

## Copper and molybdenum sorption onto selective ion exchangers

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### ABSTRACT

The sorption of Cu and Mo was carried out by dynamic experiments using glass vertical columns. Two types of sorbents were used for sorption (ion exchange). Tests proceeded under following conditions: sorbent volume – 15 mL, specific flow rate – 6 BV/h, inlet molybdenum and copper concentration – 10 mg/L, three pH scales – 3.5; 4 and 4.5. The first ion exchanger – protonized Purolite D4123 (styrene-divinylbenzene matrix and 1-deoxy-1-methyl-amino-D-glucitol functional group) was not effective for copper sorption at all studied pHs (3.5; 4; 4.5). However, due to the high sorption capacity of D4123 for molybdenum (0.82 mol/L, pH=3.5), mixed bed was made from ion exchangers. It was composed of Purolite D4123 and Lewatit TP 207 (in form of free acid) in volume ratio 1:1. Lewatit TP 207 ion exchanger contains iminodiacetate (IDA) functional group. In this case, sorption was successful at all three initial pHs. The best breakthrough capacities, reached at pH of 3.5, were 0.37 mol/L and 0.37 mol/L for copper and molybdenum, respectively. The concurrent sorption of Cu and Mo on TP207 at pH 4 showed molybdenum breakthrough capacity 0.013 mol/L. Therefore isolated sorption of Mo on TP207 was important to measure. In this case, molybdenum was probably in the form of molybdenyl cation.

**Keywords:** molybdenum, copper, ion exchange, N-methyl glucamine, iminodiacetate

### INTRODUCTION

Molybdenum and copper are essential elements for human body. However, their excessive concentrations can cause various problems (for example molybdenum causes disease molybdenosa<sup>1</sup>). Natural sources of molybdenum are minerals, especially sulphide minerals. Anthropogenic pollution originates from glass, ceramic and electrochemical industry. In water it occurs mainly in form of molybdates and their polyanions<sup>2</sup>. Its limits are 0.2 mg/L for surface waters and 0.05 mg/L for water supply rivers. Molybdenum is not limited in drinking, table water and water for babies<sup>1,3</sup>. Copper occurs mainly in sulfide form and due to decomposition of sulfide minerals it pollutes underground waters<sup>1,4</sup>. Anthropogenic source of copper in surface water can be waste water from surface finishing of metals and application of algacide chemicals against alga and anabaena. The presence of copper in drinking and supply water can be linked to dissolution of copper water piping by aggressive water. High

concentration of copper in water causes unpleasantly grip taste. Its limit concentrations are 0.1 mg/L for drinking water and 0.05 mg/L for surface waters (because of its high toxicity for fishes and other aquatic organisms)<sup>1,3</sup>. World Health Organization cites these drinking water limits: for copper – 2 mg/L and for molybdenum – 0.07 mg/L<sup>5</sup>.

Molybdenum separation by resins with glucitol functional groups and copper separation by resins with iminodiacetate functional groups were tested<sup>6,7,8</sup>. Co-removal of copper and molybdenum was tested on Chilean mine waters (initial concentrations: Cu 1.35 g/L and Mo 1g/L). There, two hollow fiber-type microporous liquid membrane extraction systems were used. After this metal removing some residual copper and molybdenum concentrations remained in water<sup>9</sup>.

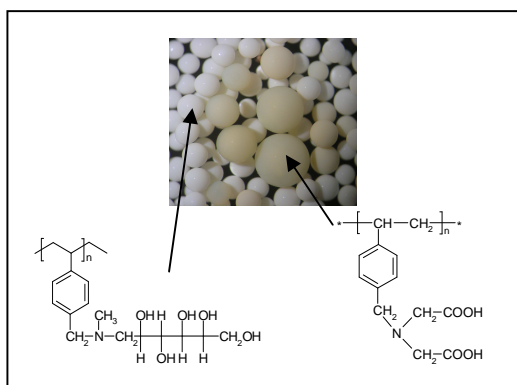
The aim of this work was finding of available ion exchangers for concurrent removal of copper and molybdenum from solution with low copper and molybdenum concentrations<sup>10</sup>.

## EXPERIMENTAL

The sorption of both metals was carried out by dynamic experiments using glass vertical columns. Two types of sorbents were used for sorption (ion exchange). Tests proceeded under following conditions: sorbent volume – 15 mL, specific flow rate – 6 BV/h, inlet molybdenum and copper concentration – 10 mg/L, three pH scales – 3.5; 4 and 4.5. Limit breakthrough concentrations were 0.1 mg/L for each element<sup>3)</sup>.

Selective sorptions were observed on two types of ion exchangers: 1: protonized Purolite D4123 (styrene-divinylbenzene matrix with 1-deoxy-1-methyl-amino-D-glucitol functional group) (FIG.1)

2: Lewatit TP 207 (in form of free acid) contains iminodiacetate (IDA) functional group (Figure1). Experiments proceeded on these ion exchanger's beds: 1/ 15 mL Purolite D4123, 2/7.5 mL Purolite D4123 + 7.5 mL Lewatit TP 207 (FIG. 1), 3/ 15 mL Lewatit TP 207



**Figure 1** Selective sorbents Purolite D4123 (left side) and Lewatit TP 207 (right side) and their mixture under microscope (in the middle)

## RESULTS AND DISCUSSION

Purolite D4123 is excellent sorbent for molybdenum sorption in form of oxoanion. Molybdenum is bound by glucitol functional group. Breakthrough capacities of molybdenum and copper on Purolite D4123 are evident from figure 2. Molybdenum and copper breakthrough concentrations were 0.1 mg/L for both elements. The highest molybdenum breakthrough capacity onto D4123 was reached at pH=3.5, i.e. 0.823 mol/L. This glucitol sorbent is not available for copper sorption, because copper is bound in cationic form.

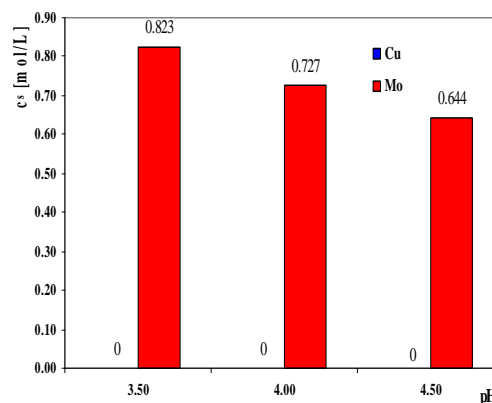
Figure 3 shows breakthrough capacities of ion exchanger mixture (D4123+TP207). Optimal and for both metals available pH is 3.5

where both metals have almost identical breakthrough capacities, i.e. 0.366 and 0.367 mol/L for copper and molybdenum, respectively. This pH appears as the well-balanced. At pH=4.5 molybdenum sorption is a little too low, e.i. 0.265 mol/L. Although, pH=4.5 is the most suitable for copper sorption ( $c_s=0.419$  mol/L).

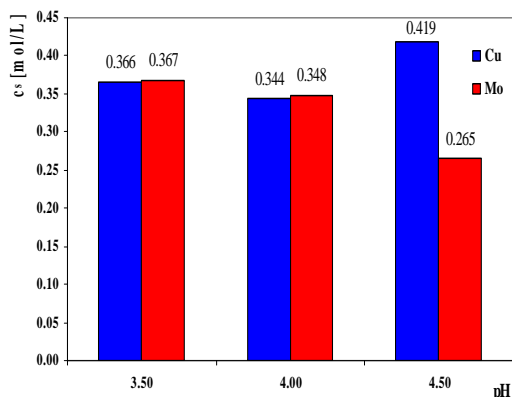
Figure 4 shows sorptions on three types of sorbent at pH=4. From the picture it is evident, that sorption on ion exchanger mixture (D4123+TP207) is well-balanced (with regards to breakthrough capacities). Lewatit TP207 is clearly the best for copper sorption, but some molybdenum sorption is also evident here. It was confirmed by molybdenum sorption under copper presence on this sorbent (FIG. 5). In the copper presence molybdenum breakthrough capacity was 0.013 mol/L and without copper it was 0.0515 mol/L. We suppose, that molybdenum was bound on TP207 in cationic form, i.e. as molybdenyl –  $\text{MoO}_2^{2+}$ . Thus, molybdenum competed with copper in sorption onto Lewatit TP207.

Both resins (TP207 and D4123) were selective for removal of copper and molybdenum, respectively.

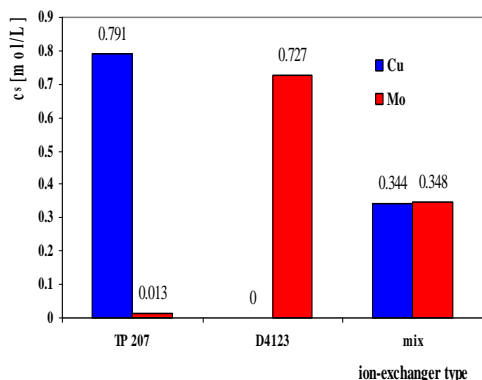
Regeneration and conditioning of mixture of ion exchangers in one column are advantage of this process. Both elements were removed eluted with 1 M NaOH and 1M HCl with 100% efficiency (Figure 6).



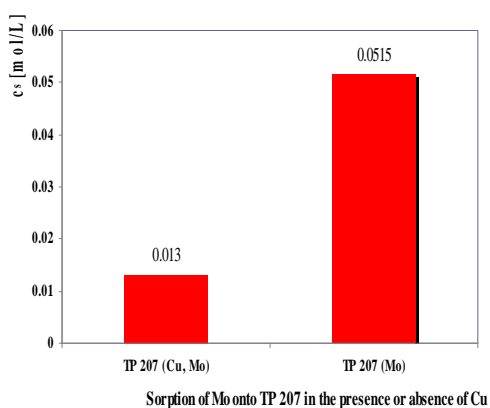
**Figure 2** Breakthrough capacities of Purolite D4123 at three pHs: 3.5; 4.0; 4.5 for sorptions of both metals, copper and molybdenum



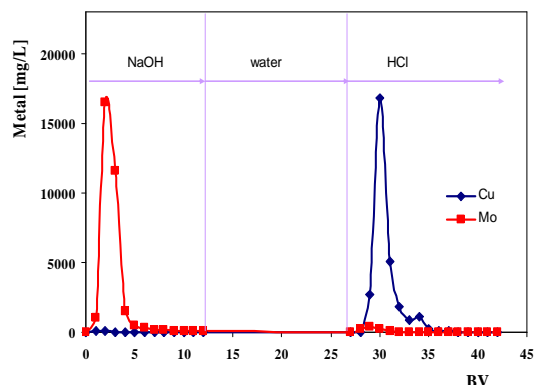
**Figure 3** Breakthrough capacities of mixed bed Purolite D4123 + Lewatit TP 207 at three pHs: 3.5; 4.0; 4.5 for sorptions of both metals, copper and molybdenum



**Figure 4** Breakthrough capacities of ion exchangers (Lewatit TP 207, Purolite D4123 and mixture of both) at pH=4



**Figure 5** Breakthrough capacities of Lewatit TP207 for molybdenum sorption (pH=4), in the presence or absence of copper



**Figure 6** Regeneration of ion exchanger mixture (D4123+TP207) by 1 M NaOH and 1 M HCl

### CONCLUSIONS

Ion exchanger mixture composed from Purolite D4123 and Lewatit TP207 was successful for concurrent sorption of copper and molybdenum at all three initial pHs (3.5;4;4.5). Generally the best and the most balanced operational capacities were reached for both element at pH=3.5, i.e. 0.366 and 0.367 mol/L for copper and molybdenum, respectively. Glucitol sorbent – Purolite D4123- is excellent for molybdenum sorption. The best breakthrough capacity was reached at pH=3.5, i.e. 0.823 mol/L. But this sorbent is not intended for copper sorption. Lewatit TP207 is mainly available for copper sorption. The best operational capacity was reached at pH=4.5. It was interesting, that this ion exchanger also bound molybdenum. Molybdenum was probably in cationic form ( $\text{MoO}_2^{2+}$ ) here. It competed with copper in sorption on Lewatit TP207.

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