated using 0.01 M HCl solution and sorption-desorption studies were carried out for three cycles. The obtained results implied that *P. platypus* may serve as suitable adsorbent material for the removal of Ag(I) from wastewater.

INTRODUCTION

Silver is a metal of economic interest and widely used in various industries viz., electroplating, photographic, imaging industries, etc. for many years. Human exposure to silver and silver compounds can occur orally, dermally, or by inhalation. Numerous diseases and disorders in organisms are reported to occur due to accumulation of silver ions through the food chain of living organisms (Schmahl & Steinhoff 1960, Rosenman et al. 1979, Rosenman et al. 1987). Accidental ingestion of silver nitrate may cause abdominal pain, diarrhoea, vomiting, discoloration of skin, damage of the gastrointestinal tract, respiratory irritation, shock, convulsions and death in human (US-EPA 1985). Allergic responses have also been noted due to dermal contact with silver (ATSDR 1990). Therefore, the effective removal of Ag(I) from wastewater was recommended (Wen et al. 2002, Mack et al. 2007).

Various treatment processes such as chemical precipitation, ion exchange, reductive exchange and electrolytic recovery are available for the removal of silver from wastewaters (Lambert & Murr 1968). Although the conventional methods can remove silver ions from the effluents, techno-economic considerations limit the wide scale application of these processes (Sonune & Grate 2004). Considerable attention has been paid to the development of a safe technology which can reduce heavy metal concentrations to environmentally acceptable levels at affordable cost (Crini 2005, Sud et al. 2008).

Biosorption, the most promising technology has been used for the removal and recovery of precious metal ions from aqueous solutions because of its high efficiency and favourable economics (Das 2010). This technology can utilize macrofungi, and of these, oyster mushroom (*Pleurotus platypus*) has already been identified for its good biosorption capacity for silver in our previous study (Das et al. 2010, Das & Das 2011). Fruit bodies of macrofungi can be used as biosorbents without the need for immobilization or sophisticated reactor configuration which is generally needed in case of microorganisms (Muraleedharan et al. 1994).

Most of the research involving biosorbents for metal removal is based on batch equilibrium studies which provide fundamental information about the effectiveness of metal sorbent system. However, these data may not be suitable for the continuous system where contact time is insufficient to attain the equilibrium (Zulfadhly et al. 2001). For a continuous process, a packed bed column is usually used and the effectiveness of a biomass can be evaluated from the breakthrough curve of the effluent concentration. A typical S-shaped breakthrough curve is usually observed (Chu 2004). In order to predict the breakthrough curve in adsorption process in a packed bed, various mathematical models have been used. As far as authors are aware, there is no report in the literature regarding the silver adsorption equilibria in column mode which is most important in understanding the biosorption process. Therefore, the objective of the present

study was to investigate the equilibria information through modelling and response surface methodology and evaluate the performance of macrofungus as potential biosorbent in column mode for wastewater treatment.

MATERIALS AND METHODS

Preparation of biosorbent: The biosorbent (fruit bodies of *Pleurotus platypus*) were purchased from the mushroom farm at Krishi Vigyan Kendra of Tamil Nadu Agricultural University at Virinjipuram, Vellore district, Tamil Nadu, India. They were washed thoroughly with deionised water, dried, pulverized and oven dried at 40°C for 24 h. Particles with 425–600 µm size were used for the experiment.

Preparation of stock solution: Stock solution (1000 mg/L) of Ag(I) was prepared by dissolving required quantity of AgNO₃ in deionized water. The solution was diluted to prepare the working solutions and pH of influent solution was adjusted to 6.0 with a pH meter (Systronics, Model-MK VI) by using 0.1 N HCl and/or 0.1 N NaOH.

Column experiments: Column studies were conducted in a glass column having internal diameter 3 cm and height 15 cm) packed with biosorbent *Pleurotus platypus*. An initial concentration of 300 mg/L Ag(I) was pumped through the column at a desired flow rate with a peristaltic pump (Rivotek™) and pH maintained at 6.0±0.3. The effect of parameters viz., inlet flow rate (1, 3, 5 mL/min), bed height (4, 8, 12 cm) and initial Ag(I) concentration (50–300 mg/L) were studied and analysed. The effluent samples were collected at regular time intervals and analysed for Ag(I) concentration using atomic absorption spectrophotometer (Varian AA-240, Australia).

The total amount of Ag(I) biosorbed in the column (M_{ad}) was calculated from the area above the breakthrough curve (outlet metal concentration versus time) which was further multiplied by the flow rate. Uptake capacity (Q) of the biomass was calculated by dividing the amount of Ag(I) biosorbed (M_{ad}) by the weight of the biosorbent (M). The total amount of metal ions sent to the column and total metal removal (%) was calculated following the standard procedure (Vimala et al. 2011, Vinodhini & Das 2011).

The amount of Ag(I) desorbed (M_d) was calculated from the area below the desorption curve (outlet Ag(I) concentration vs. time) which was further multiplied by the flow rate. The desorption efficiency was calculated using the following equation:

$$\text{Desorption efficiency (\%)} = \frac{M_d}{M_{ad}} \times 100$$

Modelling and analysis of column data: To analyse the dynamic removal of Ag(I) in column mode, breakthrough

curves (C_t/C_0 vs. time) were drawn and the data were evaluated with the help of various models viz., BDST model (Zambrano et al. 2010), Empirical model (Ruiz et al. 2001), Thomas model (Thomas 1948) and Yan model (Yan et al. 2001).

Statistical analysis: To study the effects of various parameters on a particular response is time consuming for multivariable system. Therefore, a statistical approach e.g., response surface methodology (RSM) is needed to solve this problem. The steps involved in RSM include, (1) Design experiments, (2) Response surface modelling through regression, and (3) Optimization.

The present study was carried out to investigate the effect of flow rate (mL/min) (designated as factor A), bed height (cm) (designated as factor B) and initial metal concentration (mg/L) (designated as Factor C) on breakthrough time (min). Factor A was varied over two main levels, -1 and +1 (1 and 5 mL/min) relative to the centre point denoted by 0 (3 mL/min), factor B was varied over the levels 4 cm (-1) and 12 cm (+1) relative to 8 cm (0), and factor C was varied over the levels 50 mg/L (-1) and 250 mg/L (+1) relative to 150 mg/L (0) respectively as shown in Table 1. Fourteen sets of experiments with 6 centre points were carried out in replicates with appropriate combinations of all the three factors in order to study the effect of each combination on breakthrough time of Ag(I) removal by *P. platypus*. For estimating the breakthrough time, statistical and graphical analyses were done by Design Expert software package (Version 8 Stat-ease Inc., Minneapolis, MN, USA). In order to evaluate the statistical significance of the model, coefficient of determination R^2 and F test analysis of variance (ANOVA) were used as predicted by the software. A large F value indicated that most of the variation in response could be explained by the regression equation (Das et al. 2010b). The significance of the statistical model was also determined by the associated p -value. P values less than 0.05 indicate the statistical significance of the model (Dash & Gummadi 2007). Range of predicted values at the design points are compared to the average prediction error using adequate precision. Model discrimination is indicated by ratio values greater than 4. The variation of data around the fitted model is well described by lack of fit F test.

Table 1: Experimental ranges and levels of independent variables.

Independent variables	Factor	Range and Level		
Flow rate (mL/min)	A	-1	0	+1
Bed height (cm)	B	1	3	5
Initial metal concentration(mg/L)	C	4	8	12
		50	150	250

Treatment of wastewater in column mode: Silver-plating wastewater collected from electroplating industry located at Coimbatore containing 250 mg/L Ag(I) was used in this experiment. pH of the wastewater was adjusted to 6.0 and treated in the column packed with the biosorbent *P. platypus* till the values reached the US-EPA standard (Ag: 0.1 mg/L). The treated samples collected from the exit were analysed for Ag(I) concentrations. The regeneration of the biosorbent was performed using 0.01 M HCl at the flow rate of 1 mL/min till the column reached exhaustion.

RESULTS AND DISCUSSION

Effect of bed height: In our previous study, the optimum pH and temperature were maintained at 6.0 and 20°C during biosorption of Ag(I) onto *P. platypus* in batch mode (Das et al. 2010a). Therefore, in the present study similar conditions were maintained in column mode for the adsorption of Ag(I). The effect of bed height on Ag(I) biosorption by *P. platypus* was investigated by varying the bed height from 4 to 12 cm maintaining the flow rate and inlet Ag(I) concentration at 1 mL/min and 50 mg/L, respectively. The breakthrough profile of Ag(I) biosorption at different bed heights for a given flow rate is shown in Fig. 1.

The uptake capacity of Ag(I) was found to be identical for different bed heights investigated (Table 2) due to the dependence of uptake capacity on the amount of sorbent available for sorption (Vijayaraghavan et al. 2005, Ghasemi et al. 2011). It was observed that the breakthrough time (t_b) and the exhaustion time (t_e) increased with the increase in bed height. High percentage of Ag(I) removal was noted at maximum bed height.

Effect of flow rate: The effect of flow rates on Ag(I) biosorption in packed bed column was investigated by varying the flow rate from 1 to 5 mL/min (Fig. 2). It was observed that an increase in flow rate resulted in a decrease in breakthrough and exhaustion times due to insufficient residence time of the metal ions in the column (Zambrano et al.

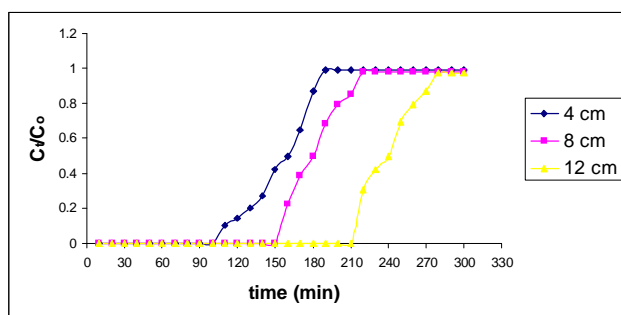


Fig. 1: Breakthrough curves for Ag(I) biosorption onto *P. platypus* at different bed heights (Initial Ag(I) concentration: 50 mg/L; Flow rate: 1ml/min; pH: 6; Temperature: 20°C).

Table 2: Column data and parameters obtained at different bed heights (Flow rate 1 mL/min; Inlet Ag(I) concentration: 50mg/L).

Bed height (cm)	t_b (min)	t_e (min)	M_{total} (mg)	M_{ad} (mg)	q (mg/g)	Percent removal of Ag(I)
4	100	170	9.5	7.66	22.53	80.62
8	150	210	11.0	9.02	23.12	81.99
12	210	280	16.5	14.0	23.42	85.30

Table 3: Column data and parameters obtained at different flow rates (Bed height: 12 cm; Metal concentration: 50mg/L).

Bed height (cm)	t_b (min)	t_e (min)	M_{total} (mg)	M_{ad} (mg)	q (mg/g)	Percent removal of Ag(I)
1	210	280	14.0	11.94	23.42	85.30
3	40	160	9.0	6.39	18.82	71.99
5	30	130	7.5	5.03	14.81	67.11

Table 4: Column data and parameters obtained at different initial metal concentrations (Bed height: 12 cm; Flow rate: 1 mL/min).

Bed height (cm)	t_b (min)	t_e (min)	M_{total} (mg)	M_{ad} (mg)	q (mg/g)	Percent removal of Ag(I)
50	210	280	14.0	11.94	23.42	85.30
75	200	270	21.0	17.20	33.73	81.92
100	180	260	26.0	20.59	40.37	79.19
150	150	240	36.0	28.34	55.56	78.71
200	140	200	40.0	30.31	59.43	75.78
259	80	180	45.0	33.33	65.35	74.07

Table 5: 2D Factorial design experimental run table of three factors along with experimental and predicted breakthrough time of Ag(I) removal by *P. platypus*.

Run	Factor A Flow rate (mL/min)	Factor B Bed height (cm)	Factor C Initial metal conc. (mg/L)	Response Breakthrough time (min)	Predicted R1
1	0	0	0	80+5.78	78.95
2	0	0	0	80+5.78	78.95
3	-1	1	-1	210+5.78	211.45
4	-1	-1	-1	150+11.54	153.95
5	0	0	0	80+5.78	78.95
6	1	1	-1	60+5.78	63.95
7	0	0	0	80+5.78	78.95
8	0	0	0	80+5.78	78.95
9	1	-1	1	40+5.78	41.45
10	0	0	0	80+0	78.95
11	1	-1	1	30+0	31.95
12	-1	-1	1	40+5.78	41.45
13	-1	1	1	20+5.78	21.45
14	-1	1	1	60+0	63.95

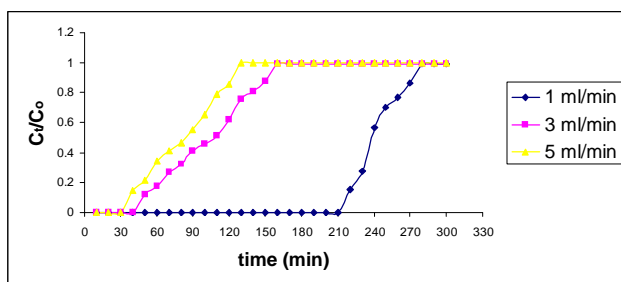


Fig. 2: Breakthrough curves for Ag(I) biosorption onto *P. platypus* at different flow rates (Initial Ag(I) concentration: 50 mg/L; Bed height: 12 cm; pH: 6; Temperature: 20°C).

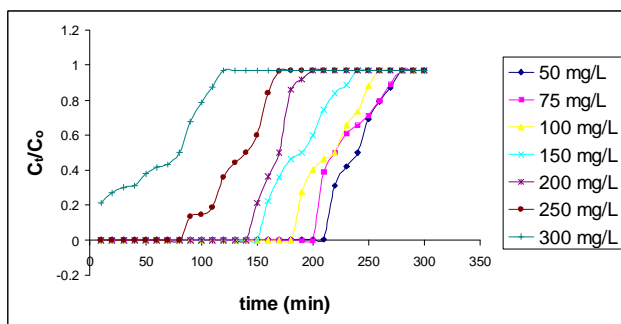


Fig. 3: Breakthrough curves for Ag(I) biosorption onto *P. platypus* at different Initial Ag(I) concentrations (Bed height: 12 cm; pH: 6; Temperature: 20°C).

2010, Muhamad et al. 2010). The breakthrough curves exhibited steep nature with a short mass transfer zone. The dependence of Ag(I) biosorption by *P. platypus* was confirmed by the values presented in Table 3.

Effect of initial metal concentration: The effect of initial metal concentration ranging from 50-300 mg/L on Ag(I) removal was instigated (Table 4). Breakthrough time was found to be maximum in case of lowest concentration (50 mg/L) and decreased with an increase in concentration up to 250 mg/L (Fig. 3). At 300 mg/L, breakthrough concentration (0.1 mg/L) was not reached and hence, a concentration up to 250 mg/L was taken into consideration for further experiments.

2D factorial design: The effect of flow rate (factor A), bed height (factor B) and initial metal concentration (factor C) on the breakthrough time of Ag(I) removal by *P. platypus* was analysed using 2D factorial design. The factors were varied over the levels -1, 0 and +1 as given in Table 1. The effect of the factors A, B and C on the breakthrough time is given by the following equation :

$$\text{Breakthrough Time} = 76.25 - 38.75A + 11.25B - 38.75C - 8.75AB + 26.25AC - 8.75BC \dots(1)$$

The experimental and predicted values of breakthrough time are presented in Table 5. The maximum predicted re-

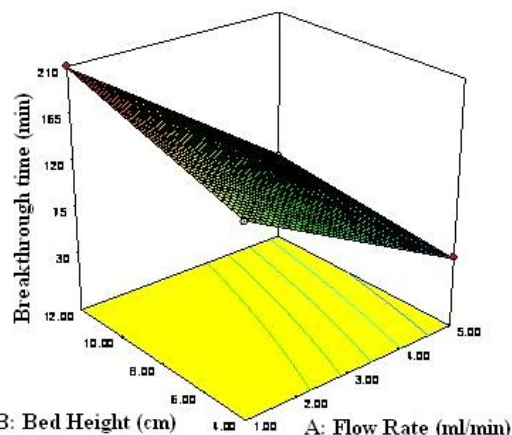


Fig. 4(a)

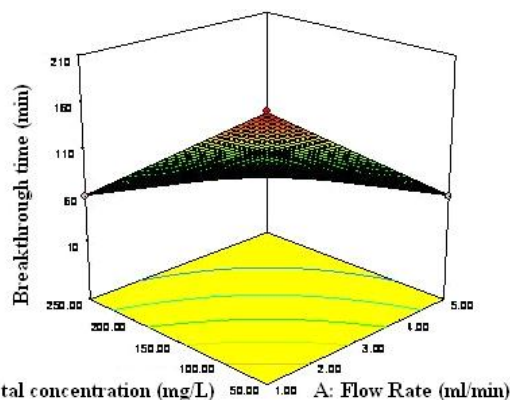


Fig. 4(b)

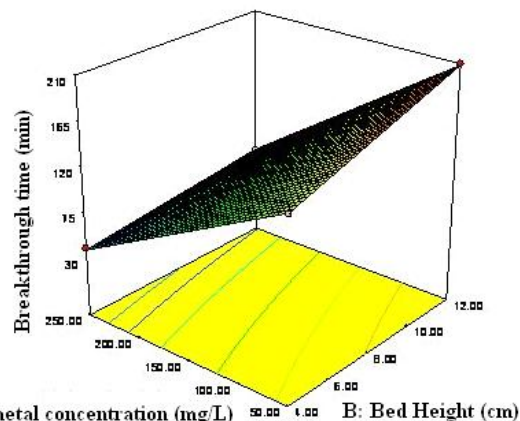


Fig. 4(c)

Fig. 4: (a) 3D mesh diagram showing (a) the effect of flow rate and bed height at initial metal concentration: 50 mg/L; (b) the effect of flow rate and initial metal concentration at bed height 12 cm; (c) the effect of bed height and initial metal concentration at flow rate: 1 mL/min) on breakthrough time.

Table 6: Analysis of variance (ANOVA) for the effect of flow rate, bed height and metal concentrations on breakthrough time for Ag(I) removal by *P. platypus*.

Source	Sum of squares	Mean square	d.f.	F Value	Probability (p)> F	
Model	31775	5295.833	6	2542	<0.0001	Significant
A-Flow rate	12012.5	12012.5	1	5766	<0.0001	
B-Bed height	1012.5	1012.5	1	486	<0.0001	
C-Initial	12012.5	12012.5	1	5766	<0.0001	
Metal Concentration						
AB	612.5	612.5	1	294	<0.0001	
AC	5512.5	5512.5	1	2646	<0.0001	
BC	612.5	612.5	1	194	<0.0001	
Curvature	0.000443	0.000443	1	1.673655	0.2433	Not significant
Residual	0.001588	0.000265	6			
Lack of fit	0.001588	0.001588	1			Not significant

R²: 0.999607; Pred. R²: 0.999214; Adequate precision : 174.14

Table 7: Bed depth service time model parameters for removal of Ag(I) on *P. platypus*.

Initial Ag(I) Conc.(mg/L)	N ₀ (mg/L)	K _a (mg/min)	Z ₀ (cm)	S	R ²
50	96.94	0.0011	7.11	14	0.999
75	145.41	0.0008	8.00	14	0.9964
100	176.25	0.0007	8.44	12	0.9989
150	211.5	0.0005	10.92	10	0.9962
200	227.76	0.0004	11.35	8	0.9901
250	276.91	0.0003	12.16	7	0.9900

sponse (211.45 min) was obtained at a combination of flow rate of 1mL/min, bed height of 12 cm and initial metal concentration of 50 mg/L which was found to be quite close to the experimental value of 210 min. *F*-test ANOVA was used to determine the significance of the model (Table 6). In the present case, linear effect of A(p<0.0001), B(p<0.0001), C(p<0.0001) and the interaction effect of AB(p<0.0001), AC(p<0.0001) and BC(p<0.0001) were found to be significant. As shown in Table 7, a high *F*-value of 2542 for breakthrough time was predicted by the software, R² value 0.9996 and an adequate precision of 174.14 thereby indicated that the model was highly significant. All the experiments were performed in replicates and showed a very narrow error percentage of 7.25 % thereby confirming the model accuracy.

The 3D mesh diagrams as shown in Fig 4(a)-4(c) indicated that the breakthrough time increased with an increase in bed height due to an increase in bed adsorption capacity. It decreased with an increase in flow rate and initial metal concentration due to decrease in contact time of Ag(I) ions with biosorbent and inadequacy of Ag(I) binding sites (Hasan et al. 2010). The effect of all the three factors viz., flow rate, bed height and initial metal concentration on breakthrough time was confirmed through the perturbation plot as shown in Fig. 5. The plot confirmed that the breakthrough time was

directly proportional to the bed height which was indicated by upraise of the line B and found to be inversely proportional to the flow rate and initial metal concentration as indicated by the downfall of the lines A and C respectively.

Modelling of the data for Ag(I) biosorption by *P. platypus*:

The BDST plot of service time (tb) against bed height (Z) at Ag(I) concentrations ranging from 50-250 mg/L was found to be linear with a high correlation coefficient of 0.9999 thereby indicating the validity of the model (Table 7). The upraise of the trend line was maximum in case of 50 mg/L and decreased with an increase in concentration up to 250 mg/L indicating that the breakthrough time decreased with an increase in Ag(I) concentration due to the inadequacy of metal binding sites and increased metal precipitation (Das & Das 2011). This was further supported by the data on bed sorption capacity (N₀) and sorption rate (K_a) calculated from the slope and intercept of the graph as shown in Fig. 6. It was noted that the sorption capacity increased from 96.94 mg/L at 50 mg/L Ag(I) to 276.91 mg/L at 250 mg/L Ag(I) concentration due to availability of higher amount of Ag(I) ions. As shown in Table 7, the K_a values were found to decrease from 0.0011 L/mg/min at 50 mg/L Ag(I) concentration to 0.0003 L/mg per min at 250 mg/L which indicated that with an increase in concentration a longer bed is needed to avoid breakthrough (Ghasemi et al. 2011). The critical bed depth (Z₀) was found to increase from 7.11 cm to 12.16 cm whereas the time needed to exhaust a unit length of the column was found to decrease from 14 min to 7 min.

Empirical model showed quite a good fit with a maximum R² value of 0.9821 (Table 8). The bed volume (BV) was found to increase with an increase in bed height whereas it was found to decrease with an increase in Ag(I) concentration. The data showed a linear fit Fig. 7(a) and the parameters α and BV₀ were calculated from the slope and intercept respectively. It was noted that the BV₀ value increased with an increase in bed height which signified that the a higher

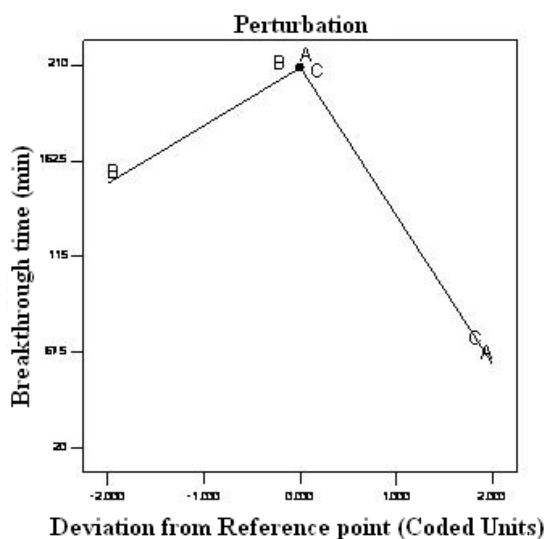


Fig. 5: Perturbation plot showing the effect of three factors viz., flow rate, bed height and initial metal concentration on breakthrough time (Flow rate: 1mL/min; Bed height:12 cm; Initial metal concentration: 50 mg/L).

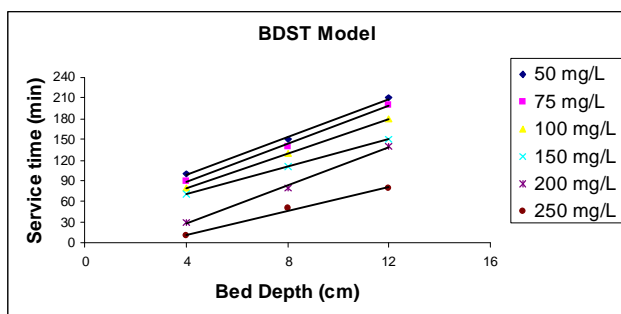


Fig. 6: Bed depth service time model at varying Ag(I) concentrations ranging from 5 mg/L to 250 mg/L.(Flow rate: 1mL/min).

volume of effluent could be treated due to an increased mass of biosorbent and increased number of Ag(I) binding sites.

The column data were analysed using Thomas model at different bed heights and Ag(I) concentrations as shown in Fig. 7(b). R^2 values were found to be less than BDST and Emperical models (Table 8). Low R^2 values indicated that adsorption of Ag(I) on *P. platypus* is limited by chemical reaction and not by the mass transfer at solid liquid interface (Araneda et al. 2011). The parameters viz., K_{Th} and q_{Th} associated with this model showed an increasing trend with an increase in bed height. Similar results were obtained by Ghasemi et al. (2011). As given in Table 8, the uptake values were found to increase from 97.9 mg/g at 50 mg/L to 490.23 mg/g at 250 mg/L of initial Ag(I) concentration and at a bed height of 12 cm, whereas the K_{Th} values were found to decrease from 0.029 to 0.006 L/mg/min respectively which

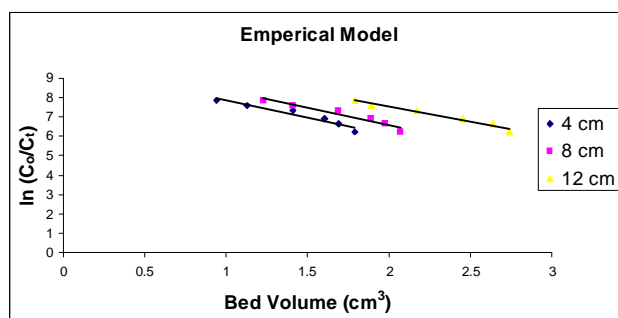


Fig. 7a

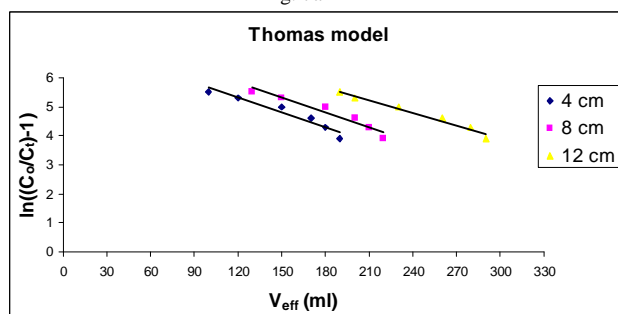


Fig. 7b

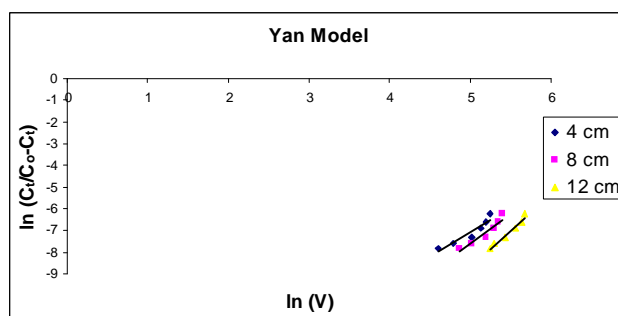


Fig. 7c

Fig. 7: Different models (a) Emperical model; (b) Thomas model; (c) Yan model at various bed heights and flow rate 1mL/min.

was attributed to the controlled rate step shifts from external to internal mass transfer limitations and increased metal precipitation (Ghasemi et al. 2011).

Yan model was found to analyse the column data as effectively as Thomas model since the R^2 values were quite similar in both the cases (Table 8). The uptake values were found to increase from 28.76 mg/L at 4 cm to 119.69 mg/g at 12cm due to an increase in adsorption sites. The rate of adsorption was found to increase with an increase in bed height, whereas it was inversely related to the metal concentration (Fig. 7c).

Treatment of electroplating wastewater in column mode: Application oriented study was conducted using biosorbent *P. platypus* which was employed for the treatment of

Table 8: Thomas, Emperical and Yan model parameters at different bed heights and initial Ag(I) concentrations (Flow rate: 1 mL/min).

Model	Bed height (cm)	Parameters	Initial Ag(I) concentration(mg/L)					
			50	75	100	150	200	250
Thomas Model	4	q_{TH} (mg/g)	79.5	119.2	158.9	238.4	317.9	397.4
		K_{TH} (L/mg/min) $R^2 - 0.9693$	0.025	0.016	0.012	0.008	0.006	0.004
	8	q_{TH} (mg/g)	82.8	124.3	165.5	248.7	330.8	413.7
		K_{TH} (L/mg/min) $R^2 - 0.9319$	0.027	0.018	0.013	0.009	0.006	0.005
	12	q_{TH} (mg/g)	97.9	146.9	195.9	293.9	391.9	490.2
		K_{TH} (L/mg/min) $R^2 - 9319$	0.029	0.019	0.015	0.009	0.007	0.006
4	$V(mL)BV\alpha = 1.77BV_0 = 5.43R^2 - 0.9643$	190	180	170	150	120	100	
		1.79	1.69	1.60	1.41	1.13	0.94	
Emperical Model	8	$V(mL)BV\alpha = 1.78BV_0 = 5.67R^2 - 0.9736$	220	210	200	180	150	130
			2.07	1.98	1.89	1.69	1.41	1.23
	12	$V(mL)BV\alpha = 1.79BV_0 = 6.45R^2 - 0.9821$	220	210	200	180	150	130
			2.74	2.64	2.45	2.17	1.89	1.79
Yan Model	4	q_i (mg/g) K_Y (L/mg/min) $R^2 - 0.9317$	28.8	43.4	57.5	86.8	113.8	157.2
			0.047	0.031	0.023	0.016	0.012	0.009
	8	q_i (mg/g) K_Y (L/mg/min) $R^2 - 0.9496$	69.9	108.4	139.8	196.4	279.6	373.9
			0.056	0.037	0.028	0.019	0.014	0.011
	12	q_i (mg/g) K_Y (L/mg/min) $R^2 - 0.9496$	119.7	185.9	239.4	335.2	478.7	522.6
			0.068	0.045	0.034	0.023	0.014	0.011

Table 9: Biosorption and elution process parameters for different biosorption-desorption cycles.

Cycle No.	t_b (min)	t_e (min)	q (mg/g)	Percent removal	Elution Efficiency (%)
1	80	180	65.35	74.07	85.50
2	70	180	64.21	73.26	84.81
3	60	170	61.33	65.91	84.30

wastewater containing silver in column mode and its reusability was assessed. As the regeneration cycles progressed, a decrease in breakthrough time and exhaustion time were noted. The removal percentage of Ag(I) was found to decrease in the successive cycles which could be attributed to the gradual deterioration of biomass on continuous usage (Table 9). It was noted that elution efficiency remained almost same in all the three desorption cycles.

CONCLUSION

The present study showed that macrofungus *P. platypus* could serve as potential biosorbent for the removal of Ag(I) from wastewater in column mode. The treated effluent reached the value of Ag(I) standard established by US-EPA. The study revealed the importance of bed height, flow rate and initial metal concentration on Ag(I) biosorption during column process. Among all the models tested, BDST model showed the best fit for the evaluation of column performance. Regeneration of biosorbent was performed using 0.01 M HCl solution and the biosorbent was efficiently reused for three cycles of sorption followed by desorption.

ACKNOWLEDGEMENTS

The authors thank VIT University for providing laboratory facilities.

REFERENCES

- Araneda, C., Basualto, C., Sapag, J., Tapia, C., Cotoras, D. and Valenzuela, F. 2011. Uptake of copper (II) ions from acidic aqueous solutions using a continuous column packed with microcapsules containing a β -hydroxyoximic compound. Chem. Eng. Res. Des., 89: 2761-2769.
- ATSDR (Agency for Toxic Substances and Disease Registry) 1990. Toxicological profile for silver. Prepared by Clement International Corporation, under Contract 205-88-0608. U.S. Public Health Service. ATSDR/TP-90-24.
- Chu, K.H. 2004. Improved fixed bed models for metal biosorption. Chem. Eng. J., 97: 233-239.
- Crini, G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog. Polym. Sci., 30: 38-70.
- Das, D. and Das, N. 2011. Response surface approach for the biosorption of Ag(I) by macrofungus *Pleurotus platypus*. Clean-Soil, Air, Water, 39: 157-161.
- Das, D., Das, N. and Mathew, L. 2010. Kinetics, equilibrium and thermodynamic studies on biosorption of Ag(I) from aqueous solution by macrofungus *Pleurotus platypus*. J. Hazard. Mater, 184: 765-774.
- Das, N. 2010. Recovery of precious metals through biosorption - An overview. Hydrometallurgy, 103: 180-189.
- Dash, S.S. and Gummadi, S.N. 2007. Optimization of physical parameters for biodegradation of caffeine by *Pseudomonas* sp.: A statistical approach. Am. J. Food Technol., 2: 21-29.
- Ghasemi, M., Keshtkar, A.R., Dabbagh, R. and Safdari, S.J. 2011. Biosorption of uranium (VI) from aqueous solutions by Ca-pretreated *Cystoseria indica* alga: Break curves studies and modeling. J. Hazard. Mater., 189: 141-149.
- Hasan, S.H., Srivastava, P. and Talat, M. 2010. Biosorption of lead using immobilized *Aeromonas hydrophila* biomass in up flow column

- system: Factorial design for process optimization. *J. Hazard. Mater.*, 177: 312-322.
- Lambert, J. and Murr, T.A. 1968. *Practical Chemistry*. 2nd Edition, Heinemann Educational Books, London.
- Mack, C., Wilhelmi, B., Duncan, J.R. and Burgess, J.E. 2007. Biosorption of precious metals. *Biotechnol. Adv.*, 25: 264-271.
- Muhamad, H., Doan, H. and Lohi, A. 2010. Batch and continuous fixed-bed column biosorption of Cd^{2+} and Cu^{2+} . *Chem. Eng. J.*, 158: 369-377.
- Muraleedharan, T.R., Venkobachar, C. and Leela, I. 1994. Investigations of fungal fruiting bodies as biosorbents for the removal of heavy metals from industrial processing streams. *Sep. Sci. Technol.*, 29: 1893-1903.
- Rosenman, K.D., Moss, A. and Kon, S. 1979. Argyria: Clinical applications of exposure to silver nitrate and silver oxide. *J. Occup. Med.*, 21: 430-435.
- Rosenman, K.D., Seixas, N. and Jacobs, I. 1987. Potential nephrotoxic effects of exposure to silver. *Br. J. Ind. Med.*, 44: 267-272.
- Ruiz, M., Sastre, A.M., Zikan, M.C. and Guibal, E. 2001. Palladium sorption on glutaraldehyde-crosslinked chitosan in fixed-bed systems. *J. Appl. Polym. Sci.*, 81: 153-165.
- Schmahl, D. and Steinhoff, D. 1960. Experimental carcinogenesis in rats with colloidal silver and gold solutions. *Z. Krebsforsch.*, 63: 586-591.
- Sonune, A. and Grate, R. 2004. Developments in wastewater treatment methods. *Desalination*, 167: 55-63.
- Sud, D., Mahajan, G. and Kaur, M.P. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review. *Bioresour. Technol.*, 99: 6017-6027.
- Thomas, C.H. 1948. Chromatography: A problem in kinetics. *Ann. N.Y. Acad. Sci.*, 49: 161-182.
- US-EPA (US Environmental Protection Agency) 1985. Drinking water Criteria Document for silver. Environmental Criteria and Assessment Office. Cincinnati, OH. ECAO-CIN-026, PB86-118288.
- Vijayaraghavan, K., Jegan, J., Palanivelu, K. and Velan, M. 2005. Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column. *Chemosphere*, 60: 419-426.
- Vimala, R., Charumathi, D. and Das, N. 2011. Packed bed column studies on Cd (II) removal from industrial wastewater by macrofungus *Pleurotus platypus*. *Desalination*, 275: 291-296.
- Vinodhini, V. and Das, N. 2010. Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust. *Desalination*, 264: 9-14.
- Wen, L. S., Santschi, P.H., Gill, G.A. and Tang, D. 2002. Silver concentration in Colorado, USA, watersheds using improved methodology. *Environ. Toxicol. Chem.*, 21: 2040-2051.
- Yan, G., Viraraghavan, T. and Chen, M. 2011. A new model for heavy metal removal in a biosorption column. *Adsorption Sci. Technol.*, 19: 25-43.
- Das, D., Charumathi, D. and Das, N. 2010b. Combined effects of sugarcane bagasse extract and synthetic dyes on the growth and bioaccumulation properties of *Pichia fermentans* MTCC 189. *J. Hazard Mater.*, 183: 497-505.
- Zambrano, J.B., Szygula, A., Ruiz, M., Sastre, A.M. and Guibal, E. 2010. Biosorption of reactive black 5 from aqueous solutions by chitosan: column studies. *J. Env. Management*, 91: 2669-2675.
- Zulfadhly, Z., Mashitah, M.D. and Bhatia, S. 2001. Heavy metal removal in fixed bed column by the macrofungus *Pycnoporus sanguineus*. *Environ. Pollut.*, 112: 463-470.

Nomenclature:

BV	Bed Volume passed through the column
BV ₀	Virtual volume of the solution for which the effluent concentration reaches a value of 0.5 C ₀
C ₀	Inlet metal ion concentration (mg/L)
F	Volumetric flow rate (mL/h)
K _a	BDST rate constant (L/mg/h)
K _{Th}	Thomas model rate constant (L/mg/min)
K _Y	Yan Model rate constant (L/mg/min)
M _{ad}	Metal mass adsorbed
M _{total}	Total amount of metal ions sent through the column
N ₀	BDST Bed sorption capacity (mg/L)
q _{Th}	Metal uptake predicted by Thomas model (mg/g)
q _i	Maximum metal uptake (mg/g)
q ₀	Equilibrium metal uptake (mg/g)
S	Time required to exhaust unit length of the column
σ	Standard deviation
τ	Time required for 50% adsorbate breakthrough (min)
t ₀	Time at which the effluent concentration is half the influent concentration (min)
t _b	Breakthrough time (min)
t _e	Exhaustion time (min)
v	Superficial flow velocity (mL/min)
V	Volume passed through the column (ml)
Z ₀	Critical bed depth (cm)