

# Adsorption of Copper on Specifically Modified Polyamide Sorbent

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**ABSTRACT:** A novel, specific sorbent based on polyamide covalently immobilized with dead yeast cells by glutaraldehyde was prepared and characterized. This sorbent exhibits a high capacity for metal complexation based on multifunctional groups of dead cells, as well as a good stability for reuse based on the crosslinking agent, glutaraldehyde. The  $\text{Cu}^{2+}$  sorption characteristics of the polyamide modified with immobilized dead cells were studied and compared to those of the polyamide chemically modified without cells. The adsorption capacity of specifically modified polyamide was about 19-fold higher than the chemically

modified polymer. The adsorption isotherms of Langmuir and Freundlich for the new specific sorbent were determined. The effect of pH, temperature and co-ions ( $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) on the  $\text{Cu}^{2+}$  sorption capacity were studied. The effectiveness of heavy metal desorption and the coefficient of recovery of sorption ability were determined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 80–85, 2003

**Key words:** polyamides; modification; adsorption

## INTRODUCTION

Over the past decade, the consumption of metals and chemicals in processing industries has increased dramatically. Industrial uses for metals, such as metal plating, tanning, and reaction catalysis, have generated large amounts of aqueous effluents that contain high levels of heavy metals.<sup>1</sup> Methods for the removal of metal ions from aqueous streams, such as chemical precipitation and reverse osmosis, result in incomplete metal removal and have high reagent or energy consumptions. Moreover, they generate toxic sludge that is difficult to dewater and other waste products that require careful disposal.<sup>2</sup>

The search for an effective treatment technology for the removal of heavy metal ions involves the production of new sorbents. Polymer sorbents containing certain functional groups, capable of forming complexes with metal ions, are widely used.<sup>3–5</sup> It may be possible to modify these polymer sorbents to obtain additional functional groups, broadening the spectrum of their application.<sup>5–8</sup> Polyamide is an interesting candidate for study based on its unwettability and porosity.<sup>9</sup> The preparation of modified polyamide beads containing predominantly amino and carboxyl groups on their surfaces has been reported by several authors.<sup>10–13</sup>

An alternative method of adding functional groups to the polymer surface is the coating of the polymer with microbial dead cells.<sup>14</sup> The immobilization of the cells on the polymer considerably increases the number of functional groups participating in the removal of metal ions from aqueous solutions. Such functional groups include the amino, amide, carboxylic and sulfahydril groups present in the proteins of the cell wall matrix.<sup>15</sup> The covalent bonding of the cells is preferred because the sorbents become more stable by reuse. Processes using dead cells for modification are interesting because of the large variety and low cost of these materials and for the potential use of multifunctional chelating groups, which guarantee a higher sorption capacity.

The aim of this work was to obtain a new chelating polymer sorbent by the covalent immobilization of dead microbial cells onto chemically modified polyamide beads, taking into account economic and environmental considerations, as well as to study  $\text{Cu}^{2+}$  sorption from aqueous solutions.

## EXPERIMENTAL

### Materials and methods

Preparation and chemical modification of a porous polymer carrier

Polyamide (PA) beads were prepared by the dissolution of 10 g of polyamide-6 in 60 mL of a 100% formic acid solution, followed by precipitation in a crystallizer with distilled water. The neutral precipitation water pH was maintained by the continuous addition

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of 50% NaOH, along with the addition of PA solution. The PA beads obtained were washed with distilled water until sodium formate was totally removed (to pH 7) and dried at 90°C to a constant weight.

The polymer beads were immersed in a 30% solution of NaOH at 50°C for 60 min for chemical modification. Then they were thoroughly washed with distilled water and a 5% solution of HCl until full neutralization. The beads obtained were immersed in 150 mL of a 10% solution of 1,2-diaminoethane for 60 min at room temperature. Then they were once again washed with distilled water until a pH of 7 was recorded. Furthermore, the chemically modified polymer beads were dried at 60°C until they established a constant weight.

#### Immobilization and treatment of the yeast cells

The immobilization of yeast was carried out using a cross-linking agent, glutaraldehyde. Chemically modified polymer beads were immersed in a 5% solution of glutaraldehyde for 1 h at room temperature. Then they were washed thoroughly with distilled water, until total removal of the residual glutaraldehyde, proven by qualitative reaction.<sup>16</sup>

The strain used in this study, *Saccharomyces cerevisiae* RD1, was obtained from the Bulgarian Academy of Science (Sofia, Bulgaria).

The biomass of a 24 h *S. cerevisiae* culture of beer agar was washed out with sterile physiological solution (0.9% NaCl) and suspended in 45 mL of nutrition medium in 500 cm<sup>3</sup> Erlenmeyer flasks. To the suspension with an initial cell concentration corresponding to 0.03 g dry weight was added 1g of modified polymer beads (treated with glutaraldehyde). For the production of biomass, the flask was incubated on a rotary shake (220 rpm) at 25°C for 24 h.

Then the beads with the covalently immobilized cells were filtered and washed thoroughly with distilled water to remove the unbound cells. They were then boiled in 50 mL of distilled water for 20 min (to obtain dead cells), cooled to room temperature, and rewashed with distilled de-ionized water.

#### Removal experiments

Copper was supplied as CuSO<sub>4</sub> at concentrations from 50 to 500 mg/L. The obtained sorbent with a known concentration of the immobilized yeast (0.05 g dry cell weight/g carrier) was suspended in 50 mL of metal solution in an Erlenmeyer flask, which was then agitated at room temperature and pH 5. Samples were taken at certain intervals.

The effect of the pH and the temperature on the Cu<sup>2+</sup> sorption capacity was studied by varying pH in the range from 3 to 6 and varying temperature between 15 and 50°C.

The co-ions Zn<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, with initial concentrations of 50 – 200 mg/L, were added to the copper solution (200 mg/L) to investigate the effect of the co-ions on the Cu<sup>2+</sup> sorption.

All experiments were performed in triplicate.

#### Recovery experiments

After contact with Cu<sup>2+</sup> the exhausted PA/yeast cell beads were washed with distilled water and transferred to a glass column. Hydrochloric acid (0.1N or 1N) was washed through the column (1 mL/min) to recover the metal ions from the sorbent. Samples were taken at certain intervals and were analyzed for copper ion content. The adsorption/desorption cycles were repeated six times.

The coefficient of distribution of metal ions between the solution and fresh sorbent can be expressed as

$$K'_d = \frac{a}{C}$$

where *a* is the concentration of metal ions in the sorbent (mg/L) and *C* is the concentration of metal ions in the solution (mg/L).

The coefficient of recovery was calculated by the following formula:

$$K_d = \frac{K_{df}}{K'_d}$$

where *K<sub>df</sub>* is the coefficient of distribution of the metal ions between the solution and the regenerated sorbent.

#### Analysis

The surface area and porosity of the beads were measured by mercury porosimetry, using a Porometer 1500-Carlo Erba.

The amounts of the functional groups introduced into the polyamide were determined quantitatively by residual titration in a heterogeneous medium.<sup>17</sup>

Metal ions taken up by the specific modified polymer were determined by measuring the residual metal ions in the samples using an atomic absorption spectrophotometer (AAS1, Carl Zeiss Jena).

## RESULTS AND DISCUSSION

The surface area and average pore size of the specific modified PA beads were measured to be approximately 20 m<sup>2</sup>/g and 2,500 Å, respectively. The majority of the beads were 3 – 10 mm in diameter and their coefficient of uniformity (*C<sub>n</sub>*) was calculated to be 3.17.

TABLE I  
Active Groups in Modified Polyamide Beads [mgeq/g]

Unmodified PA		Chemically Modified PA		PA/Cells	
Carboxyl Groups	Amino and Amido Groups	Carboxyl Groups	Amino and Amido Groups	Carboxyl Groups	Amino and Amido Groups
0.2448	0.2489	0.1545	0.5894	0.6033	0.9323

The effective size of the beads was calculated to be 5 mm<sup>2</sup>.

The polyamide beads were chemically modified to produce active amino groups necessary for the covalent binding of the cells. The amount of the functional groups present was quantitatively measured and compared with that of unmodified PA (Table I).

The covalent immobilization was carried out with glutaraldehyde, simultaneously immobilizing the cells and making the sorbent more stable for reuse. The immobilized microbial cells on the PA bore active groups in their cell walls responsible for separating metal ions from solution. The surface of a yeast cell consists of polysaccharides and proteins containing carboxyl, amino and amide groups, which provide sites where the metal cations can bind.<sup>18</sup> The yeast cells also possess latent binding sites that were activated by treatment with boiling water. The amounts of functional groups introduced into the PA/cell beads are presented in Table I. As can be seen, the amounts of the amino, amide and carboxylic groups in the polymer/cells sorbent are significantly higher than the amounts of the same functional groups observed in chemically modified and unmodified polymer.

#### Adsorption capacity

The sorption characteristics of both sorbents, the chemical modified polymer and the PA with immobi-

lized dead biomass, were compared. The experiments were performed under static conditions with model solutions of copper sulphate. The kinetic sorption characteristics were investigated at a pH of 5 and an initial concentration of Cu<sup>2+</sup> of 200 mg/L (Fig. 1.). Complete saturation was reached after 15 min of contact, but high sorption rates were observed during the first 10 min. The adsorption capacity of PA specifically modified with dead cells (PA/cells) was shown to be 19-fold higher than that of chemically modified polymer.

#### Adsorption isotherms

The two widely accepted equilibrium adsorption isotherm models, those of Langmuire and Freundlich, were used to evaluate the sorption behavior of the examined specifically modified polymer.

$$\text{Langmuir: } \frac{C_t}{q} = \frac{1}{Am} \times b + \frac{C_t}{Am}$$

$$\text{Freundlich: } \log(q) = \log k + \frac{1}{n} \times \log C_t$$

where  $q$  is the adsorption capacity,  $Am$  is the maximum uptake,  $C_t$  is the equilibrium concentration of

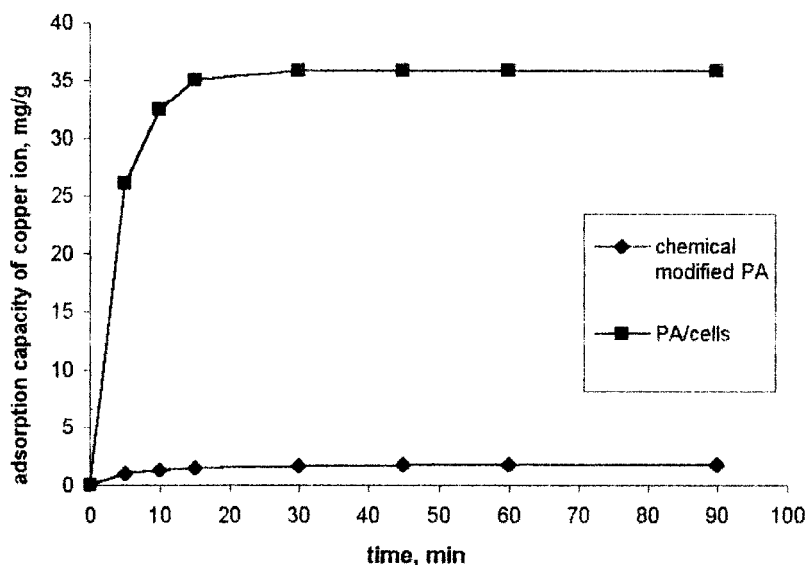


Figure 1 Kinetics of sorption of Cu<sup>2+</sup> on the modified polyamide sorbents; the initial concentration was 200 mg/L, with neutral pH at room temperature

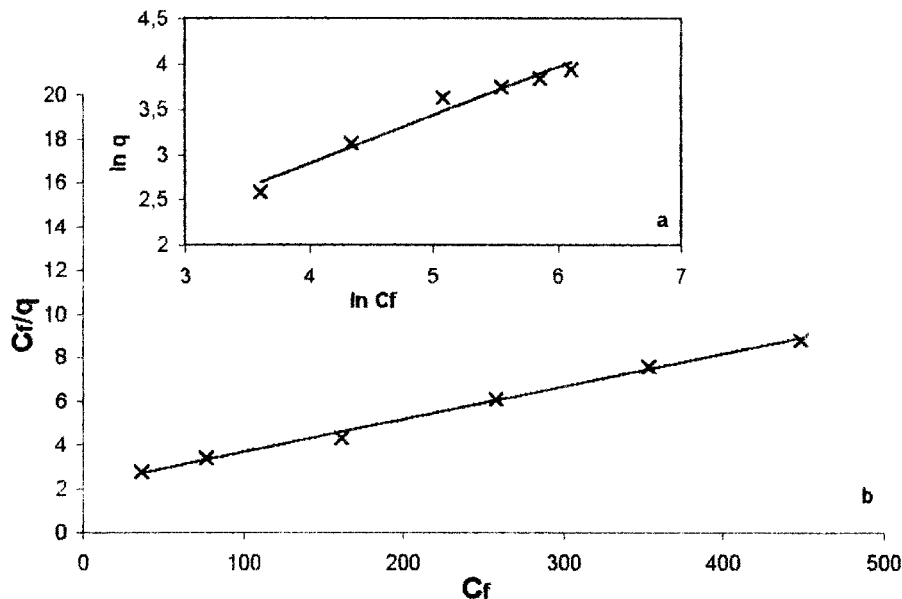


Figure 2 Sorption isotherms for PA/cell sorbent: (a) Freundlich isotherm; (b) Langmuir isotherm

metal ions in the solution,  $b$  and  $n$  are constants related to the energy of adsorption, and  $k$  is a constant.

The adsorption isotherms for the sorbent were drawn at a pH of 5 and an initial concentration of  $\text{Cu}^{2+}$  from 50 to 500 mg/L [Fig. 2(a,b)]. To determine which isotherm gives a better description of the process, the theoretical parameters obtained from both isotherms were compared to the experimental data (Table II), and the standard error of estimate (SEE) values were calculated. A comparison of the SEE values shows that although both fit the sorption data for the examined concentration range reasonably well, the fit of Freundlich equation resulted in lower SEE values, thus indicating the slightly better suitability of this model.

To enhance the process of the sorption of  $\text{Cu}^{2+}$  by PA/cell beads, the influence of some other factors was also studied. These factors include pH, temperature and the presence of other cations ( $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the copper solution.

**Influence of pH and temperature**

The influence of pH on the formation of complexes is well known. The change of pH affects the concentra-

tions of the active ionogenic groups, their electron donating properties, and mutual deposition of the ligand groups in the solution. Complex forming properties depend to a greater extent on the pH of the contact solution than on that of the ion exchange solution. This effect can be observed in the formation of the coordination bond between nitrogen and metal. The pH value is a powerful factor in determining the mechanism of sorption. Copper ions form strong coordination bonds with amino and amide groups at optimal pH.<sup>19</sup>

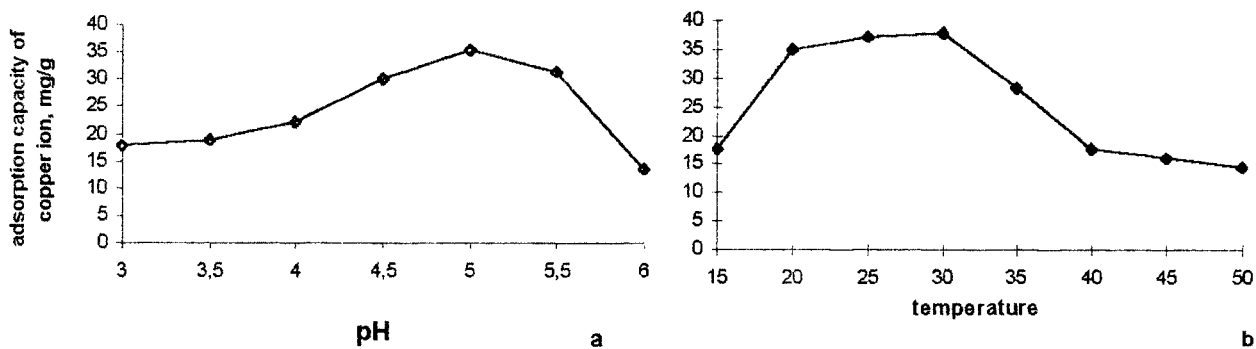
Adsorption efficiency was studied at various pH values, stabilized during the sorption process with a pH-stat laboratory system [Fig. 3(a)]. When the pH value was raised from 3 to 5, the adsorption capacity was enhanced. Therefore, as pH decreases, the sorbent surface becomes more positively charged, reducing the attraction between active sites and metal ions. In contrast, a higher pH results in facilitation of the metal uptake because the beads surface is more negatively charged. Investigation with pH values at and above 6 was not possible since metal precipitation took place at those levels as copper hydroxide. The maximal adsorption capacity was observed at a pH of 5 [Fig. 3(a)]. The obtained optimal pH was same as that used

TABLE II  
Experimental and Calculated Copper Uptake by Polyamide Beads Modified with Immobilized Dead Cells

Experimental		Freundlich Parameters <sup>a</sup>				Langmuir Parameters <sup>a</sup>				SEE <sup>b</sup>			
$q_{50}$ %	$q_{200}$ %	$q_{50}$ %	$q_{200}$ %	$k$	$n$	$q_{50}$ %	$q_{200}$ %	$A_m$	$b(\times 10^2)$	Freundlich		Langmuir	
										$q_{50}$ %	$q_{200}$ %	$q_{50}$ %	$q_{200}$ %
13.3	37.94	14.70	32.35	2.173	1.884	11.45	29.85	66.96	0.70	9.38	4.84	28.4	8.40

<sup>a</sup>  $q_{50}$  and  $q_{200}$  metal uptake at the residual concentrations of 50 and 200 mg/l, respectively.

<sup>b</sup>  $(q_{exp} - q_{cal}) \cdot 100 / q_{cal}$



**Figure 3** Effect of (a) pH and (b) temperature on the sorption of  $\text{Cu}^{2+}$  by polyamide modified with immobilized dead cells; initial copper concentration of 200 mg/L

for conventional cation exchangers.<sup>19</sup> The uptake of copper reached a plateau very rapidly (for 10–15 min), depending on pH value. Thus, at the optimal pH, the sorption equilibrium was reached for about 10 min, and the sorption capacity was highest (35.38 mg/g).

Results of the experiments to determine the effect of temperature on sorption kinetics are presented in Figure 3(b). Increasing the temperature of the solution from 15 to 30°C led to an increase of diffusion of metal ions from the solution bulk to the sorption sites. Maximal adsorption capacity was achieved at 30°C (37.9 mg/g). The decrease of adsorption capacity after 30°C was probably due to reduction of active sites of the sorbent.

#### Co-ion effect on copper sorption

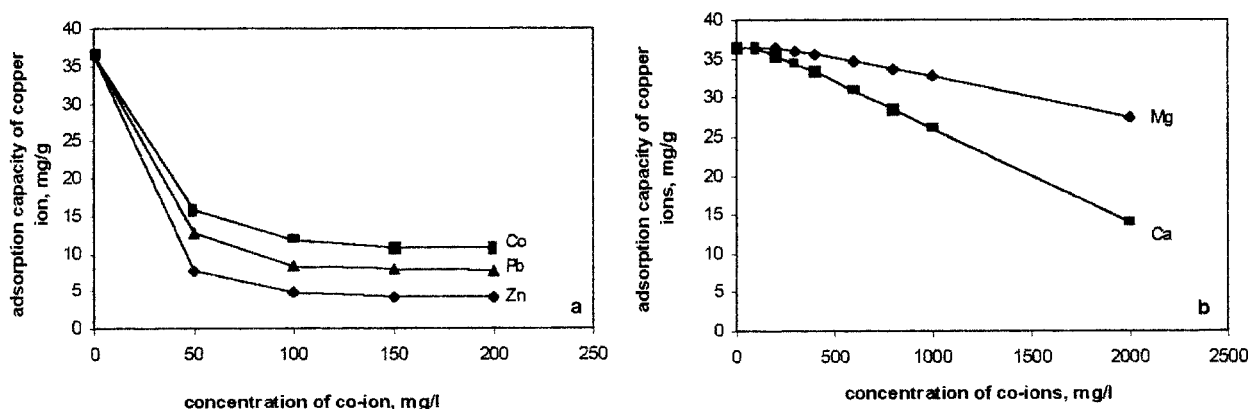
The effect of the presence of co-ions in the solution on the copper uptake capacity of the PA/cell beads was examined by adding other heavy metals ( $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ ), as well as the bivalent ions of Ca and Mg. As seen from Figure 4(a), the three heavy metal ions had a strong effect on the copper uptake capacity. Of the three, the Zn ions most negatively affected the sorption of  $\text{Cu}^{2+}$ . The strong inhibition of the copper adsorption capacity of the polymer by the presence of

bivalent heavy cations is due to their competition for the chelating surface sites of the PA/cell beads.

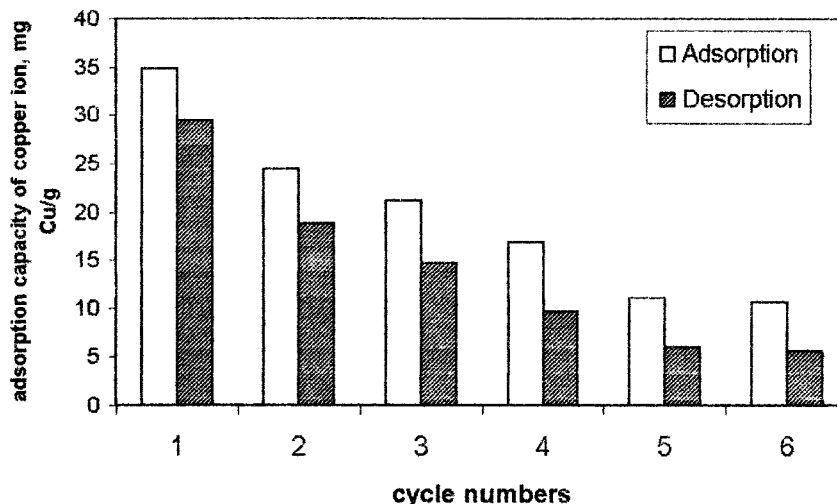
At low concentrations, the other metal ions studied ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) did not suppress the overall sorption of  $\text{Cu}^{2+}$  [Fig. 4(b)]. At higher concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , however, the ions were in strong competition with  $\text{Cu}^{2+}$  for the complex forming sites of the cell wall of the PA/cell sorbent, and the adsorption capacity was greatly inhibited.

#### Recovery of the sorbent

An important characteristic of the obtained specific sorbent is the possibility of its regeneration for further use. The recovery of heavy metals from the sorbents was studied by utilizing desorption agents 0.1N HCl and 1N HCl. Hydrochloric acid was selected because it was reported to have the best desorption efficiency compared to many other chemical reagents tested.<sup>17,20</sup> Copper ions were desorbed very rapidly and reached desorption equilibrium within 20 min. The desorption efficiency was about 84% with 0.1N HCl and 72% with 1.0N HCl. Therefore, 0.1N HCl was assumed to be the better eluent. Besides, the use of 1N HCl was considered risky because it can detach the bound cells from the polyamide beads.



**Figure 4** Co-ion effect on the sorption of  $\text{Cu}^{2+}$  by PA modified with immobilized dead cells



**Figure 5** Adsorption/desorption cycles of PA/cell sorbent and the coefficient of recovery ( $K_d$ ) of the sorbent. The eluent was 0.1N HCl, and the flow rate was 1 mL/min

Repeated adsorption/desorption (A/D) cycles were performed to examine the reusability and metal recovery efficiency of the sorbent. As shown in Figure 5, the  $\text{Cu}^{2+}$  adsorption capacity of the PA/cell beads decreased from 37.9 mg/g dry sorbent to about 10.6 mg/g dry sorbent for six cycles. Acid treatment may alter the conformation of Cu-adsorption sites on the sorbent. Figure 5 presents the coefficients of recovery of the sorbent for each adsorption cycle. It is very important to note that no loss of biomass was observed during the six A/D cycles, which makes the polymer modified in this way very suitable for the design of a continuous sorption process.

### CONCLUSIONS

A novel specific sorbent based on polyamide covalently immobilized with dead yeast cells was prepared. This sorbent exhibits a high capacity for metal complexation. The adsorption capacity of specifically modified polyamide was about 19-fold higher than the chemically modified polymer. The isotherms of Langmuire and Freundlich were used to evaluate the sorption behavior of the examined specifically modified polymer. The Freundlich model was more suitable for this sorption process. The optimal process conditions were determined to be a pH of 5 and a temperature of 30°C. The HCl-induced desorption of  $\text{Cu}^{2+}$  achieved nearly 100% recovery. However, after six A/D cycles, the recovery efficiency dropped significantly. With the advantages of high metal adsorption capacity, satisfactory recovery efficiency and the receptiveness to repeated uses, the specific sorbent (PA/cell beads) has the possibility of being an effective adsorbent for the

removal and recovery of heavy metals from polluted wastewaters.

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