

Biosorptive recovery of platinum from platinum group metal refining wastewaters by immobilised *Saccharomyces cerevisiae*

C. L. Mack, B. Wilhelmi, J. R. Duncan and J. E. Burgess

ABSTRACT

The process of platinum group metal (PGM) refining can be up to 99.99% efficient at best, and although it may seem small, the amount of valuable metal lost to waste streams is appreciable enough to warrant recovery. The method currently used to remove entrained metal ions from refinery wastewaters, chemical precipitation, is not effective for selective recovery of PGMs. The yeast *Saccharomyces cerevisiae* has been found capable of sorbing numerous precious and base metals, and is a cheap and abundant source of biomass. In this investigation, *S. cerevisiae* was immobilised using polyethyleneimine and glutaraldehyde to produce a suitable sorbent, capable of high platinum uptake (150–170 mg/g) at low pH (<2). The sorption mechanism was found to be a chemical reaction, which made effective desorption impossible. When applied to PGM refinery wastewater, two key wastewater characteristics limited the success of the sorption process; high inorganic ion content and complex speciation of the platinum ions. The results proved the concept principle of platinum recovery by immobilised yeast biosorption and indicated that a more detailed understanding of the platinum speciation within the wastewater is required before biosorption can be applied. Overall, the sorption of platinum by the *S. cerevisiae* sorbent was demonstrated to be highly effective in principle, but the complexity of the wastewater requires that pretreatment steps be taken before the successful application of this process to industrial wastewater.

Key words | effluent, platinum group metals, sorption, yeast

C. L. Mack
B. Wilhelmi
J. R. Duncan
J. E. Burgess (corresponding author)
Department of Biochemistry Microbiology and
Biotechnology,
Rhodes University,
PO Box 94,
Grahamstown, 6140,
South Africa

J. E. Burgess (corresponding author)
Present address: Water Research Commission,
P/bag X03,
Gezina, 0031,
South Africa
E-mail: job@wrc.org.za

INTRODUCTION

The process of platinum group metal refining can be up to 99.99% efficient at best, and although it may seem small, the amount of valuable metal lost to waste streams is appreciable enough to warrant recovery. The method currently used to remove entrained metal ions from refinery wastewaters, chemical precipitation, is not an effective means for selective recovery of precious metals from a wastewater. Biosorption, the ability of certain types of biomass to bind and concentrate metals from even very dilute aqueous solutions, may be an effective point-source metal recovery strategy. The removal and recovery of heavy metals from platinum group metal (PGM) wastewater have become increasingly important in light of both increasing environmental burdens and non-renewable resource depletion. Biosorption has been

identified as a potential replacement for conventional physico-chemical processes for the recovery of metals from dilute aqueous wastes such as chemical precipitation, solvent extraction and electrochemical methods as biosorption is inexpensive and in some cases more efficient than the conventional methods. The yeast, *Saccharomyces cerevisiae*, has been found capable of sorbing numerous precious and base metals, and is a cheap and abundant source of biomass (Wang & Chen 2006). Suitably immobilised, it has successfully sorbed both base and precious metals from aqueous solutions.

Industrial wastewater streams often comprise a matrix of several metal ions, one of which is the metal of interest, along with any number of inorganic and organic constituents.

The other components may be capable of interaction with the target metal, thus modifying their behaviour towards the sorbent material (Matis *et al.* 1994), in some cases forming complexes that are displaced with great difficulty in the presence of the sorbent material (Sankaramakrishnan *et al.* 2007). These impurities could include light metal ions, several heavy metal ions, surfactants and chelating agents. For example, gold mine tailings have been found to contain many other metal ions such as copper, lead, iron, zinc, calcium and magnesium (Gamez *et al.* 2003). The effect of multiple-metal solutions on the sorption of a specific metal depends on the number of metals competing for the same sorption sites, the particular metal combinations, and the concentrations in which the metals are present (Aksu & Dönmez 2006). This behaviour cannot be predicted based on single metal studies (Puranik & Paknikar 1999). For this reason, we examined the effects of co-ions on the uptake of the target metal platinum in order to better represent the sorption ability of the sorbent in the environment for which it is being developed.

MATERIALS AND METHODS

Biosorbent preparation

Bakers' yeast biomass was purchased from a bakery supplied by Anchor Yeast, RSA. The biomass was immobilised using polyethyleneimine (50% aqueous polyethyleneimine, Sigma-Aldrich, Germany) and glutaraldehyde (50% aqueous glutaraldehyde, Sigma-Aldrich, Germany) as embedding and crosslinking agents, respectively, and subsequently treated with hot alkali (3% potassium hydroxide) solution according to the method described by Stoll & Duncan (1997).

Effect of contaminant cations and anions on platinum(IV) sorption

The effect of ionic strength on the sorption process was studied by using various concentrations to bracket the concentrations found in the refinery wastewater (0.01, 0.1 and 1.0 M in deionised water) of NaCl, NaNO₃ and Na₂SO₄ solution as indicated in Table 1 (all Saarchem, Merck Chemicals (Pty) Ltd, Johannesburg, RSA) as a dilution agent for the platinum solutions (1000 mg/l atomic absorption spectrometry standard solutions, EC Labs, Port Elizabeth, RSA). The effect of light metal ions on sorption was investigated by addition of Ca(II), Mg(II), K(I) and Na(I) from 1000 mg/l atomic absorption standard solutions (EC Labs) to achieve

Table 1 | The concentrations of contaminant ions used to investigate the impact of ionic strength on platinum uptake

Molar concentration	NaCl	NaNO ₃	Na ₂ SO ₄
0.01	544.43 mg/l	849.89 mg/l	1.42 g/l
0.1	5.443 g/l	8.449 g/l	14.204 g/l
1.0	54.443 g/l	84.989 g/l	142.037 g/l

concentrations of 20, 100 and 200 mg light metal/l in a 50 mg/l platinum solution. Similarly, the effect of base metals (Ni(II), Co(II), Fe(II), Cu(II)) and precious metals (Rh(III), Au(III) and Pd(II)) were determined by the addition of metal from 1000 mg/l atomic absorption standard solutions (EC Labs) to achieve concentrations of 20, 100 and 200 mg contaminant metal/l in a 50 mg/l platinum solution. The sorbent (0.05 g) was added separately to 50 ml solution containing the contaminant and platinum in 100 ml Erlenmeyer flasks and agitated (170 rpm) on a bench top shaker (Labcon, South Africa) at room temperature (20 ± 1°C) for 24 h. The pH of all experiments was adjusted to < 1.5 using 1 M HCl (univAR, Merck).

Biosorption from PGM wastewater

A simple comparison was performed in order to gauge the difference between platinum sorption from the PGM wastewater and the aqueous solutions, using PGM refinery wastewater and a single synthetic solution at the same platinum concentration. The synthetic solution was made up to a similar platinum concentration as the PGM wastewater (approximately 18 mg/l). A sorbent dose of 1 g/l was added to flasks containing 50 ml of either wastewater or synthetic solution. These were agitated on an orbital bench top shaker at 170 rpm for 24 hours at room temperature, after which a sample was removed for metal analysis. In all experiments, sorbent-free controls were analysed alongside the experimental flasks.

A second experiment determined the effect of increasing the sorbent dosage on the uptake of platinum from the PGM wastewater. This experiment was run in the same way as those detailed previously, except that increasing concentrations of sorbent (1.0–20.0 g/l) were added to flasks containing 50 ml of PGM wastewater. All experiments were conducted in triplicate and the arithmetic means are reported. Error bars indicate the standard deviation from the calculated means, and in some cases are not visible on the graphs.

Sample analysis

Samples were removed and centrifuged (2000 g for 5 minutes (Labofuge, Heraeus, Germany)) in order to separate the sorbent from the solution. The platinum ion concentrations were measured by atomic absorption spectrometry (GBC 909 AA, GBC, Australia).

Refinery wastewater characterisation

Wastewater samples were taken from the aqueous wastewater originating from the solvent extraction separation of platinum from the matte concentrate of a PGM refinery. The PGM wastewater was analysed using *Standard Methods for the Examination of Water and Wastewater* (APHA *et al.* 1998). The characteristics of the wastewater were: pH, 1.2; settleable solids, 4 mg/l; total suspended solids (TSS), 166.1 mg/l; chloride, 27.5 g/l (0.78 M), nitrate, 660 mg/l (0.01 M); sulphate, 5.7 g/l (0.06 M); platinum, 18.2 mg/l; copper, 0.3 mg/l; nickel, 0.6 mg/l; sodium, 2.1 g/l; zinc, 4.4 mg/l.

RESULTS AND DISCUSSION

Influence of solution matrix on platinum sorption

The sorption mechanisms within a mixed metal matrix are far more complex than that of a single metal solution. One or more of three possible types of behaviour can be expected; synergism, antagonism and non-interaction. Synergism implies that the effect of the mixture is greater than that of the sum of the effects of the individual constituents, i.e. will result in a higher uptake of the target ion. Antagonism refers to the opposite situation, where the effect of the mixture is less than that of the sum of the individual constituents. When no change in effect is brought about by the mixture, it is termed non-interaction (Li *et al.* 2004).

Table 2 illustrates the effect of the light and heavy base metals on the platinum removal efficiency of the sorbent. The light metals exerted a low influence on platinum sorption. At 20 mg/l, calcium suppressed platinum uptake by 8%, whereas magnesium, potassium and sodium showed very low suppression (<5%). At higher concentrations (100 and 200 mg/l), calcium and magnesium suppressed platinum uptake by approximately 20%, while sodium and potassium only decreased platinum uptake by 8–10%. Suppression of platinum sorption by light metals followed the trend: magnesium ≈ calcium > potassium > sodium. The light metals investigated all carry positive charge, ensuring that they are unable to compete with platinum for similar binding sites, because the overall positive charge of the sorbent surface should repel all positively charged ions. Yet, they were still capable of reducing the uptake efficiency of platinum by the sorbent to a small degree. Sodium and potassium have shown similarly low impact on sorption of base metals such as lead and copper at concentrations up to 50 mg/l (Dahiya *et al.* 2008). López *et al.* (2004) evaluated the effects of calcium and magnesium on gold uptake by hop biomass. It was found that at pH 2, calcium decreased gold uptake by 25%, whereas magnesium increased gold sorption by 5–10%. Parsons *et al.* (2003) studied the effects of calcium, magnesium and sodium on platinum binding to alfalfa and found that calcium had the greatest effect on platinum binding (pH 2). In general, it has been observed that the light metals provide little competition for binding sites (even with similarly charged base metals), and seldom reduce the heavy metal sorption capacity of the sorbent (Tobin *et al.* 1993).

The suppression of platinum sorption by cobalt, copper, nickel and iron is shown in Table 2. No major effects were noted at 20 mg/l of base metal. Copper reduced platinum uptake by 5%, while nickel cobalt and iron had only a small effect. At the highest concentration of base metal (200 mg/l), a trend with respect to suppression of platinum uptake was apparent. Nickel and iron decreased uptake by 25–30%, copper by 40%, and cobalt achieved the highest suppression,

Table 2 | The effect of selected light and heavy metals on the sorption of platinum by immobilised *S. cerevisiae* sorbent

[Metal] (mg/l)	Platinum removal efficiency (%) ± (standard deviation)							
	Mg	K	Ca	Na	Co	Fe	Ni	Cu
0	96.6 (0.8)	96.6 (0.8)	96.6 (0.8)	96.6 (0.8)	96.6 (1.1)	96.6 (1.1)	96.6 (1.1)	96.6 (1.1)
20	92.8 (0.9)	92.4 (2.3)	89.4 (1.2)	96.5 (0.6)	95.2 (1.1)	94.1 (0.6)	97.0 (0.8)	91.1 (0.1)
100	75.0 (5.3)	88.1 (3.5)	78.1 (2.1)	96.1 (3.7)	77.7 (1.2)	82.4 (1.0)	86.8 (1.9)	69.9 (0.5)
200	76.5 (5.4)	87.4 (2.4)	76.6 (12.2)	88.9 (2.5)	32.5 (2.1)	69.0 (2.5)	65.9 (1.1)	51.9 (0.2)

at 60%. The suppression trend was thus: cobalt > copper > nickel > iron. The base metals investigated (copper, iron, nickel and cobalt) are often associated with the platinum group metals (PGMs) in the Earth's crust, and as such persist as contaminant metals throughout the PGM refining process, thus representing a real impact on platinum sorption. With regard to base metal interference with base metal biosorption, it is no surprise that interactions occur; since the metal ions share the same characteristics they may be direct competition for binding sites. The differences in the degree of inhibition of uptake of one base metal due to the presence of another have been linked to a number of characteristics specific to a particular metal, such as ionic radius (El-Naas *et al.* 2006), electronegativity (Al-Rub *et al.* 2006), and far more complex characteristics such as the metal acid hardness/softness as categorised by Pearson (1968), who crystallised the theory of Hard and Soft Acids and Bases (HSAB). Tsezos *et al.* (1996) tested this theory, and in the case of precious metals (soft/ borderline acids), they showed that the presence of a hard acid (yttrium) had no effect on the biosorption of a soft acid (silver). The presence of a borderline/hard acid (nickel) also had no effect on silver (soft acid) adsorption. However, when testing the effects of a second soft acid (gold) on the biosorption of a target soft acid (palladium) there was a significantly negative effect on the sorption of palladium.

All four of the base metals tested are classified as borderline acids, but iron and copper tend more towards soft acid characteristics, whereas nickel and cobalt tend towards hard acid characteristics. Platinum is a soft acid, which may explain the strong influence of the copper ions on the sorption of platinum. Iron did not exert the same effect, and cobalt decreased platinum uptake the most. It is therefore necessary to consider the hard/soft character of the chloro-platinum anion rather than the platinum(IV) cation alone in order to determine a reason for the cobalt effect based on the HSAB theory. However, this still does not satisfactorily explain the

reduction in platinum sorption, as no base metal sorption was observed. The decrease must, therefore, be due to interactions between the positively charged base metal ions and the platinum anions, resulting in complexes with reduced binding affinity for the sorbent, similar to the much lower influence of the light metals. It is possible that the chloro-platinum was hydrolysed, a possibility which should be investigated.

Competing precious metal anions exerted a profound effect on the selective sorption of platinum from solution (Table 3). Even at low concentration (20 mg/l), where the platinum concentration was higher (50 mg/l), uptake was reduced by > 30% by all three metals. At 100 and 200 mg/l, the suppression trend became apparent: rhodium reduced uptake by 35 and 40%, gold decreased platinum uptake by 45 and 55%, and palladium reduced platinum removal by 65 and 75%, respectively. Hence, the suppression trend followed: palladium > gold > rhodium. The presence of precious metal chloro-complexes other than platinum in solution had a significant impact on the sorption of platinum from solution. This indicated that the sorption mechanism was non-specific, and governed by electrostatic interactions at low pH. This is supported by Chassary *et al.* (2005), and confirmed by the strong competition effect of chloride and sulphate anions on platinum sorption. The competitive effects between platinum and palladium have also been investigated for sorption onto modified chitosan (Chassary *et al.* 2005). The authors stated that platinum and palladium will compete for the same binding sites regardless of the sorbent type, but that platinum sorption is greatly decreased in the presence of excess palladium. The palladium sorption is also faster and more efficient than that of platinum. The reactivity trends of the PGMs, as described by Lee (1991), increase from ruthenium to rhodium to palladium, and from osmium to iridium to platinum, with gold the most reactive. These trends corroborate the apparent affinity series exhibited in the results obtained. A further possible explanation of the affinity trend is the shape of the

Table 3 | The effect of precious metals and anionic ligands on the sorption of platinum by immobilised *S. cerevisiae* sorbent

[Metal] (mg ^g -1)	Platinum removal efficiency (%) ± (standard deviation)			[Anion] (M) ^a	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
	Au	Pd	Rh				
0	96.6 (0.8)	96.6 (0.8)	96.6 (0.8)	0	96.6 (0.8)	96.6 (0.8)	96.6 (0.8)
20	61.8 (7.6)	56.4 (8.6)	66.9 (2.5)	0.01	79.9 (1.5)	91.8 (1.0)	71.0 (4.8)
100	43.2 (0.2)	30.3 (1.7)	53.3 (0.5)	0.1	72.1 (1.9)	72.0 (3.2)	46.5 (1.9)
200	33.8 (3.8)	18.3 (0.8)	39.1 (0.3)	1.0	34.9 (1.7)	29.3 (0.8)	36.4 (5.6)

^aMolar conversions to mg/l and g/l are shown in Table 1

metal chloro-complexes, where the most compact shape would be sorbed to a higher degree by allowing a higher number of anions to bind than would a larger shape. The chloro-palladate anion and the chloro-aurate anion are both compact, square planar molecules, whereas the chloro-platinate and chloro-rhodate anions are larger octahedral structures, thus allowing fewer ions to bind via steric hindrance (Lee 1991).

Nitrate had little effect at (0.01 M, but reduced the platinum removal efficiency by 20% at 0.1 M and 60% at 1.0 M. The presence of both chloride and sulphate (even at low concentration, 0.01 M) decreased the removal efficiency by 10 and 20%, respectively. The suppression of platinum sorption by these anionic ligands appeared to follow the trend sulphate > chloride > nitrate (based on suppression of platinum uptake at 0.01 M). In all cases the effect was inhibitory to platinum uptake. The anionic ligands competed directly with the platinum chloride anions for sorption sites. In general, when dealing with precious metal sorption, chloride is thought to be of most importance as an inhibitor of biosorption (Godlewska-Żyłkiewicz 2003; Uheida *et al.* 2006).

Sanyahumbi *et al.* (2005) investigated the effect of sulphate, chloride and nitrate on the biosorption capacity of *Desulfovibrio desulfuricans* for platinum and palladium. They found that NaNO₃ had a negligible effect on uptake. Chloride ions, in the form of NaCl, were found to completely abolish platinum uptake at 0.2 M, while a 0.1 M concentration reduced the palladium uptake by 50%. Sulphate, as Na₂SO₄, stimulated palladium uptake, but at 0.1 M decreased platinum removal by 80%, and completely abolished it at 0.5 M. These results corroborate the trend found in the present study with regard to platinum sorption; sulphate had the highest antagonistic effect, followed by chloride, and lastly nitrate.

Platinum recovery from platinum group metal refinery wastewater

Of the non-metal components present in the wastewater, the high concentration of chloride and sulphate are of most interest. In general, there is only a very small concentration of metal ions other than platinum in the wastewater. The high concentration of sodium along with the high concentrations of chloride and sulphate indicate the high ionic strength of the wastewater. Figure 1 compares the removal efficiency and uptake capacity of the sorbent in wastewater and in synthetic solution. In both cases the performance of the sorbent was better with the synthetic solution than with the wastewater. This was largely due to the high concentration of inorganic

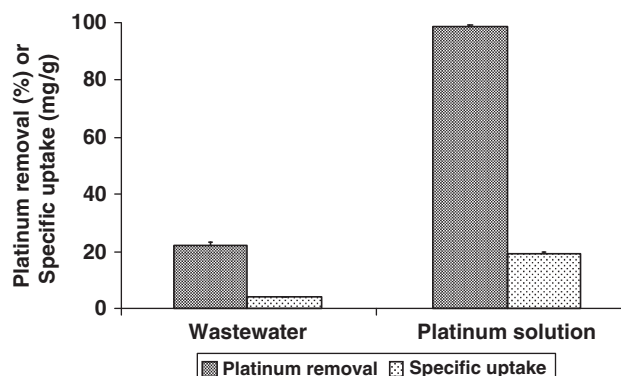


Figure 1 | A comparison of the platinum removal efficiency and specific uptake capacity (mg Pt/g sorbent) of the sorbent in synthetic solution and in PGM wastewater. Error bars represent standard deviation from the mean ($n = 3$).

anions such as chloride and sulphate present in the wastewater. As has been shown, these anions would compete with the platinum chloride anions for similarly-charged binding sites on the sorbent surface.

Figure 2 shows the removal efficiency and specific uptake capacity of the sorbent at increasing sorbent concentration. A five-fold increase in the sorbent dose resulted in a doubling of the removal efficiency. This did not improve significantly as the sorbent dose was further increased to 20 g/l. It had been expected that co-sorption of platinum with other inorganic ions would occur if sufficient sorbent were added. However, an increase in the concentration of sorbent would also lead to increased wastage of sorbent surface area, as more would be sacrificed for the sorption of inorganic anions. An explanation for the insignificant increase in platinum uptake beyond a sorbent dose of 5 g/l may be that the speciation of the platinum within the PGM wastewater is such that only 40% is in a form easily sorbed by the sorbent material, whereas the

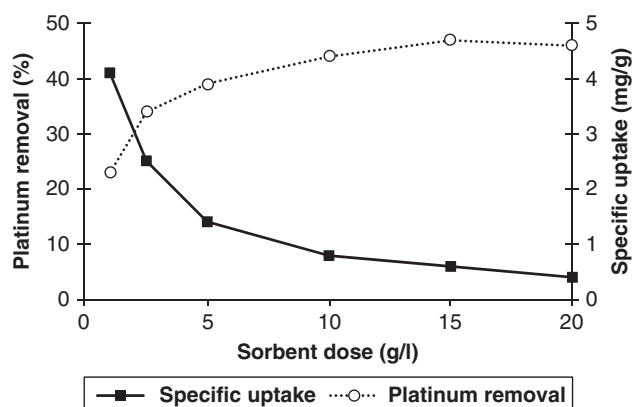


Figure 2 | The effect of increased sorbent dose on the removal efficiency and specific uptake capacity of the sorbent for platinum from PGM wastewater. Error bars represent the standard deviation from the mean ($SD < 1\%$) and are all too small to be visible ($n = 3$).

speciation of platinum in the synthetic solution was such that over 90% of metal was readily sorbed when no other metals were present.

When considering the effect of platinum speciation on its effective extraction from wastewater, factors such as the acidity, chloride and PGM concentration, temperature and age of the wastewater usually determine the extent of hydrolysis and/or aquation (Kramer & Koch 2006). Kramer & Koch (2006) studied the speciation and preferential extraction of platinum(IV) halide complexes by a modified silica-based anion exchanger, and demonstrated that the PtCl₆²⁻ species was extracted preferentially over the aquated species. This study suggests that only 40% of the total platinum in the PGM wastewater is in a similarly extractable form. Further, previous experiments (Mack *et al.* 2008) showed that the single metal synthetic solution evinced rapid initial sorption resulting in removal of approximately 70% of the metal from a 50 mg/l platinum solution in 5 min, while the PGM wastewater required a much longer contact time to attain the maximum removal from this solution.

Other studies have produced better results upon transfer of information from a synthetic solution sorption to one from wastewater. Bahadir *et al.* (2007) removed up to 95% of lead contained in a storage battery industry wastewater (approximately 3 mg Pb/l) using *Rhizopus arrhizus*. Deng *et al.* (2007) were also able to remove lead, copper, chromium and cadmium from an industrial wastewater to levels below the Chinese wastewater discharge standard using *Cladophora fascicularis*. Some wastewaters have required pretreatment before successful metal recovery was possible (Sankararamakrishnan *et al.* 2007; Lu & Gibb 2008).

CONCLUSIONS

The presence of anionic ligands, especially chloride and sulphate, had an antagonistic effect on the sorption of platinum by competing directly with the platinum anions for similar binding sites. The light metals exerted a low impact on platinum sorption, possibly due to the formation of mildly lower-affinity complexes. In the presence of excess base metal (in particular, cobalt and copper), platinum sorption significantly decreased. This may also be due to the formation of lower-affinity complexes between the base metal cations and the platinum anions. No evidence of base metal sorption was observed. The sorption of platinum in the presence of other precious metals was profoundly affected. This can be explained in a number of ways: electrostatic attraction via non-specific binding; reactivity, where one precious metal

forms an extractable species faster than, and at the expense of, another; and molecular shape and size.

There are two major factors influencing the sorption of platinum from the PGM refinery wastewater; the contaminant ions, and possibly even organic compounds, occupying binding sites; and the complex speciation chemistry of the wastewater. The results suggested that only approximately 40% of the available platinum is present in the wastewater in a form that can be extracted via sorption onto the immobilised yeast surface, which may indicate that the technology is not cost-effective for this wastewater under current economic conditions.

ACKNOWLEDGEMENTS

The authors would like to thank Anglo Platinum Ltd for funding towards the completion of this research. C. Mack would like to acknowledge financial assistance from the Atlantic Philanthropies Scholarship and the National Research Foundation of South Africa. Opinions expressed and conclusions drawn are those of the authors and are not necessarily to be attributed to Rhodes University or the donors mentioned herein.

REFERENCES

- Aksu, Z. & Dönmez, G. 2006 Binary biosorption of cadmium(II) and nickel(II) onto dried *Chlorella vulgaris*: Co-ion effect on mono-component isotherm parameters. *Process Biochemistry* **41**, 860–868.
- Al-Rub, F. A., El-Naas, M. H., Ashour, I. & Al-Marzouqi, M. 2006 Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions. *Process Biochemistry* **41**, 457–464.
- Bahadir, T., Bakan, G., Altas, L. & Buyukgungor, H. 2007 The investigation of lead removal by biosorption: An application at storage battery industry wastewaters. *Enzyme and Microbial Technology* **41**, 98–102.
- Chassary, P., Vincent, T., Marcano, J. S. & Macaskie, L. E. 2005 Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives. *Hydrometallurgy* **76**, 131–147.
- Dahiya, S., Tripathi, R. M. & Hegde, A. G. 2008 Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass. *Bioresource Technology* **99**, 179–187.
- Deng, L., Su, Y., Su, H., Wang, X. & Zhu, X. 2007 Sorption and desorption of lead(II) from wastewater by green alga *Cladophora fascicularis*. *Journal of Hazardous Materials* **143**, 220–225.
- El-Naas, M. H., Abu Al-Rub, F., Ashour, I. & Al-Marzouqi, M. 2006 Effect of competitive interference on the biosorption of lead(II) by *Chlorella vulgaris*. *Chemical Engineering and Processing* **46**(12), 1391–1399.

- Gamez, G., Gardea-Torresdey, J. L., Tiemann, K. J., Parsons, J., Dokken, K. & Yacaman, M. J. 2003 Recovery of gold(III) from multi-elemental solutions by alfalfa biomass. *Advances in Environmental Research* **7**, 563–571.
- Godlewska-Żyłkiewicz, B. 2003 Biosorption of platinum and palladium for their separation/preconcentration prior to graphite furnace atomic absorption spectrometric determination. *Spectrochimica Acta Part B: Atomic Spectroscopy* **58**(8), 1531–1540.
- Kramer, J. & Koch, K. R. 2006 195Pt NMR study of the speciation and preferential extraction of Pt(IV)-mixed halide complexes by diethylenetriamine-modified silica-based anion exchangers. *Inorganic Chemistry* **45**, 7843–7855.
- Lee, J. D. 1991 4th Edn. *Concise inorganic chemistry*. Chapman and Hall, London.
- Li, Q., Wu, S., Liu, G., Liao, X., Deng, X., Sun, D., Hu, Y. & Huang Y. 2004 Simultaneous biosorption of cadmium(II) and lead(II) ions by pretreated biomass of *Phanerochaete chrysosporium*. *Separation and Purification Technology* **34**, 135–142.
- López, M. L., Gardea-Torresdey, J. L. & Peralta-Videa, J. R. 2004 Study of calcium(II), copper(II), magnesium(II), and iron(III) interference on Au(III) binding to native hop biomass using ICP-OES. *Spectroscopy Letters* **37**(2), 201–215.
- Lu, S. & Gibb, S. W. 2008 Copper removal from wastewater using spent-grain as biosorbent. *Bioresource Technology* **99**(6), 1509–1517.
- Mack, C. L., Wilhelmi, B., Duncan, J. R. & Burgess, J. E. 2008 A kinetic study of the recovery of platinum ions from an artificial aqueous solution by immobilized *Saccharomyces cerevisiae* biomass. *Minerals Engineering* **21**(1), 31–37.
- Matis, K. A., Zouboulis, A. I. & Hancock, I. C. 1994 Waste microbial biomass for cadmium ion removal: application of flotation for downstream separation. *Bioresource Technology* **49**, 253–259.
- Parsons, J. G., Gardea-Torresdey, J. L., Tiemann, K. J. & Gamez, G. 2003 Investigation of trace level binding of PtCl₆ and PtCl₄ to alfalfa biomass (*Medicago sativa*) using Zeeman graphite furnace atomic absorption spectrometry. *Analytica Chimica Acta* **478**, 139–145.
- Pearson, R. G., 1968 Hard and soft acids and bases, HSAB, Part I Fundamental principles. *Journal of Chemical Education* **45**, 581–587.
- Puranik, P. R. & Paknikar K. M. 1999 Influence of co-cations of biosorption of lead and zinc – a comparative evaluation in binary and multimetal systems. *Bioresource Technology* **70**, 269–276.
- Sankararamakrishnan, N., Sharma, A. K. & Sanghi, R. 2007 Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater. *Journal of Hazardous Materials* **148**, 353–359.
- Sanyahumbi, D., de Vargas, I., Climo, M., Mabbett, A. N., Yong, P. & Macaskie, L. E. 2005 Selective biosorption of palladium and platinum from bi- and multi-metallic solutions. In: Harrison, S. T. L., Rawlings, D. E. & Peterson, J. (eds) Proceedings of the 16th International Biohydrometallurgy Symposium, Cape Town, South Africa, 2005, 571–579.
- American Public Health Association/American Water Works Association/Water Environment Federation. 1998 *Standard Methods for the Examination of Water and Wastewater*. 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- Stoll, A. & Duncan J. R. 1997 Comparison of the heavy metal sorptive properties of three types of immobilized, non-viable *Saccharomyces cerevisiae* biomass. *Process Biochemistry* **32**(6), 467–472.
- Tobin, J. M., L'homme, B. & Roux, J. C. 1993 Immobilization protocols and effects on cadmium uptake by *Rhizopus arrhizus*. *Biotechnology Techniques* **7**(10), 739–744.
- Tsezos, M., Remoudaki, E. & Angelatou, V. 1996 A study of the effects of competing ions on biosorption of metals. *International Biodegradation and Biodegradation* **38**(1), 19–29.
- Uheida, A., Iglesias, M., Fontàs, C., Hidalgo, M., Salvadó, V., Zhang, Y. & Muhammed, M. 2006 Sorption of palladium(II), rhodium(III) and platinum(IV) on Fe₃O₄ nanoparticles. *Journal of Colloid and Interface Science* **301**, 402–408.
- Wang, J. & Chen, C. 2006 Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review. *Biotechnology Advances* **24**(5), 427–451.