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Original Article

Assessment of Copper and Lead Biosorption from Aqueous Solutions by Brewer's Yeast

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Abstract

Adsorption of Cu(II) and Pb(II) ions by a non-conventional biosorbent, brewer's yeast (a waste by-product from the brewing industry) was investigated. Copper and lead ions were studied, taking into account their ubiquitous presences in various types of industrial waste waters. In order to determine the adsorption capacity (q_e) of copper and lead ions by brewer's yeast, in accordance with the data present in specialty literature, experimental tests regarding the study of the concentrations dynamics of metal ions in synthetic aqueous solutions treated with known quantities of biosorbent were performed. The impacts of various parameters such as contact time, pH and biosorbent dose on the removal efficiency were assessed. The results demonstrate that the brewers yeast adsorption capacity of metals increases with yeast-metal solution contact time, however it appears that adsorption weakens after 60 minutes, proving that the systems reach equilibrium. It was determined that the pH of solutions is one of the important factors in biosorption. The increase of yeast concentration also affects the metal ions adsorption capacity (doubling the yeast concentration causes a decrease of q_e values). The optimum results were obtained for the biosorbent concentration of 0.5% and contact time 60 min., copper at pH 6, and lead at pH 5 respectively.

Keywords: Biosorption, Brewery Yeast, Heavy Metal, Adsorption Capacity.

1. Introduction

The presence of heavy metals in an aquatic ecosystem is an important environmental and social problem. Heavy metals are not only a concern in the academic world but also to environmental regulators. Metals discharged into water bodies are not biodegradable, and can accumulate along the food chain, creating a large impact on the environment as well as on public health.

Therefore, increasing awareness on waters heavy metals pollution is rapidly growing worldwide and one of its offshoots, is the treatment and removal of heavy metals from effluents to permissible limits before discharging into surface waters. The need for low-cost, economical, effective and safe technologies for the removal of heavy metals in wastewaters has resulted in the search for unconventional materials which may be useful in reducing the levels of accumulation of heavy metals in the environment [1-3]. Among the various biosorbent materials, the brewer's yeast deserves and has received considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment. Previous literature data has proved that the

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brewer's yeast can remove toxic heavy metals from aqueous solutions to various extents [4-16].

Copper and lead ions were chosen for this biosorption study with regard to their wide industrial use and their potential polluting impact. Copper is a metal widely used in our daily life, but like any other heavy metal it is potentially toxic for all living organisms. Lead can contaminate the environment either via anthropic sources as well as through natural geochemical processes. It can accumulate along the food chain and is not amenable to biological degradation [17].

2. Material and Method

2.1. Biosorption experiments

Yeast was supplied as a lyophilized by-product from industrial ethanol production. Prior to use as a biosorbent, it was pretreated through washing with deionized water, stirring, and centrifugation at 3000 rpm for 20 minutes.

The supernatant was discarded and the pellet was reslurried in deionized water. The procedure was repeated for three times until the supernatant was clear. The pellet was then dried in a vacuum drying oven at 80°C for 48 h. The dried biomass was grounded with a mortar and pestle and stored in a sealed bottle to prevent readsorption of moisture.

A synthetic stock solution containing 100 mg L^{-1} concentration of Cu^{2+} and Pb^{2+} was prepared by dissolving $Pb(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$ in deionized water. The stock solution was diluted as required in order to obtain a working solution containing 1 mg L^{-1} concentration of Cu^{2+} and Pb^{2+}.

The pH of the working solution was adjusted with addition of HCl 0.1 M or NaOH 0.1 M. All the chemicals used for this study were analytical grades purchased from Merck (Darmstadt, Germany).

Metal ion binding experiments were performed by incubation of biomass (200 mg and 400 mg dry weight) with 40 mL working solution (1 mg L^{-1} Cu, Pb) in 50 mL Falcon test tube.

Samples, in triplicate, were placed on a magnetic stirrer (200 rpm) in a water bath at a constant temperature of 21°C and maintained for different contact time (15 min, 30 min, 60 min and 120 min). The biosorbent was separated from the solution through centrifugation at 3500 rpm and the residual metal concentration in the supernatant was analyzed by GFAAS.

2.2. Cu(II) and Pb(II) ions quantification by GFAAS

The samples were digested using a Speedwave MWS-2 Microwave Pressure Digestion microwave digestion system (Berghof Products + Instruments, Germany). 20 mL of the sample was digested in a duplicate with 3 mL of nitric acid 65% (Suprapure, Merck, Darmstadt, Germany) in pre-cleaned HF100 PTFE vessels.

All samples were completely digested and diluted to a final volume of 50 mL deionized water (≥18 MΩ). Samples were further diluted as necessary in the same manner.

Preparation blanks were taken through the same digestion and preparation process as the samples and analysed accordingly. Details of the procedure are provided in Table 1.

Table 1. Program used for the digestion

Step	1	2	3
Temperature [°C]	200	130	100
Power [%]	60	40	40
Time [min]	20	5	5

Total Copper Al, Fe and Cu were measured using an AAnalyst 800 atomic absorption spectrometer with a transversely heated graphite atomizer (THGA) and longitudinal Zeeman-effect background corrector as well as an AS-800 autosampler with WinLab32 software (Perkin Elmer, USA). The operating parameters were set according to the recommendations of the manufacturer and are described in Table 2.

The ultrapure deionized water (resistivity of 18.2 MΩ cm) obtained with a water purification system Direct Q UV3 (Millipore, USA) was used for preparing the solutions and for all dilutions. Standard stock solutions with a concentration (1000 mg L^{-1}) of the individual metal element were used to prepare the requested concentrations by dilution using a 1% (v/v) nitric acid solution.

The diluted standard solutions were used to build the calibration curves. In all experiments carried out, the glass /plastic containers were cleaned by soaking in10%, v/v HNO_3 for at least 24 h and rinsing with distilled water prior to use.

Table 2. The GFAAS instrument parameters and temperature programmes for the measurement of copper and lead

Instrument Parameters	Cu					Pb				
Lamp Type	HCL					HCL				
Lamp Current [mA]	15					10				
Wavelength [nm]	324.8					283.3				
Mode	AA-BG					AA-BG				
Slit Width (nm)	0.7					0.7				
Measurement Type	Peak Area					Peak Area				
Matrix Modifier [mg]	0.005 mg Pd + 0.003 mg $Mg(NO_3)_2$					0.05 mg $NH_4H_2PO_4$ + 0.003 mg $Mg(NO_3)_2$				
Calibration	Linear through zero					Linear through zero				
Temp [°C]	100	140	1000	2300	2600	100	140	700	1800	2600
Ramp (s)	5	15	10	0	1	5	15	10	0	1
Hold (s)	20	15	20	5	5	20	15	20	5	3
Internal Ar flow [mL min^{-1}]	250	250	250	0	250	250	250	250	0	250

The instrument response was periodically checked with known Cu^{2+} and Pb^{2+} solution standards. The experiments were performed in triplicate and the samples were analyzed in triplicate as well.

For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error.

The adsorptive capacity for lead and copper ions was calculated using the following equation:

$$q_e = (c_i - c_t)\frac{v}{m} \quad [1]$$

where q_e is the amount of metal ions adsorbed onto per unit weight of beer yeast (µg g^{-1}); c_i is the initial concentration (µg L^{-1}); c_t is the concentration of the solution at different contact time (µg L^{-1}); v is the volume of the solution (L); m is the weight of the dry biomass (g).

3. Results and discussions

The results are given in the tables below:

Table 3. Adsorptive capacity [µg g^{-1}] of brewer´s yeast for copper ions at different experimental parameters

Contact time [min]	q_e [µg g^{-1}] (yeast concentration 0.5%)			q_e [µg g^{-1}] (yeast concentration 1%)		
	pH=3.5	pH=5	pH=6	pH=3.5	pH=5	pH=6
15	30.72	53.08	59.94	33.65	55.39	60.49
30	47.68	77.29	77.74	46.79	62.21	76.57
60	48.44	78.20	81.34	45.98	60.17	67.23
120	51.28	79.36	82.3	50.07	61.34	69.16

Table 4. Adsorptive capacity [µg g^{-1}] of brewer´s yeast for lead ions at different experimental parameter

Contact time [min]	q_e [µg g^{-1}] (yeast concentration 0.5%)			q_e [µg g^{-1}] (yeast concentration 1%)		
	pH=3.5	pH=5	pH=6	pH=3.5	pH=5	pH=6
15	36.29	38.68	29.61	39.45	42.12	33.15
30	41.39	44.15	36.43	40.06	44.73	37.73
60	46.14	48.68	37.24	44.38	47.96	33.24
120	48.05	50.19	39.08	45.49	48.44	34.69

3.1. The effect of contact time

Experimental data confirms that the adsorptive capacity (q_e), of both copper and lead ions, increases with the increase of yeast-metal solution contact time until the equilibrium stage was obtained. The biosorption process was rapid in the first 15 min. value close to equilibrium was reached after 60 min. with a very slow increase until 120 min. These results are consistent with the literature data [10, 18-19], which has have demonstrated that the biosorption of the metals proceeds in two distinct phases: a fast phase, between 15 and 30 minutes, followed by a slow phase, in which a balance between the concentration of metal ions in solution and in the biomass is observed. After a certain time interval the biomass (yeast) is saturated with metal ions through physical adsorption processes or via ion exchanges, following with a process of stagnation or even an increase in the concentration of metals in the solution

due to desorption. Adsorption capacity was found to be lower for lead (50.19 µg g^{-1}) compared to copper (82.3 µg g^{-1}).

3.2. Effect of pH

The pH values chosen for experiments were 3.5, 5 and 6. The experiments were not conducted above pH 6.0 to avoid possible hydroxide precipitation. The pH of the solution is one of the most important factors in the biosorption process, because if it reaches above the isoelectric point, the cell wall components get negatively charged, promoting the binding of certain ligands (carboxyl, amino, phosphate) with positive metal ions. As the pH values decrease the amount of cell membrane surfaces which are positively charged which will inhibit the attraction of positive metal ions. The effect of pH on the biosorption capacity can be interpreted by the competition of the hydronium ions [H3O+] and metal ions for binding sites.

The experimental results confirm these findings. There was an increase in biosorption capacity of biomass with the increasing of the pH for both metals and the effect of pH was in the order Cu >Pb. The highest metal uptake values obtained for copper and lead ions were 82.3 µg Cu g^{-1} (pH: 6, contact time: 120 min and yeast concentration 0.5%) and 50.19 µg Pb g^{-1} (pH: 5, contact time: 120 min and yeast concentration 0.5%) respectively.

At low pH values, the ligands on the cell are closely associated with the hydronium ions, but when the pH is increased, the hydronium ions are gradually dissociated and the positively charged metal ions are associated with the free binding sites. These results are also consistent with other literature data [9, 20].

3.3.The effect of the biomass amount on adsorption capacity

Increasing the concentration of yeast affects in a similar way the adsorption capacity of the two metal ions namely doubling the concentration causes a decrease in the qe values. Increasing the dose of biomass should favor biosorption of metal ions due to the availability of adsorption sites. The decrease of adsorption capacity can be explained by a mechanism of yeast aggregation [21] or due to interference occurring between functional groups of cell membrane components [20] or due to insufficient concentrations of metal ions in solution compared to the yeast amount [22].

Experimental data confirms these theories, pointing out a slight increase in the adsorption capacity in the first stage of contact, following with a stagnation or decrease.

4. Conclusions

In this study, the biosorption of copper and lead ions from aqueous solutions by brewer's yeast was investigated and the following conclusions were drawn.

1. The brewer's yeast, a low-cost biosorbent, has the ability to adsorb Cu(II) and Pb(II) ions from aqueous solutions.

2. The biosorption ability is influenced by the experimental parameters such contact time, solution pH and yeast concentration

3. The metal uptake increased with increasing contact time. The optimum contact time for the maximum adsorption capacity was 60 minutes.

4. The uptake capacity increased with increasing pH and was maximum at pH 5.0 (for Pb) and pH 6.0 (for Cu) and the maximum metal uptakes at 60 minutes were 81.34 mg Cu g^{-1} and 48.68 mg Pb g^{-1}, respectively.

5. The uptake capacity of copper and lead decreased with increasing biosorbent concentration.

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