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HEAVY METALS REMOVAL USING RESIDUAL FUNGAL BIOMASS

C. BUMBAC*, E. PENA LEONTE, C. DUMITRESCU, I. GHITA, M. STEFANESCU

National Research and Development Institute for Industrial Ecology – ECOIND, 90–92 Panduri Street, Sector 5, 76 231 Bucharest, Romania
E-mail: ecoind@incdecoind.ro

Abstract. Heavy metal pollution has become one of the most serious environmental problems today. Biosorption, using biomaterials such as bacteria, fungi, yeast and algae, is regarded as a cost-effective biotechnology for the treatment of high volume and low concentration wastewaters containing heavy metal(s) in the order of 1 to 100 mg/l. This paper presents the results obtained in the biosorption experiments for metal ions removal from wastewater emphasising the influence of pH, contact time and initial concentration of heavy metals and biomass on the biosorption process. The experiments were conducted using active residual brewing yeast biomass for Pb and Cd biosorption and baker yeast biomass for Zn and Mn biosorption. Maximum removal efficiency for Pb and Cd were obtained after a contact time of 48 h, at pH 5, initial biomass concentration of 2 mg d.w./l, initial Pb concentration of 3.4 mg/l and, respectively, 7.5 mg/l initial Cd concentration. Maximum removal efficiency for Zn and Mn was obtained after a contact time of 48 h, at pH 5, and 4 mg d.w./l initial biomass concentration.

Keywords: heavy metals, wastewater, biosorption, fungal biomass.

AIMS AND BACKGROUND

With the rapid development of various industries, wastes containing metals are directly or indirectly discharged into the environment increasingly, especially in developing countries, having brought serious environmental pollution, and threatened biolife[1,2].

Conventional methods for removing metal ions from aqueous solution such as chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, etc. have been studied in details. However, chemical precipitation and electrochemical treatment are ineffective, especially when metal ion concentration in aqueous solution is as low as 1 to 100 mg/l, while ion exchange, membrane technologies and activated carbon adsorption processes are extremely expensive, especially when large amounts of water and wastewater containing low concentrations of heavy metals are treated, so they can not be used at large scale.

* For correspondence.

Alternative process for this task is biosorption, which utilises various natural materials of biological origin, which possesses metal sequestering properties and can decrease the concentration of heavy metal ions in solutions from ppb to ppt level. Biosorption, using biomaterials such as bacteria, fungi, yeast and algae, is regarded as a cost-effective biotechnology for the treatment of high volume and low concentration complex wastewaters containing heavy metal(s) in the order of 1 to 100 mg/l (Refs 3 and 4).

Some potential biomaterials with high metal-binding capacity have been identified in part. Among those biosorbents, there are marine algae (e.g. *Sargassum natans*), bacteria (e.g. *Bacillus subtillis*), fungi (e.g. *Rhizopus arrhizus*), yeast (e.g. *S. cerevisiae*) and waste microbial biomass from fermentation and food industry. For the economical reason, researchers have paid much attention to various by-products from fermentation industry, because they are produced in large quantities. *S. cerevisiae* is widely used in the food and beverage industry and it is a kind of solid waste[5,6]. Although *Sacharomyces* sp. is a mediocre biosorbent, it is still a concerned biomaterial in biosorption study because of its unique characteristics in comparison with other microorganisms for metal removal:

- is easy to cultivate at large scale;
- the biomass of *S. cerevisiae* can be obtained from various food and beverage industries;
- is generally regarded as safe;
- is an ideal model organism to identify the mechanism of biosorption in metal ion removal because it is the best known yeast biological model[6].

EXPERIMENTAL

The experiments for Pb and Cd biosorption were conducted in 100 ml flasks with 50 ml fluid volume and 2 g d.w./l residual active brewing yeast biomass.

The biomass was previously washed with distilled water and centrifuged at 3000 rpm – operation, which was repeated three times. The experiments were performed using municipal wastewater enriched with metal ions (Pb or Cd) and corrected to pH 5 – favourable for biosorbent (yeast) development. The concentrations tested were 1.4, 2.63, and 3.4 mg/l for Pb and 1, 2.63, 6.62 and 7.5 mg/l for Cd.

The flasks containing the synthetic solution and biosorbent were placed on a mechanical shaker at 200 rpm, at room temperature. The biosorption capacity of residual active brewing yeast biomass was evaluated by analysing the remaining concentration after 1, 3, 24 and 48 h, respectively.

Another set of experiments was set up using lyophilised biomass of baker yeast biomass for Zn and Mn biosorption from chemically pretreated mine water with residual heavy metal concentration of 6.84 mg/l Mn and 1.04 mg/l Zn. The

biosorption experiments on pretreated mine water were conducted in 100-ml shaking flasks in two variants at different biosorbent concentration, 2 and 4 g d.w./l, and different initial pH value of pretreated mine water, 7 and 5, respectively.

The biosorption capacity of baker yeast biomass was evaluated by analysing the remaining heavy metal concentration in the shaking flasks after 1, 3, 24 and 48 h for the variants at pH = 7 and after 1, 24, 48 and 69 h for the variants at pH = 5.

RESULTS AND DISCUSSION

Pb biosorption using brewery residual yeast (*2 g d.w./l*). The residual concentration of Pb after biosorption emphasised the followings aspects (Table 1, Figs 1 and 2):

– for the same initial concentration of Pb, residual metal concentrations decreased with the increasing of reaction time and removal efficiencies increased in the same way. The optimal contact time for 3 different initial lead concentrations, in order to be in the frame of discharging limit were: 3 h for 1.4 mg Pb/l (<0.01 mg residual Pb/l; η = 99.3%), 24 h for 2.63 mg Pb/l (0.14 mg residual Pb/l; η = 94.7%), 48 h for 3.4 mg Pb/l (0.16 mg residual Pb/l; η = 95.3%);

– for the same contact time, the residual concentration of Pb increased with initial metal concentrations. The biosorption process is able to remove lead contents ≤ 3.4 mg Pb/l, in case of 48-hour contact time, below discharging limit (0.2 mg Pb/l). In this initial concentration range the efficiencies for lead removal were between 20.6 (maximum initial concentration, 1-hour contact time) and 99.6 (2.63 mg Pb/l influent, 48-hour contact time).

Table 1. Pb biosorption using brewery residual yeast (2 g d.w./l)

Parameter		Contact time (h)				
		initial	1	3	24	48
A	Pb (mg/l)	1.4	0.73	0.01	0.01	0.01
	adsorption η (%)	–	47.9	99.3	99.3	99.3
B	Pb (mg/l)	2.63	1.71	0.33	0.14	0.01
	adsorption η (%)	–	35	87.5	94.7	99.6
C	Pb (mg/l)	3.4	2.7	2.56	1.16	0.16
	adsorption η (%)	–	20.6	24.7	65.9	95.3

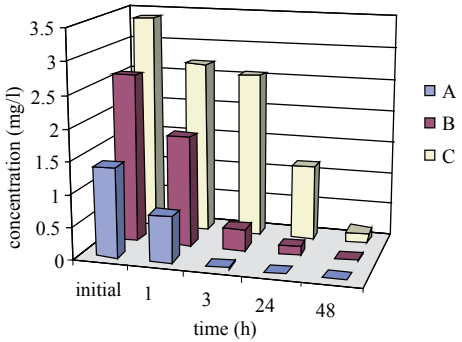

Fig. 1. Pb concentration variation in time

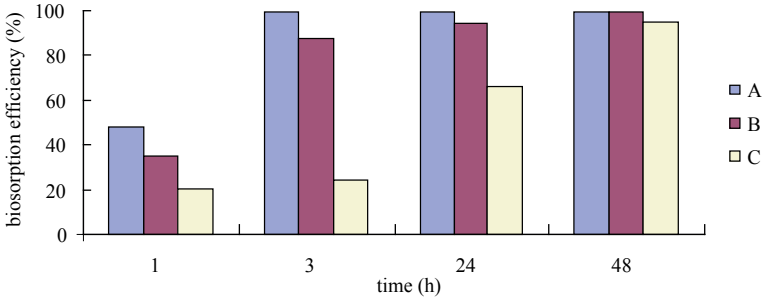

Fig. 2.Evolution in time of Pb biosorption removal efficiency

Cd biosorption using brewery residual yeast (*2 g d.w./l*). Biosorption of Cd revealed the following (Table 2, Figs 3 and 4):

– for the same initial concentration of Cd, residual metal concentration decreased with higher reaction time and removal efficiencies increased. The optimum contact time for 3 different initial cadmium concentrations was: 3 h for 1 mg Cd/l (0.12 mg residual Cd/l; η = 88%), 48 h for 2.63–7.5 mg Cd/l (0.12–0.16 mg residual Cd/l; η = 95.4–98%);

– for the same contact time, residual concentrations of Cd increased with influent concentrations. The biosorption process is able to remove cadmium concentrations $\leq$ 7.5 mg Cd/l in case of 48-hour contact time, below discharging limit (0.2 mg Cd/l). For tested initial cadmium concentrations, the removal efficiencies of cadmium were between 4.9 (maximum initial concentration, 1-hour contact time) – 97.9% (maximum initial concentration, 48-hour contact time).

Table 2. Cd biosorption using brewery residual yeast (2 g d.w./l)

Parameter		Contact time (h)				
		initial	1	3	24	48
A	Cd (mg/l)	1	0.45	0.12	0.1	0.07
	adsorption η (%)	–	55	88	90	93
B	Cd (mg/l)	2.63	2.46	0.32	0.25	0.12
	adsorption η (%)	–	6.5	87.8	90.5	95.4
C	Cd (mg/l)	6.62	4.74	0.35	0.18	0.13
	adsorption η (%)	–	28.4	94.7	97.3	98
D	Cd (mg/l)	7.5	7.13	0.45	0.27	0.16
	adsorption η (%)	–	4.9	94	96.4	97.9

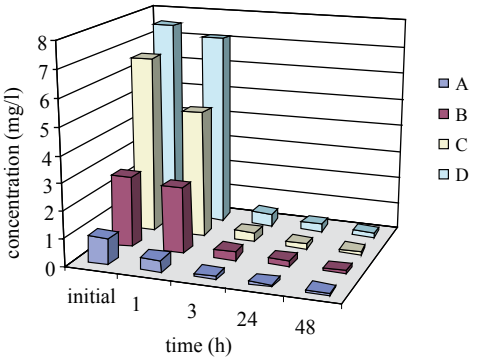

Fig. 3. Evolution in time of Cd concentration during biosorption experiments

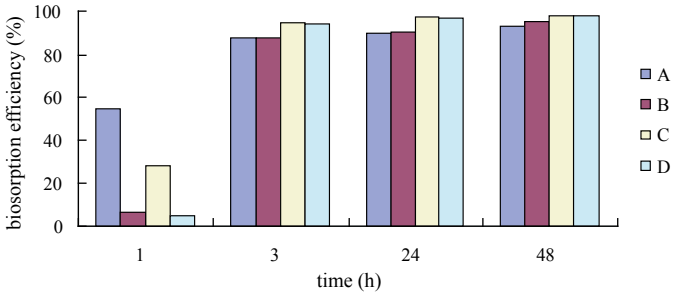

Fig. 4. Evolution in time of Cd biosorption removal efficiency

Zn and Mn biosorption using bakery yeast (*pH = 7; 2 or 4 g d.w./l biosorbent*). The results obtained from Zn and Mn biosorption experiments at pH 7 were disappointing, with maximum removal efficiencies of 23%, being unable to assure the quality requested by NTPA 001.

Zn and Mn biosorption using bakery yeast (*pH =5; 2 g d.w./l biosorbent*). The biosorption process in case of Zn and Cd emphasised the followings (Tables 3 and 4, Figs 5–8):

– for 2 g d.w./l biosorbent the removal efficiencies of Zn and Mn increased with contact time (88.5 and 80.4%, respectively for 69-hour contact time). Only residual Zn concentration (0.22 mg Zn/l) was below admitted limit for discharge for 48-hour contact time;

– for 4 g d.w./l biosorbent, removal efficiencies of Zn and Mn were in the frame of stipulated limits for 48-hour contact time: 0.001 mg Zn/l, 0.003 mg Mn/l.

Table 3. Zn and Mn biosorption using bakery yeast (2 g d.w./l)

2 g d.w./pH 5	Contact time (h)				
	initial	1	24	48	69
Zn conc. (mg/l)	1.04	0.78	0.54	0.22	0.12
Biosorption η (%)	–	25.0	48.1	78.8	88.5
Mn conc. (mg/l)	6.84	4.94	4.02	1.52	1.34
Biosorption η (%)	–	27.8	41.2	77.8	80.4

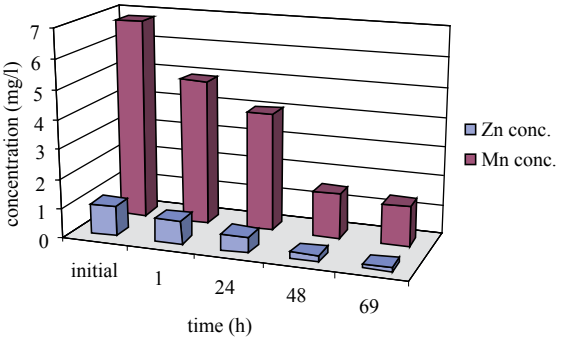

Fig. 5. Evolution in time of Zn and Mn concentration during biosorption experiment (pH – 5; 2 g d.w./l biosorbent)

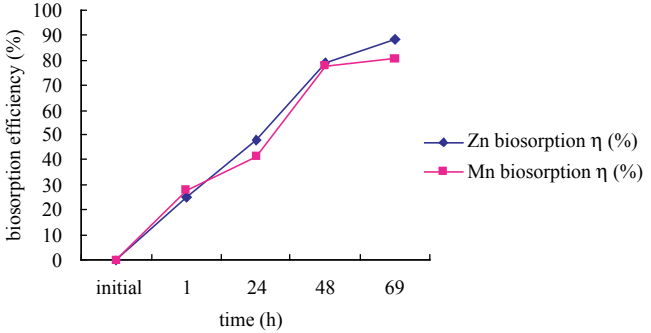

Fig. 6. Evolution in time of Zn and Mn biosorption removal efficiency (pH – 5; 2 g d.w./l biosorbent)

Table 4. Zn and Mn biosorption using bakery yeast (pH – 5; 4 g d.w./l biosorbent)

4g d.w./pH5	Contact time (h)				
	initial	1	24	48	69
Zn conc. (mg/l)	1.04	1.02	0.55	0.001	0.001
biosorption η (%)	0	1.92	47.12	99.90	99.90
Mn conc. (mg/l)	6.84	6.04	4.68	0.003	0.003
biosorption η (%)	0	11.70	31.58	99.96	99.96

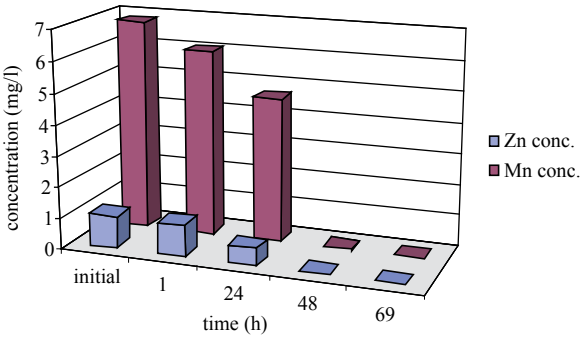

Fig. 7. Evolution in time of Zn and Mn concentration during biosorption experiment (pH – 5; 4 g d.w./l biosorbent)

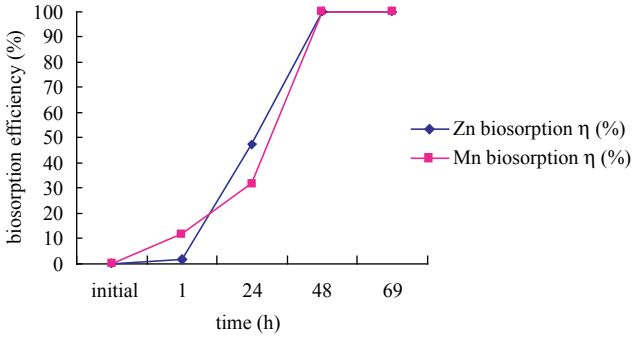

Fig. 8. Evolution in time of Zn and Mn biosorption removal efficiency (pH – 5; 4 g d.w./l biosorbent)

CONCLUSIONS

Maximum removal efficiency for Pb and Cd was obtained after a contact time of 48 h, at pH 5, initial biomass concentration of 2 mg d.w./l initial Pb concentration of 3.4 mg/l and, respectively, 7.5 mg/l initial Cd concentration.

Maximum removal efficiency for Zn and Mn was obtained after a contact time of 48 h, at pH 5, and 4 mg d.w./l initial biomass concentration.

More systematic researches are needed to assess the impact of influential factors (pH, temperature, contact time, competing ions/co-ions, initial concentration of metal ions and biomass) on the efficiency of the biosorption process at higher initial heavy metal concentration.

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