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CHEM 489 – DIRECTED RESEARCH II

Instructor Professor Timur Atabaev

Mesoporous silica particles for removal of toxic, heavy metal cations from the water samples

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Abstract: Pollution of terrestrial and aquatic ecosystems with toxic and heavy metals is a major environmental concern with serious public health implications. In this study, we investigated the size effects of synthesized mesoporous silica particles (~ 50 nm, ~ 200 nm, ~ 500 nm) on the removal rate of toxic and heavy metals in tap and river water. Chemical analysis before and after adsorption experiments revealed that mesoporous silica particles can effectively remove the As, Se, V, Sn, Sr, Al, and Fe elements from water. In particular, ~200 nm SiO₂ particles (surface area ~ 748.46 m²/g) showed the highest As (91.4%), Al (98.5%), Fe (72.5%) and Sr (61.9%) removal rates after 30 min. Other factors, such as water pH and contact time, were investigated as well. The results showed that fabricated mesoporous silica particles can be used for the effective removal of some toxic and heavy metals from water.

Keywords: silica particles, adsorbent, toxic and heavy metal ions removal.

1. Introduction

As the population of human grows, there is a notable escalation in the volume of solid waste and wastewater generated each year. Additionally, the utilization of harmful substances like metals, fertilizers, volatile organic compounds, organic halogenated compounds, and dyes is on the rise. Studies have identified 278 distinct emerging pollutants present in samples of surface water and groundwater collected from various regions globally.¹

The aim of implementing this research is to eliminate heavy metal cations released by various industries. There are 60 natural metal elements from the Periodic table and 54 of them are classified as heavy metals, as they have a density of more than 4.5g/cm³.² Among these metals Iron, Zinc, Copper, and Chromium are necessary elements for metabolism and physiological processes in the human body. Therefore, there is some concentration of them in the human body and it means some amount of these metals are permissible. According to World Health Organization³ (WHO), limited standards for heavy metal ions are Se (0.02 ppm), Fe (0.3 ppm), As (0.01 ppm) and Hg (0.006 ppm) and higher concentrations of these metals will cause health disorders. Each element can cause different illnesses Hg and Cd make defects in the reproductive and respiratory systems, while arsenic and chromium are cancerogenic.⁴ In addition, harmful effects of mercury include causing Minamata disease, while cadmium exposure can lead to itai-itai disease.⁵ Heavy metals can cause harm to particular organs in the human body, such as the kidneys, nerves, liver, skin, and heart, among other effects.⁶

There are several sources of heavy metal ion entry into water sources, including natural processes and anthropogenic activities. Natural processes contributing to the release of heavy metal ions into water include weathering, volcanic eruptions, and leaching processes.⁶ The anthropogenic effect includes agricultural, mining and industrial sectors which play a substantial role in introducing detrimental heavy metals, including arsenic (III), cadmium (II), lead (II), chromium (VI), nickel (II), mercury (II), and copper (II), into water sources.⁷ Nevertheless, chemical fertilizers, cosmetics, and their byproducts represent minor sources of heavy metals from human activities that are spread into water.⁸

To deal with these challenges, the decision was made to employ cost-effective and reusable mesoporous silica particles. These particles offer the advantage of tunable pore diameter and surface area, which can be adjusted using NaOH as a base. The silica surface features hydroxy groups and ethereal linkages, resulting in a negative charge that attracts species deficient in

electrons, such as metal cations. Positively charged heavy metal ions are spontaneously drawn and adsorbed onto the surface of mesoporous silica (MPS). The novelty of this research lies in the use of a more environmentally friendly base which is sodium hydroxide, instead of the commonly used ammonia. Previous studies, like that of Trofimova et al.⁹, synthesized mesoporous silica using an alcohol-water mixture with ammonia as a base, resulting in a surface area of 800m²/g, pore volume of 0.63cm³/g, and average diameter of 3nm. According to a similar study by Kobylinska et al.¹⁰ who also treated the water with mesoporous silica with surface functionalization achieved Removal efficiency (RE) of 90% for Cu and Mn within 10 minutes of adsorption with 45-50 mg/g adsorption capacity which is good results.

This research aims to characterize Mesoporous Silica particles of different sizes MPS-1, MPS-2 and MPS-3 which are synthesized with different amount of base and perform adsorption experiments under various pH conditions and at different time intervals, using both tap and river water sources. The objective is to determine how the size variation of Mesoporous Silica influences the efficiency of heavy metal cation removal.

2. Materials and Methods

2.1. Sample synthesis

60 mg of cetyl-trimethylammonium bromide (CTAB) was dissolved in 30 mL of DI water. The solution was then stirred at 700 rpm and heated to 75°C. After reaching the desired temperature, different amounts (100, 200, and 300 µL) of 2M NaOH were added under continuous stirring. After 5 minutes, 500 µL of 99.9% tetraethyl orthosilicate (TEOS) was added to the solution and stirred for an additional 2 hours. After that, the mixture was centrifuged for 10 minutes at 800 rpm, and the solid precipitate was dried in the oven at 60°C overnight.

To wash the mesoporous silica (MPS) samples, dry silica powder was first suspended in a solution of 100 µL of HCl in 10 mL of 70% ethanol by sonication. The suspension was then stirred for 1 hour at 700 rpm. After that, the mixture was centrifuged and dried in the oven, similar to the previous stage.

Finally, the powders were calcined in an oven at 500°C for 1 hour. **MPS-1** (with 100 µL of NaOH), **MPS-2** (with 200 µL of NaOH), and **MPS-3** (with 300 µL of NaOH).

2.2. Adsorption experiments

For each type of MPS, 3 time-dependent (10 min, 20 min, and 30 min) adsorption experiments were performed. For each experiment, 10 mg of silica nanoparticles were suspended in 10 mL of filtered tap water by ultrasonication (2 min) and stirred at 700 rpm for a designated time. After that, the silica nanoparticles were filtered out using a syringe with a 0.1 µm filter. The time dependence experiment for river water was performed in exactly the same procedure as for tap water. The amount of metals in the samples was determined by ICP-OES.

Negligible amounts of HCl and NaOH were added until pH=6 and pH=8, respectively to the water samples to for the pH experiment. The procedure of the adsorption experiment was the same as the previous one, but the experiment time was only 30 minutes due to limited time and resources.

2.3. Characterization

The surface morphology of the samples was investigated by a field-emission scanning electron microscope (FE-SEM, Zeiss Crossbeam 540). In addition to that, imaging was performed by a transmission electron microscope (TEM) JEOL JEM - 1400 Plus. X-ray diffraction (XRD) was

performed using the Smartlab Rigaku system with Cu Ka radiation ($\lambda = 1.54056 \text{ \AA}$). The porosity of the nanoparticles was assessed using Brunauer-Emmett-Teller (BET) analysis on nitrogen porosimeter Autosorb iQ. Vibrational modes present in nanoparticles were measured using Nicolet iS10 Fourier-transform infrared (FT-IR) spectrometer. The Zeta potential of the nanoparticles was measured by Microtrac Nanotrack wave II. The amount of metal ions dissolved in the water samples was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 7500ce) and inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fischer Scientific iCAP).

3. Results and Discussion

3.1. Instrumental analysis

SEM images (Figure 1) showed that the synthesized MPS nanoparticles all have near spherical shape.

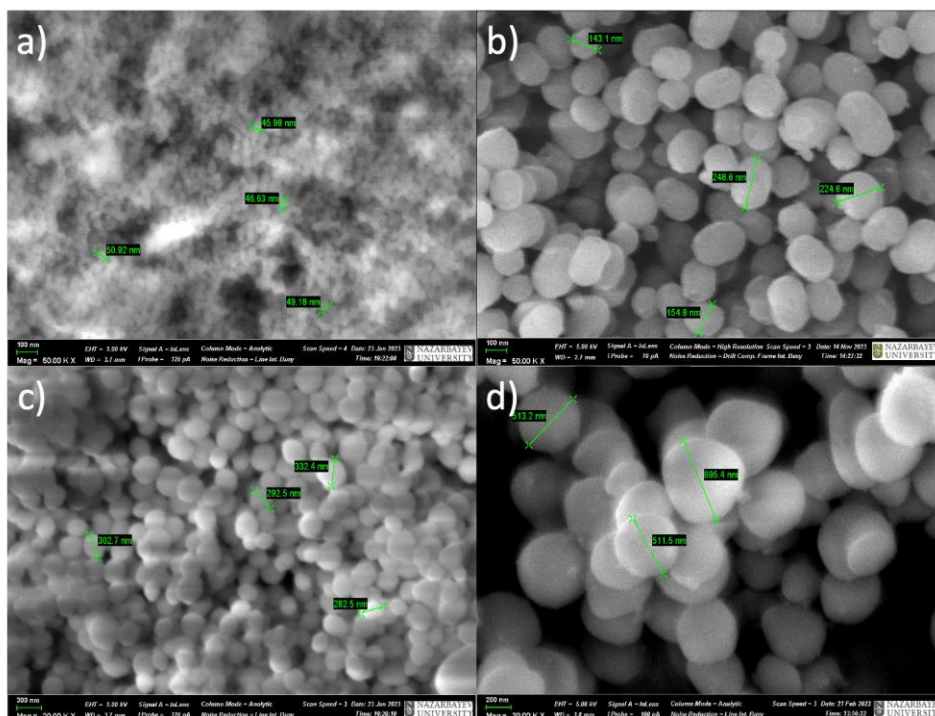


Figure 1. SEM images of a) MPS-1, b) MPS-2, c) and d) MPS-3

The size of the nanoparticles was found to have a correlation with the amount of added NaOH during synthesis. According to Table 1, as the amount of NaOH increases, the diameter of MPS also increases. The change in 100 μL of 2M NaOH increases the MPS diameter 2-4 times.

Table 1. Average silica nanoparticle sizes from SEM

NaOH volume	MPS-1	MPS-2	MPS-3
Particle diameter range, nm	45-55	150-250	300-600

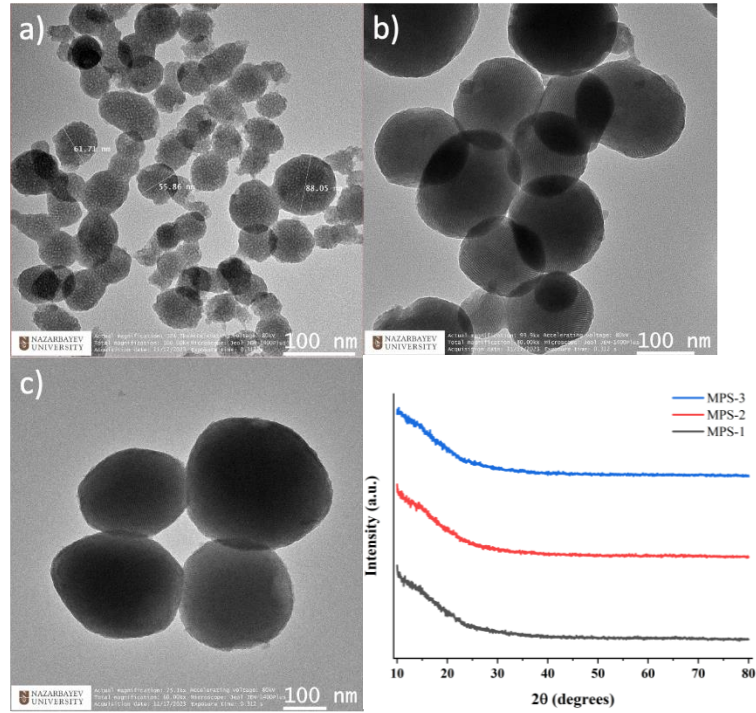


Figure 2. TEM images of a) MPS-1, b) MPS-2, c) MPS-3 d) XRD spectrum of the samples

The TEM images (Figure 2) confirm the spherical geometry of nanoparticles and show small pores on the surface. According to the XRD results, it can be concluded that the nanoparticles consist of amorphous silica because there are no distinct peaks that would signify crystalline structure. BET analysis shows that the highest porosity, i.e. largest pore size and surface area 0.721 cc/g and 748.46 m²/g, respectively, is achieved in the case of the **MPS-2** sample. The **MPS-3** sample has the lowest pore size and surface area 0.472 cc/g and 651.173 m²/g. Detailed BET data is given in Table 2.

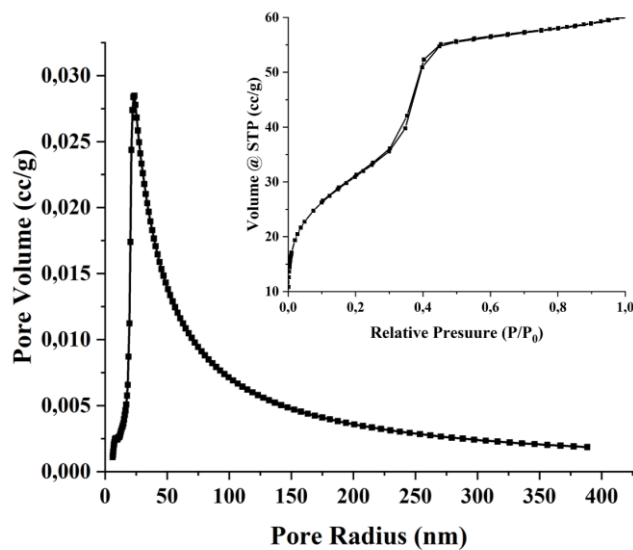
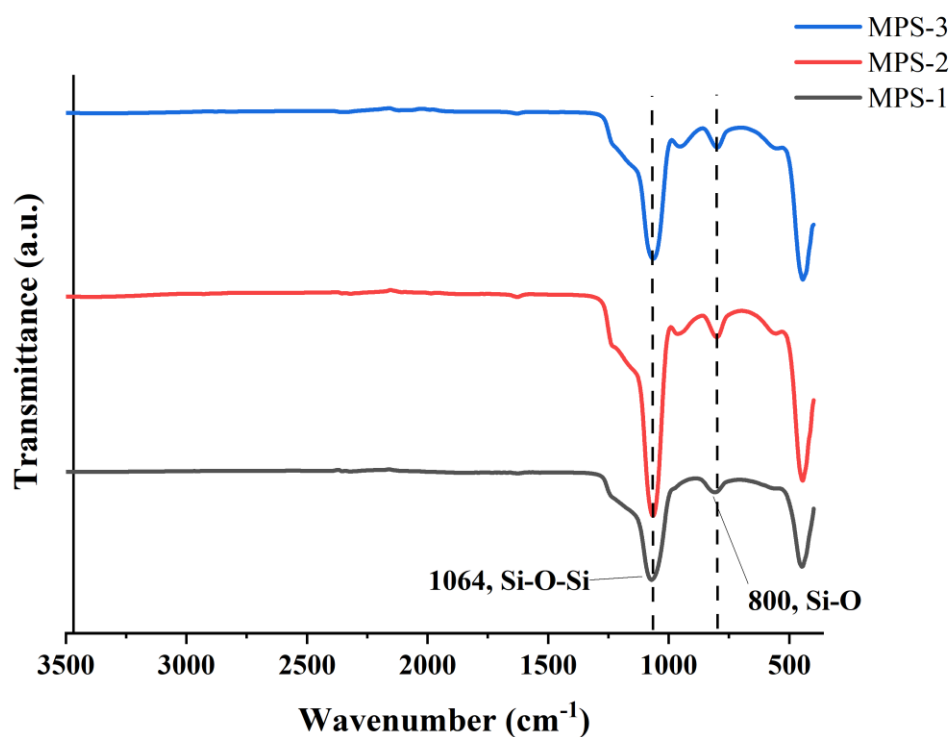


Figure 3. Results of BET analysis for MPS-2

Table 2. BET results

	Pore volume cm ³ /g	Surface area m ² /g
MPS-1	0.718	667.781
MPS-2	0.721	748.46
MPS-3	0.427	651.173

As seen from Figure 4, FT-IR analysis reveals two peaks at 1064 cm⁻¹ and at 800 cm⁻¹, which correspond to Si-O-Si and Si-O, respectively. The obtained results prove that desired SiO₂ was successfully synthesized in all **MPS-1-3**.

**Figure 4.** FT-IR analysis of powder MPS-1, MPS-2, and MPS-3**Table 3.** Zeta potential analysis

	MPS-1	MPS-2	MPS-3
Zeta Potential, mV	29.2	46.1	23.9
Polarity	Negative	Negative	Negative

As an additional characterization, we decided to measure the zeta potential of MPS nanoparticles. All of them had negative charge as expected. MPS-2 exhibited the highest zeta potential at 46 mV, indicating strong repulsive forces and good stability in solution. Other samples such as MPS-1 and MPS-3 shows incipient stability which provide the evidence for comparable poor adsorption. Since MPS-2 has a higher zeta potential, it exhibits improved cation adsorption due to enhanced electrostatic interactions, increased surface charge, and minimized particle aggregation.

3.2. Adsorption experiments

Table 3. Concentrations in ppm of elements determined by ICP-OES analysis for **MPS-1**

Elements	Al	As	Se	Sn	V
Tap water	0.0131	0.02095	0.0322	0.0183	0.0279
10 min	0	0.0028	0.0035	0.0026	0.0105
Removal %	100	86.63	89.13	85.79	62.37
20 min	0	0.0025	0.0008	0.0015	0.0068
Removal %	100	88.07	97.52	91.80	75.63
30 min	0	0.0026	0.001	0.0015	0.0142
Removal %	100	87.59	96.89	91.80	49.10
pH 6	0.0014	0.00205	0	0.0023	0.0129
Removal %	89.31	90.21	100	87.43	53.76
pH 8	0.001	0.0001	0.0005	0.0016	0.0069
Removal %	92.37	99.52	98.45	91.26	75.27

Table 4. Concentrations in ppm of elements determined by ICP-OES analysis for **MPS-2**

Elements	Al	As	Se	Sn	V
Tap water	0.0131	0.02095	0.0322	0.0183	0.0279
10 min	0	0.00385	0.0006	0.0013	0.0111
Removal %	100	81.62	98.14	92.90	60.22
20 min	0	0.003	0.0003	0.0014	0.0088
Removal %	100	85.68	99.07	92.35	68.46
30 min	0	0.0018	0.0021	0.0016	0.0062
Removal %	100	91.41	93.48	91.26	77.78
pH 6	0.0002	0.0008	0	0.0016	0.0053
Removal %	98.47	96.18	100	91.26	81.00
pH 8	0	0	0.002	0.0014	0.0056
Removal %	100	100	93.79	92.35	79.93

Table 5. Concentrations in ppm of elements determined by ICP-OES analysis for **MPS-3**

Elements	Al	As	Se	Sn	V
Tap water	0.0131	0.02095	0.0322	0.0183	0.0279
10 min	0	0.0024	0	0.0017	0.0097
Removal %	100	88.54	100	90.71	65.23
20 min	0	0.0011	0	0.0014	0.0095
Removal %	100	94.75	100	92.35	65.95
30 min	0	0.002	0.0027	0.0017	0.0063
Removal %	100	90.45	91.61	90.71	77.42
pH 6	0.0005	0.0011	0	0.0013	0.007
Removal %	96.18	94.75	100	92.90	74.91
pH 8	0.0004	0.0033	0	0.0015	0.0039
Removal %	96.95	84.25	100	91.80	86.02

The mesoporous silica (MPS) synthesized in this study was subjected to efficiency testing for the removal of heavy metal cations from tap water sourced from Nazarbayev University in Astana, Kazakhstan. Among the different samples tested (MPS-1, MPS-2, and MPS-3), MPS-2 exhibited superior removal results. This is in line with the BET results that showed higher porosity for MPS-2 compared to two other samples

Furthermore, relatively good removal efficiencies (Figure 5) were shown by Al^{3+} , As^{3+} , Se^{4+} , Sn^{4+} , and V^{3+} , whose removal efficiency after 10 minutes was more than 90% except for vanadium and arsenic cations which were 60.2% and 81.6%. However, the removal efficiency increases for these metals with time, up to 91.4% for arsenic, while for vanadium the value was 77.8%.

Interestingly, heavy metals exhibiting excellent removal efficiency did not display a significant time dependency, as their removal rates were already notably high. It is important to highlight that the mesoporous silica demonstrated exceptional removal efficiency for various heavy metals, including molybdenum, antimony, cadmium, etc. However, due to their low concentrations (less than 0.001 ppm), these metals were excluded from further consideration in the analysis.

Experiments with MPS-2 at different pH (Figure 6) showed that in basic conditions removal of Al, As, and Se are slightly better than in acidic conditions. This can be partially due to the formation of insoluble hydroxides of these elements. More detailed explanation is given in discussion for river water experiments.

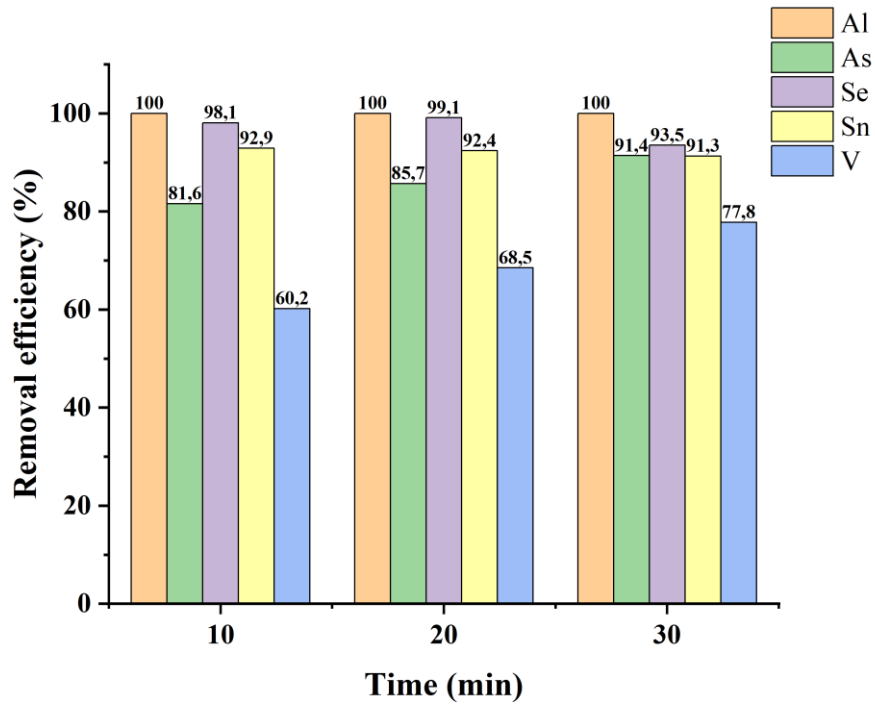


Figure 5. The time dependence of removal efficiency in tap water of selected heavy metals for MPS-2

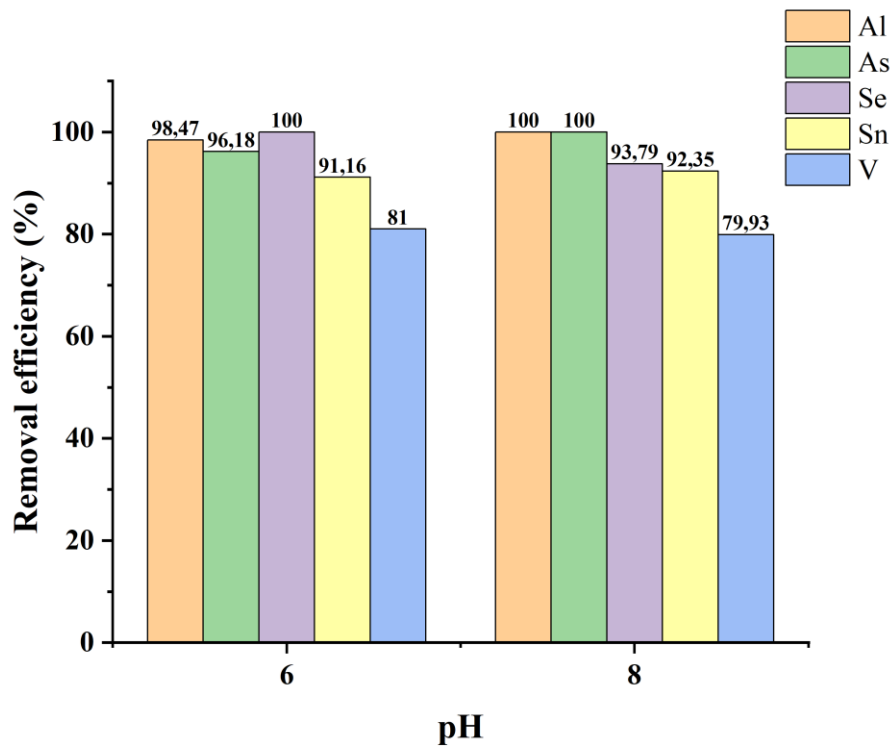


Figure 6. The pH dependence of removal efficiency in tap water of selected heavy metals for MPS-2

Table 6. ICP-MS analysis of river water samples for **MPS-1** (concentrations in ppm)

	Na	Mg	K	Ca	Fe	Sr
Filtered river water	32.988	7.911	1.173	11.674	0.070	0.229
10 min	15.850	3.512	0.571	5.322	0.027	0.082
RE%	51.95	55.61	51.27	54.41	61.14	64.32
20 min	17.296	3.908	0.942	5.930	0.021	0.090
RE%	47.57	50.60	19.63	49.20	70.12	60.50
30 min	16.461	3.735	0.546	5.479	0.018	0.089
RE%	50.10	52.79	53.47	53.06	74.50	61.09
pH 6	15.895	3.623	0.590	5.533	0.010	0.088
RE%	51.82	54.21	49.72	52.61	86.11	61.34
pH 8	40.966	1.338	0.713	2.739	0.021	0.044
RE%	0.00	83.08	39.24	76.54	69.39	80.83

Table 7. ICP-MS analysis of river water samples for **MPS-2** (concentrations in ppm)

	Na	Mg	K	Ca	Fe	Sr
Filtered river water	32.988	7.911	1.173	11.674	0.070	0.229
10 min	18.672	4.127	0.840	6.049	0.031	0.098
RE%	43.40	47.83	28.35	48.19	55.46	57.29
20 min	16.569	3.640	0.571	5.618	0.019	0.090
RE%	49.77	53.99	51.35	51.87	72.49	60.87
30 min	16.164	3.615	0.556	5.474	0.023	0.087
RE%	51.00	54.30	52.55	53.11	66.37	61.93
pH 6	16.378	3.819	0.602	5.726	0.023	0.090
RE%	50.35	51.73	48.69	50.95	66.58	60.62
pH 8	40.309	1.098	0.625	2.400	<LOD	0.037

RE%	0.00	86.12	46.74	79.44	0.00	83.67
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Table 8. ICP-MS analysis of River water samples for **MPS-3** (concentrations in ppm)

	Na	Mg	K	Ca	Fe	Sr
Filtered river water	32.988	7.911	1.173	11.674	0.070	0.229
10 min	16.572	3.562	0.557	5.461	0.015	0.084
RE%	49.76	54.97	52.47	53.22	77.87	63.11
20 min	16.280	3.576	0.584	5.410	0.019	0.084
RE%	50.65	54.80	50.24	53.65	72.43	63.15
30 min	16.674	3.657	0.539	5.538	0.017	0.089
RE%	49.46	53.77	54.01	52.56	75.12	60.96
pH 6	16.904	3.825	0.704	5.922	0.024	0.090
RE%	48.76	51.64	39.95	49.27	64.73	60.42
pH 8	39.488	1.112	0.571	2.511	<LOD	0.043
RE%	0.00	85.94	51.31	78.49	0.00	81.38

After the filtration of the river water, an adsorption experiment with the same methodology as tap water was conducted. As can be seen from Tables 6, 7, and 8, there are relatively high concentrations of Na, Mg, K, and Ca cations in river water which only affect water's hardness, but do not contribute to its toxicity. Approximately 50% of these metal cations were removed by all types of synthesized silica. The only two heavy metals, the concentrations of which were somewhat noticeable but still quite low, were Fe and Sr ions with 0.294 ppm and 0.841 ppm concentrations respectively, without dilution, while the concentrations of other heavy metals and toxic elements were negligible. This analysis of river water is not sufficient to analyze the effectiveness of MPS because only two heavy metal ions (Fe and Sr) were present. Nevertheless, Fe and Sr ions adsorbed approximately 70% and 60% respectively which is a good result for a 30 min adsorption. Fe adsorbed better under slightly acidic conditions (86%), while Sr adsorbed better at slightly basic conditions (80%). The effect of pH were investigated in the tap and river water samples. The effect of pH can be explained by the following reasons. First of all, at higher pH levels, the surface of SiO₂ becomes more negatively charged. This is due to the deprotonation of surface hydroxyl groups (Si-OH turning into Si-O⁻). Heavy metals, which are often in cationic forms (positively charged ions) in solutions, are attracted to these negatively charged sites on the SiO₂ surface. Secondly, the chemical forms (or species) of heavy metals in solution can change with pH. At higher pH, many heavy metals tend to form hydroxide species, which are less

soluble and more likely to adsorb onto surfaces like SiO₂. For example, lead (Pb²⁺) might form Pb(OH)₂ under higher pH conditions, which is more prone to adsorption.¹¹ Thirdly, at lower pH (more acidic conditions), more H ions are in the solution. These protons can compete with heavy metal cations for the adsorption sites on SiO₂. At higher pH, the concentration of H⁺ ions decreases, reducing this competition and allowing more heavy metal ions to be adsorbed.

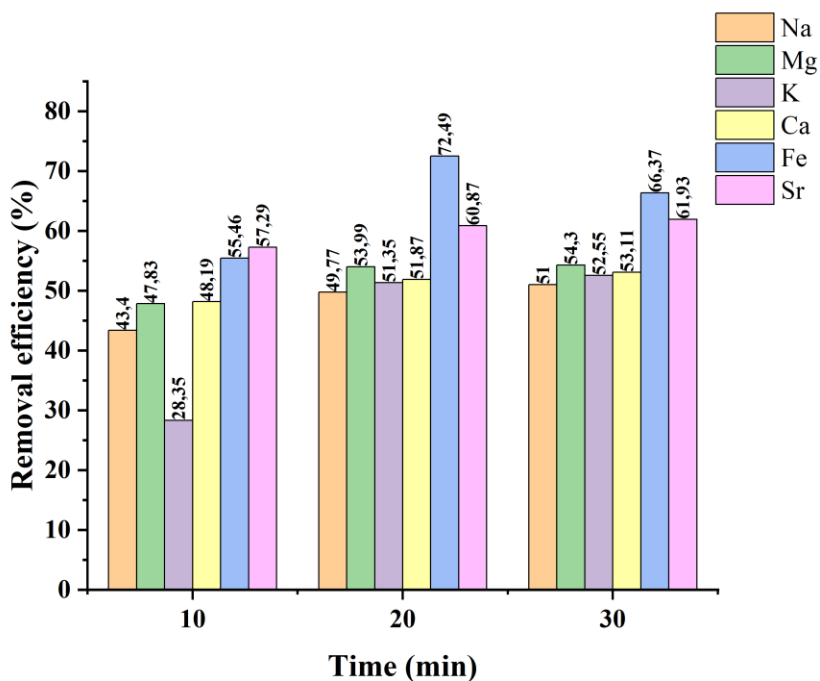


Figure 7. The time dependence of removal efficiency of selected metals for ICP-MS of river water samples with **MPS-2**

4. Conclusion

Water sources that suffer from heavy metal pollution could potentially be filtered using mesoporous silica (MPS) through the adsorption of heavy metals. The MPS was prepared with different added NaOH (2M) amounts, such as **MPS-1**, **MPS-2**, and **MPS-3**. Obtained MPS's adsorption performance tested with two parameters such as time and pH dependence. The **MPS-2** showed the best adsorption result in tap water where the removal efficiency was higher than 90%, while in the river water, the values were near 50%. The morphological characterization revealed that the **MPS-2** has an optimal nanoparticle size of 150 - 250 nm, while BET analysis showed slightly good porosity for **MPS-2** with the highest surface area and pore volumes while **MPS-3** demonstrated low porosity due to low surface area and pore sizes. The major effect of pH was observed because the adsorption should be higher at high pH values due to deprotonated silicon nanoparticles attracting more positively charged cations. As a result, the removal efficiency was higher at pH=8 than at pH=6.

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