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A NOVEL METHODOLOGY FOR METAL ION SEPARATION BASED ON MOLECULARLY IMPRINTING

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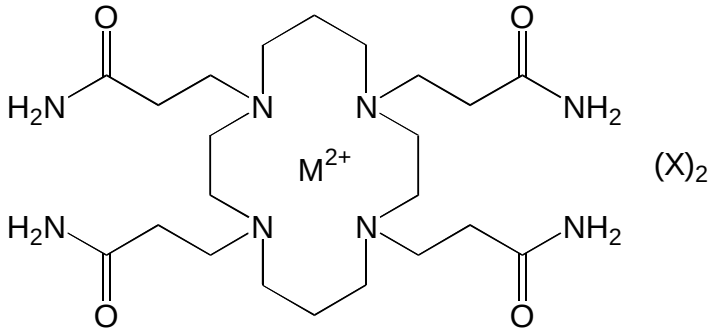
Microbes satisfy their need for iron by secreting extremely powerful ligands called siderophores into their surroundings to extract iron from the iron oxides in the soil, after which the microbe's cell membrane recognizes the iron-siderophore complex and selectively brings it back into its interior.[1] Mimicking this natural behavior, we propose a new separation methodology which also consists of two consecutive recognition steps: (1) metal ion binding to a macrocyclic ligand and (2) the macrocyclic complex as imprints binding into a polymer matrix. This combination favors effective selectivity even in the presence of competing metal ions.

A series of non-covalently imprinted polymers were synthesized by using 4 mol% of macrocyclic complex (Chart 1), 16 mol% of functional monomer (acrylamide or 4-vinyl pyridine) and 80 mol% of crosslinker (ethylene glycol dimethacrylate, EGDMA or *N*,*N'*-ethylenebisacrylamide, EBA). As shown in Table 1, **P2** is a nickel complex **1** imprinted polymer based on hydrogen bonding (Chart 2) formed between acrylamide and the dangling amide groups of the template during the copolymerization with EGDMA. After removal of the imprint by soxhlet extraction, the polymer showed a re-uptake of 26.1%, a value superior to those previously reported for polymers imprinted by hydrogen bonding. To further increase the rebinding capacity, a second mode of interaction-electrostatic attraction was introduced to the polymer system by employing the imprint **2** with a polymerizable counter ion. The nickel re-uptake of **P3** was achieved as high as 54.3%. At the same time, enhanced capacity due to the imprinting effect was much

more pronounced when compared to that of the blank polymer **P1**. A substantial increase was also observed on **P4**, the polymer templated *via* minor metal-ligand coordination with 4-vinyl pyridine as the functional monomer.



1 (M: Ni, X: ClO_4^-); **2** (M: Ni, X: $CH_2{=}CHSO_3^-$); **3** (M: Cu, X: ClO_4^-)

Chart 1

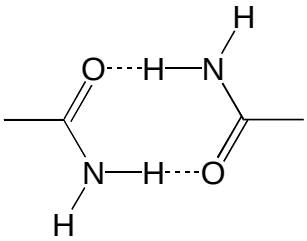


Chart 2

Table 1. Synthesis and nickel re-uptake of EGDMA-polymers

Polymer [a]	Imprint	Functional monomer	Nickel re-uptake (%) [b]
P1 (blank)	---	acrylamide	18.3
P2	**1**	acrylamide	26.1
P3	**2**	acrylamide	54.3
P4	**1**	4-vinyl pyridine	52.2

[a] Polymerization temperature: 50ºC; solvent: MeCN/MeOH=1; initiator: AIBN. [b] Based on the starting nickel complex or acrylamide.

The imprinted polymer **P2** can be resistant to concentrated nitric acid, a very strong oxidizing agent. This was shown by the investigation of reuse in which the rebound polymer was digested in concentrated nitric acid to completely remove the imprint before the next re-uptake experiment. As shown in Table 2, the rebinding capacity of **P2** tended to increase during the re-use, reaching 38.2% in the 5th run, after its digestion in concentrated nitric acid over four nights (between rebinding experiments, total time > 50 h).

Table 2. Reuse of molecularly imprinted polymer **P2**

Rebinding run	% Ni re-uptake [a]
1	26.1
2	26.6
3	31.3
4	32.3
5	38.2

[a] Based on the starting nickel complex.

Finally, a preliminary study was performed to observe the combination of the two selective processes (complexation and rebinding). One molar equivalent each of nickel(II) perchlorate, copper(II) perchlorate and the macrocyclic ligand were combined in a methanol solution and treated with the previously extracted, copper complex **3** imprinted polymer **P5** (EBA as the crosslinker). ICP analyses revealed a considerable 12 to 1 selectivity in favor of copper.

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REFERENCES

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