Removal of metal ions on activated carbon from aqueous solutions in the presence of nitrilotri(methylphosphonic acid)

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ABSTRACT

This work investigates the enhancing effect of nitrilotri(methylphosphonic acid) (NTMP) on the adsorption of metal ions onto unmodified, cheap, market activated carbon Norit made from coal. Different metal ion's initial concentrations and molar ratios of NTMP to metal ions were tested. In single element system adsorption of 0.07–0.1 mg Cd/g (0.6–0.9 mmol Cd/kg), 0.11 mg Cu/g (1.7 mmol Cu/kg) and 0.01–0.09 mg Mn/g (0.2–1.6 mmol Mn/kg) were achieved. The addition of NTMP allowed for about a 10% increase in sorption capacity towards cadmium and about 140% towards copper. The 1:1 NTMP to metal ions molar ratio achieved about 2-times better performance than 1:2 molar ratio. Sorption capacity towards manganese was decreased by about 40% after applying NTMP to the system. The experiment with all three metal ions (cadmium, copper, and manganese) showed a correlation to the first part of the research. Adsorption of 0.004 to 0.01 mg Cd/g (0.03–0.09 mmol Cd/kg), 0.04 to 0.07 mg Cu/g (0.6–1.1 mmol Cu/kg) and 0.005 to 0.02 mg Mn/g (0.09–0.4 mmol Mn/kg) were achieved followed by 250%–300% increase towards cadmium, 150%–200% increase towards copper and 40%–70% decrease after applying NTMP.

Keywords: Heavy metals removal; Purification processes; Activated carbon; Nitrilotri(methylphosphonic acid)

1. Introduction

Water is the basic substance used in everyday life for consumption as well as for municipal and industrial purposes [1]. However, water that occurs in the natural environment is often polluted. Pollution comes mainly from industrial centers, cities, and agricultural areas. Harmful substances dissolve in surface waters and flow into larger rivers and water reservoirs. Depending on the area and the business activity conducted nearby, the concentrations of individual substances in water vary [2].

The most common impurities present in water are ammonium, nitrate(III), nitrate(V), phosphate(V), and metal (including heavy metal) ions [2]. Sources of heavy metals pollution are primarily mining, fertilizer, fuel, and energy industries [3]. The increasing concentration of heavy metals in the environment is toxic to all living organisms [4]. Therefore, contaminated water must be purified in order to use it. A method with high efficiency and low complexity and operating costs is still being sought [3].

Adsorption is an often used method to purify contaminated water from metal ions [5–17]. However, activated carbon is typically more effective towards the removal of organic compounds than metals due to the nature of sorption processes. Sorption of organic compounds is mainly physical, while metals are sorbed on the surface of activated carbon by the cation-exchange ability [5]. Complexing heavy

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metal ions is an effective method to enhance the efficiency of adsorption onto activated carbon [18]. The use of chelating compounds is frequent in cleaning water or wastewater from metal ions [18–21].

Nitrilotri(methylphosphonic acid) (NTMP) belongs to the group of organophosphorus compounds chelating agents [22,23]. The acid has one nitrogen atom and three methylphosphonic groups which are attached to all available sites. NTMP structure is presented in Fig. 1. Phosphonic groups are arranged tetrahedronically. These groups form bridges with a central metal atom and the two-dimensional layers. These layers are separated from each other by hydrophobic groups from the organic parts of the molecule. Such structure ensures high stability of complexes formed by nitrilotri(methylphosphonic acid).

NTMP has a high selectivity for chelating metal ions and can precipitate them. Nitrilotri(methylphosphonic acid) forms complexes with: copper(II), iron(II), iron(III), silver(I), nickel(II), zirconium(IV) and mercury(II) ions [23]. Complexes with iron(III), zirconium(IV) and mercury(II) are precipitated in strongly acidic solution (pH < 5). Other elements form soluble complexes with NTMP over a wide pH range. Complexes with a molar ratio of metal ions to NTMP equal to 2:1 are more stable than molar ratio 1:1. However, these results include an error related to the hydrolysis process. Negatively charged phosphonic groups in the molecule can either increase or decrease the stability of the complexes – the effect depends on the bounded metal ion. For example, complexes with calcium and nitrilotri(methylphosphonic acid) are less stable than complexes with the same ion but with the different organic ligand. For comparison, complexes with iron(III) and nitrilotri(methylphosphonic acid) are more stable than complexes with the different organic ligand. This is due to the fact that negatively charged phosphonic groups are compensated by a positively charged iron(III) ion.

NTMP is also widely used in the textile and paper industry, as a corrosion inhibitor, detergent, fire retardant, anti-abrasion and stone removal agent. It is also used to slow down the crystallization process by reducing crystal nucleation and in the descaling process in the water. Due to the presence of phosphorous atoms in the structure, nitrilotri(methylphosphonic acid) is easily degraded by soil microorganisms.

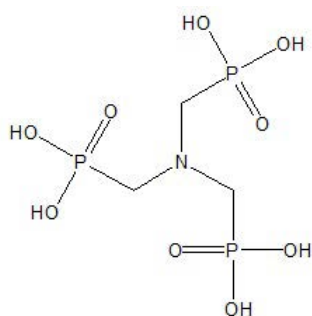This work investigates the enhancing effect of nitrilotri(methylphosphonic acid) on the adsorption of metal ions onto activated carbon. Different metal ion's initial concentrations and molar ratios of NTMP to metal ions were tested.

2. Materials and methods

2.1. Synthesis of NTMP

Nitrilotri(methylphosphonic acid) was synthesized by the Department of Chemical Technology and Processes at the Wrocław University of Science and Technology. Diethylenetriamine (99%, Sigma-Aldrich, Poznań, Poland), phosphonic acid (98%, Sigma-Aldrich, Poznań, Poland), and paraformaldehyde (MW, POCH, Gliwice) were used for the synthesis. A complexing agent – ethylenediaminetetraacetic acid was purchased at POCH Gliwice.

2.2. Metal ions removal from water

Samples of 10, 25, and 50 mg/L of chosen metal ions were mixed with 1,000 mg/L NTMP solution to obtain 1:2 and 1:1 complexing agent to metal ions molar ratio. Prepared solutions along with the blank sample (without NTMP) were shaken for 15 min to allow for complex compounds of NTMP with metal ions to form. Then 0.5 g of activated carbon was added to each solution. Mixtures were shaken for 1 h and separated on hard filters. The concentration of relevant metal ions in samples was determined by the flame atomic absorption spectrometry (FAAS) technique. The prepared analytical procedure applied for experiments is presented in Fig. 2. All experiments were carried out three times. The final values are the averages of the measurements repetition.

Activated carbon used in the study was Norit RB2 produced from coal (S_{BET} = 911 m²/g). This activated carbon has been researched extensively in the literature [24–27]. Characteristics of the activated carbon as provided by the supplier are presented in Table 1.

2.3. Concentration determination

The concentration of cadmium, copper, and manganese in samples was determined by the FAAS technique using a universal 50 mm slot burner with the air/acetylene (A/A) flame.

Cadmium was determined at 228.8 nm wavelength with a stoichiometric flame (fuel flow 1.1 min⁻¹) and 0.5 nm band-pass.

Copper was determined at 324.8 nm wavelength with a lean flame (fuel flow 0.9 min⁻¹) and 0.5 nm band-pass.

Manganese was determined at 279.5 nm wavelength with a lean flame (fuel flow 1.0 l/min) and 0.2 nm band-pass.

3. Results and discussion

Nitrilotri(methylphosphonic acid) ability to enhance the removal process of metal ions by adsorption onto the activated carbon was tested. Unmodified, cheap, market activated carbon Norit made from coal was used. Such carbon should have a low affinity to metal ions due to the lack of functional groups on the surface resulting in bad ion-exchanging properties.

Fig. 1. Nitrilotri(methylphosphonic acid) (NTMP) chemical structure.

In the first part of the experiment effect on cadmium, copper, and manganese ions were investigated individually. The study was then repeated in similar conditions in the presence of all three ions.

The experiment with only cadmium ions showed that NTMP was only partially capable of enhancing the removal of cadmium ions onto the activated carbon in investigated conditions. Determined concentration in samples before and after the purification process are presented in Table 2.

Activated carbon in blank solutions according to the presented procedure was capable to adsorb 0.07–0.1 mg Cd/g (0.6–0.9 mmol Cd/kg). These values correlate to the results

obtained by Dębowski and Lach [6] (0.1 mmol Cd/dm^3 adsorption from 141 mg Cd/dm^3 initial solution) and by Sikorska-Sobiegraj and Zieliński [5] (0.09 mg Cd/cm^3 adsorption form 100 mg Cd/dm^3 initial solution). The addition of NTMP to samples increased the sorption capacity towards cadmium by about 6% for 1:2 molar ratio of NTMP:Cd(II) and by about 10% for molar ratio 1:1. The results are presented in Fig. 3.

The experiment with only copper ions showed that NTMP greatly enhanced the adsorption process of copper ions onto the activated carbon. Determined concentration in samples before and after the purification process are presented in Table 3.

Activated carbon in blank solutions according to the presented procedure was capable to adsorb about 0.11 mg Cu/g (1.7 mmol Cu/kg). These values are about 2 times better than the results obtained by Dębowski and Lach [6] (0.1 mmol Cu/dm^3 adsorption from 141 mg Cu/dm^3 initial solution) Addition of NTMP to samples increased the sorption capacity towards copper by about 50% for 1:2 molar ratio of NTMP:Cu(II) and by about 140% for molar ratio 1:1. The results are presented in Fig. 4.

The experiment with only manganese ions showed that NTMP decreased the sorption capacity of manganese ions onto the activated carbon. Determined concentration in samples before and after the purification process are presented in Table 4.

Activated carbon in blank solutions according to the presented procedure was capable to adsorb 0.01–0.09 mg Mn/g (0.2–1.6 mmol Mn/kg). The addition of NTMP
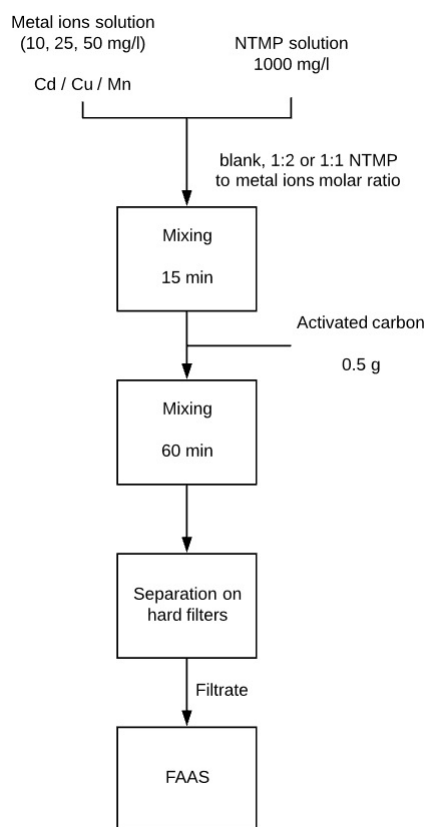

Fig. 2. The analytical procedure applied for experiments flame atomic absorption spectrometry.

Table 1
Characteristics of activated carbon used in the study as provided by the supplier

Pores width	Pores surface (m^2/g)
<0.4	0
0.4–2	983
2–3	9.9
3–5	14.6
5–10	1.3
10–50	1.2

Table 2
The concentration of cadmium ions in investigated samples before and after the purification process in a single element experiment

Experiment no.	ROclean:metal relation	Initial cadmium concentration	Final cadmium concentration
1.1	–	10.000 ± 0.011	9.29 ± 0.09
1.2	1:2	9.870 ± 0.011	9.13 ± 0.02
1.3	1:1	9.741 ± 0.011	8.992 ± 0.044
2.1	–	25.000 ± 0.013	24.4 ± 0.2
2.2	1:2	24.196 ± 0.012	23.352 ± 0.082
2.3	1:1	23.442 ± 0.012	22.620 ± 0.072
3.1	–	50.000 ± 0.018	49.02 ± 0.15
3.2	1:2	46.891 ± 0.017	45.9 ± 0.2
3.3	1:1	44.148 ± 0.016	43.19 ± 0.11

to samples decreased the sorption capacity towards manganese by about 35% for 1:2 molar ratio of NTMP:Mn(II) and by about 40% for molar ratio 1:1. The results are presented in Fig. 5.

The experiment with all three metal ions (cadmium, copper, and manganese) showed a correlation to the first part of the research. Sorption capacity towards each metal was, however, decreased. Determined concentration in samples before and after the purification process are presented in Tables 5–7.

In the case of multielement experiment sorption capacity of blank samples towards each metal was decreased
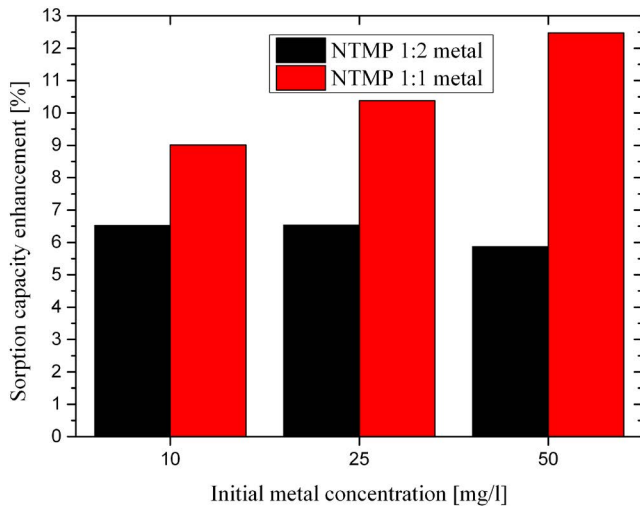
Fig. 3. Enhancement of sorption capacity towards cadmium from samples varying in initial cadmium concentration in a single element experiment.
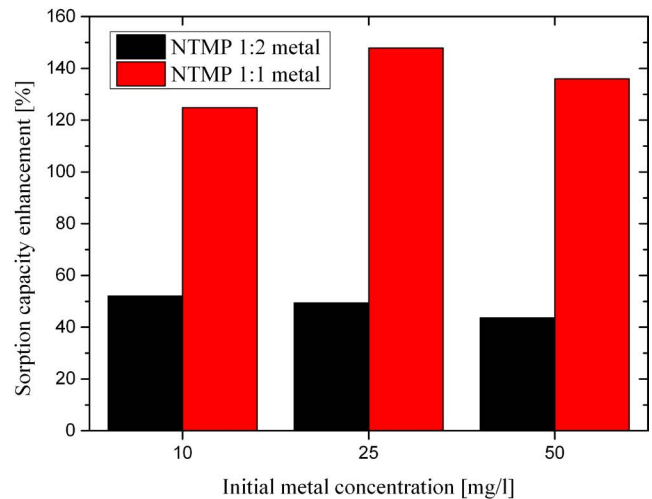
Fig. 4. Enhancement of sorption capacity towards copper from samples varying in initial copper concentration in a single element experiment.

Table 3
The concentration of copper ions in investigated samples before and after the purification process in a single element experiment

Experiment no.	ROclean:metal relation	Initial copper concentration	Final copper concentration
4.1	–	10.000 ± 0.011	8.93 ± 0.04
4.2	1:2	9.770 ± 0.011	8.149 ± 0.022
4.3	1:1	9.55 ± 0.01	7.272 ± 0.021
5.1	–	25.000 ± 0.013	23.89 ± 0.11
5.2	1:2	23.607 ± 0.012	22.04 ± 0.05
5.3	1:1	22.367 ± 0.012	19.88 ± 0.08
6.1	–	50.000 ± 0.018	48.85 ± 0.09
6.2	1:2	44.732 ± 0.016	43.26 ± 0.13
6.3	1:1	40.488 ± 0.015	38.33 ± 0.17

Table 4
The concentration of manganese ions in investigated samples before and after the purification process in a single element experiment

Experiment no.	ROclean:metal relation	Initial manganese concentration	Final manganese concentration
7.1	–	10.000 ± 0.011	9.11 ± 0.03
7.2	1:2	9.771 ± 0.011	9.221 ± 0.015
7.3	1:1	9.55 ± 0.01	9.031 ± 0.032
8.1	–	25.000 ± 0.013	24.49 ± 0.08
8.2	1:2	23.613 ± 0.012	23.30 ± 0.09
8.3	1:1	22.371 ± 0.012	22.103 ± 0.091
9.1	–	50.000 ± 0.018	49.94 ± 0.06
9.2	1:2	44.746 ± 0.016	44.71 ± 0.17
9.3	1:1	40.498 ± 0.015	40.47 ± 0.11

compared to single element analyses. For cadmium it varied from 0.004 to 0.01 mg Cd/g (0.03–0.09 mmol Cd/kg), for copper from 0.04 to 0.07 mg Cu/g (0.6–1.1 mmol Cu/kg) and for manganese from 0.005 to 0.02 mg Mn/g (0.09–0.4 mmol Mn/kg). Addition of NTMP to samples in 1:2 molar ratio

of NTMP:M(II) increased the sorption capacity towards cadmium by 60%–160%, towards copper by about 100% and decreased sorption capacity towards manganese by 30%–60%. Addition of NTMP to samples in 1:1 molar ratio of NTMP:M(II) increased the sorption capacity towards cadmium by 250%–300%, towards copper by 150%–200% and decreased sorption capacity towards manganese by 40%–70%. The results are presented in Figs. 6–8.
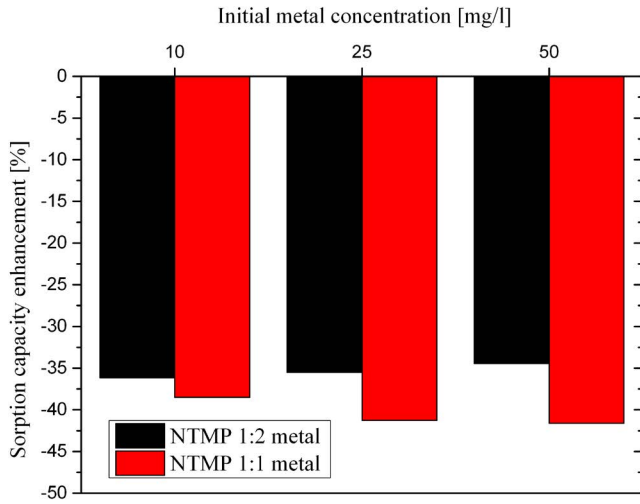
4. Conclusions

Nitrilotri(methylphosphonic acid) is a great sorption capacity enhancing agent for copper ions. Applying it to the system in correct quantity (1:1 NTMP to copper ions molar ratio) can lead to about 200% enhancement of sorption capacity in the multielement environment and about 140% in the single element environment. The 1:1 NTMP to copper ions molar ratio achieved about 2-times better performance than 1:2 molar ratio.

NTMP can be also applied as a sorption capacity enhancing agent for cadmium removal. The effect was strong in a multielement environment (more than 250%), however, achieved sorption capacity was very low (only about 0.05 mg Cd/g). In a single element system it allowed for about 10% increase in sorption capacity towards cadmium.

NTMP cannot be used to enhance the removal of manganese ions by adsorption. Applying it to the system decreased sorption capacity towards manganese by more than 30%.

Fig. 5. Enhancement of sorption capacity towards manganese from samples varying in initial manganese concentration in single element experiment.

Table 5
The concentration of cadmium ions in investigated samples before and after the purification process in the multielement experiment

Experiment no.	ROclean:metal relation	Initial cadmium concentration	Final cadmium concentration
10.1	–	10.000 ± 0.011	9.96 ± 0.04
10.2	1:2	9.39 ± 0.01	9.33 ± 0.04
10.3	1:1	8.86 ± 0.01	8.74 ± 0.03
11.1	–	25.000 ± 0.013	24.915 ± 0.071
11.2	1:2	21.534 ± 0.011	21.389 ± 0.018
11.3	1:1	18.91 ± 0.01	18.69 ± 0.03
12.1	–	50.000 ± 0.018	49.9 ± 0.1
12.2	1:2	37.850 ± 0.014	37.651 ± 0.091
12.3	1:1	30.438 ± 0.011	30.19 ± 0.09

Table 6
The concentration of copper ions in investigated samples before and after the purification process in the multielement experiment

Experiment no.	ROclean:metal relation	Initial copper concentration	Final copper concentration
10.1	–	10.000 ± 0.011	9.609 ± 0.013
10.2	1:2	9.39 ± 0.01	8.586 ± 0.023
10.3	1:1	8.86 ± 0.01	7.757 ± 0.016
11.1	–	25.000 ± 0.013	24.44 ± 0.05
11.2	1:2	21.534 ± 0.011	20.606 ± 0.012
11.3	1:1	18.91 ± 0.01	17.692 ± 0.043
12.1	–	50.000 ± 0.018	49.28 ± 0.11
12.2	1:2	37.850 ± 0.014	36.80 ± 0.06
12.3	1:1	30.438 ± 0.011	29.26 ± 0.09

Table 7
The concentration of manganese ions in investigated samples before and after the purification process in the multielement experiment

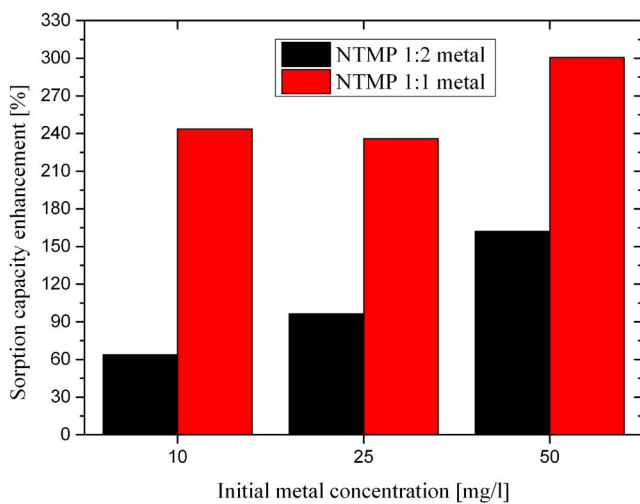| Experiment no.	ROclean:metal relation	Initial manganese concentration	Final manganese concentration
10.1	–	10.000 ± 0.011	9.801 ± 0.063
10.2	1:2	9.39 ± 0.01	9.263 ± 0.025
10.3	1:1	8.86 ± 0.01	8.76 ± 0.03
11.1	–	25.000 ± 0.013	24.942 ± 0.027
11.2	1:2	21.534 ± 0.011	21.51 ± 0.07
11.3	1:1	18.91 ± 0.01	18.891 ± 0.041
12.1	–	50.000 ± 0.018	49.9 ± 0.2
12.2	1:2	37.850 ± 0.014	37.82 ± 0.07
12.3	1:1	30.438 ± 0.011	30.418 ± 0.052

Fig. 6. Enhancement of sorption capacity towards cadmium from samples varying in initial cadmium concentration in the multielement experiment.
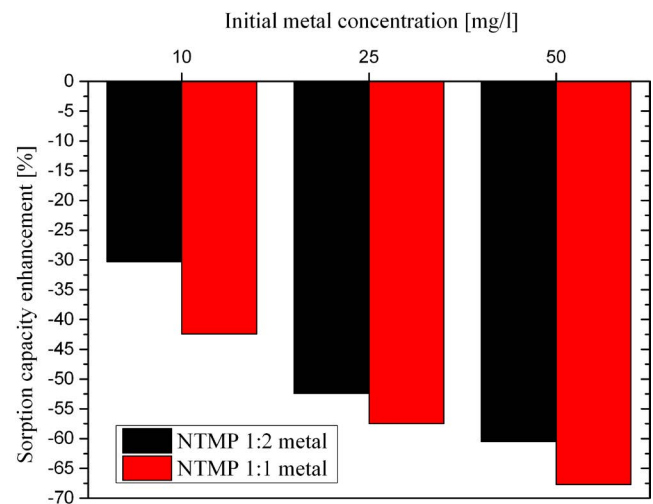

Fig. 8. Enhancement of sorption capacity towards manganese from samples varying in initial manganese concentration in the multielement experiment.
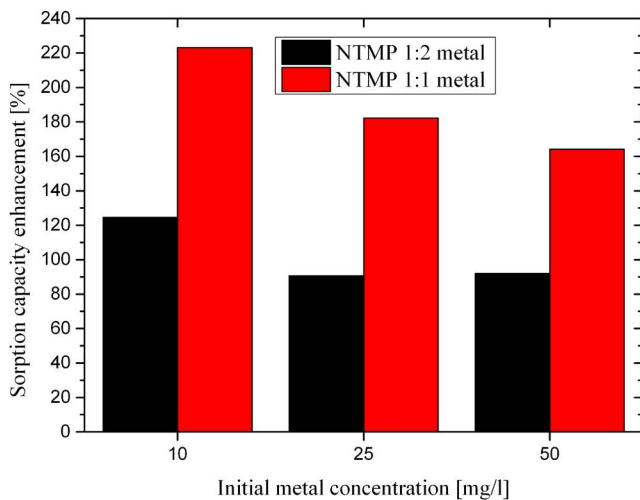

Fig. 7. Enhancement of sorption capacity towards copper from samples varying in initial copper concentration in the multielement experiment.

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