TREATMENT OF WASTEWATER CONTAINING HEAVY METALS USING FILTERS MADE OF ADVANCED SILICA-BASED MATERIALS

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Mesoporous silica is a form of SiO_2 with relatively recent use in the field of nanomaterials for environmental protection. Given the hexagonal mesoporous silica structure, characterized by a high specific surface, well defined shape and dimensions of its pores, the interest in its absorbent and catalytic properties has increased.

In this context, mesoporous silica was synthesized by the hydrothermal method. The chemical composition and microstructural properties of the obtained materials were determined by X-ray fluorescence (XRF), electronic scanning microscopy (SEM) and X-ray diffraction (XRD) analysis, while the heavy metal retention efficiency was determined for wastewater containing Cu (II), Zn (II), Pb (II) and Ni (II) ions.

Keywords: mesoporous silica; SiO_2; heavy metals; filtration; environmental protection; wastewater treatment

1. Introduction

Due to the huge increase of industrialization, the wastewaters are loaded with important quantities of various pollutants such as heavy metals. The actual applied removal methods are not entirely satisfactory. Therefore, a new approach is needed. Taking into account the size of the wastewater treatment plants, removal parameters as production, maintenance cost and the efficiency of treatment, could be improved by introducing a thin mesoporous silica filter.

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In mean time, as the mesoporous based filters have a refreshment capability, their production price may be significantly lower than for a conventional filter. The obtained mesoporous silica could be considered an advanced material, meaning that an organic, inorganic or mixed chemical substance presents a specific composition with several tailored physical and chemical properties. In the current context, thermal processing of advanced materials is used in a very broad sense to cover all sets of technologies and processes for a wide range of industrial applications [1]. This refers to materials development with a specific application potential. Among the various technologies available today in advanced materials processing, hydrothermal technology occupies an unique place thanks to its advantages over conventional technologies [2].

Hydrothermal technology becomes one of the most important tools for advanced materials processing, especially due to its benefits in the processing of nanostructural materials, with applications in a wide range of technological domains, such as: electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biophotonics, etc. [1]. Nanomaterials require control over their physicochemical characteristics if they are used as functional materials. Because the size is downgraded to nanometric scale, the materials exhibit distinct and special properties due to the quantization effect, namely: increased mechanical strength, high surface area, increased diffusivity, specific heat and higher electrical resistivity compared to their coarse-grain counterparts [2]. For this investigation, the hydrothermal technique was used to synthesize the silica materials. The synthesis of mesoporous silica is often a linear process with a rather low degree of difficulty. The wet-chemical procedure applied for nanomaterials synthesis supposes a bottom-up approach [3].

Lately, a lot of efforts have been directed towards the design of selective heavy metal adsorbents for environmental cleanup [4]. Ordered mesoporous silicas were first reported in 1992. Since then, significant progress has been made in their morphology control, pore size adjustment, composition variation and application developments. During the last two decades, various mesoporous structures have been synthesized, which can be roughly classified into three categories based on the pore types: nearly spherical cage, cylindrical channel and bi-continuous channel [5], [6].

The mesoporous silica material prepared in the present work used poly (alkaline oxide) triblock copolymer as structure directing agent, has the largest pore size found for siliceous mesostructured materials [7], [8]. Therefore, the material synthesized in this research could be an ideal support for designing general purpose adsorbents. The proposed objectives of this paper were the SiO_2 nanomaterial synthesis and testing of the material's ability to act as adsorbent for the following metals: copper, nickel, zinc and lead present in wastewater.

2. Materials and methods

2.1. Materials and preparation of SiO_2 nanoparticles

Two types of SiO_2 nanopowders identified through codes: R2 and R4 with a well-defined hexagonal structure have been developed by varying both the number of reagents used in the synthesis process and the parameters of the synthesis process: mixing and contact time and the synthesis temperature. All reagents used and laboratory supplies were purchased from MERCK.

R2 / R4 synthesis

The surfactant, Pluronic P123 - Poly (ethylene glycol) – block – poly (propylene glycol) – block – poly (ethylene glycol), was dissolved in 2 mol/L hydrochloric acid solution, after which the TEOS (tetraethyl orthosilicate) silica precursor is added. The obtained solution was mixed for 6 h 20 min for R4 and 7 h for R2 at a temperature of 35 °C, respectively 40 °C. Subsequently, the hydrothermal treatment was applied at T=100 °C, for t=24 h. The mesoporous silica was washed on filter paper (MN 640 d) with distilled water and then calcinated at 500 °C - 550 °C for 5 h 30 min to remove the surfactant, finally resulting a white siliceous powder. The chemical compositions used to obtain the two varieties of mesoporous silica are presented in Table 1.

Table 1

Weight ratios of chemicals used to obtain mesoporous silica

Identification code	***P 123/TEOS***	***TEOS / HCl 2mol/L***	***HCl 2mol /L / Water***
R2	1/2	1/10	1/2
R4	1/2	3/1	4/1

In order to accomplish the efficiency tests, the two nanopowders, corresponding to R2 and R4, were pressed as pills. For each pill, it was used 1 g of nanopowder in order to obtain a thickness around 5 mm. To ensure the compaction of without loss of material upon contact with water and at the same time not to deform the filamentous structure of SiO_2 particles, the applied pressure was of 200 daN, for 15 min.

2.2. Characterization techniques

In order to characterize the obtained SiO_2 nanoparticles and the wastewater water, a series of analysis were performed: X-ray fluorescence, X-ray diffraction, scanning electron microscopy (SEM) and respectively, atomic absorption analysis (AAS).

For X-ray fluorescence measurements, Rigaku Supermini equipment was used to perform a qualitative analysis of the obtained nanomaterials, allowing a rapid evaluation of the oxide composition.

X-ray diffraction studies were performed with a Bruker D8 Advance applying for 2θ a range between 0-10° in order to obtain precise information on

the chemical composition and crystalline structure of the obtained nanomaterials. SEM micrographs were performed on a HITACHI SU-70 FE-SEM to determine the morphology and granulometric distribution of SiO_2 nanoscale crystals. For the quantitative determination of the chemical elements in the wastewater filtered with the developed nanomaterials, the Atomic Absorption Spectrometer (HRCS-AAS ContrAA 700, Analytik Jena) was used.

3. Results and discussion

Following the X-ray fluorescence analysis, the oxidic composition of mesoporous silica was determined, as shown in Table 2. The proportions over 99.5% SiO_2 proved the accuracy of the synthesis process and the advanced purity of the precursors used.

Table 2

Oxidic composition of mesoporous silica determined by XRF

Structure	***Major element – SiO_2 (%)***
R2	99.6886
R4	99.6868

The mesoporous silica crystalline phase formation (hexagonal structure) was investigated by X-ray diffraction. The XRD pattern for R2 silica nanopowder is presented in Fig. 1, while for R4 silica nanopowder, the XRD pattern is shown in Fig. 2.

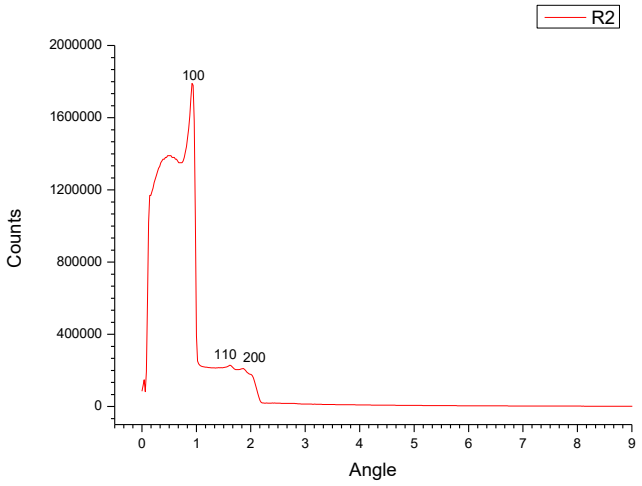


Fig. 1. X-ray diffractogram of R2 structure

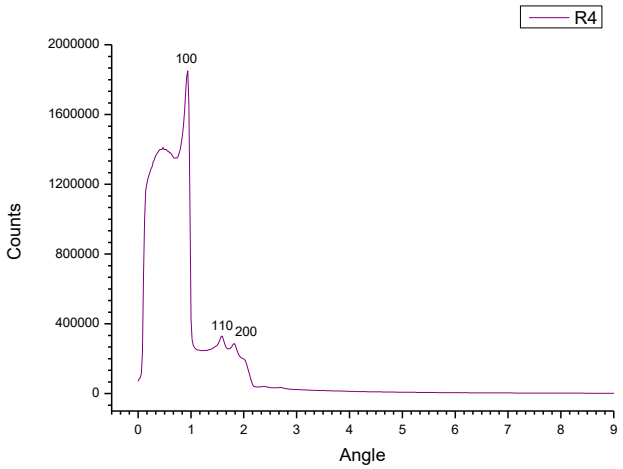
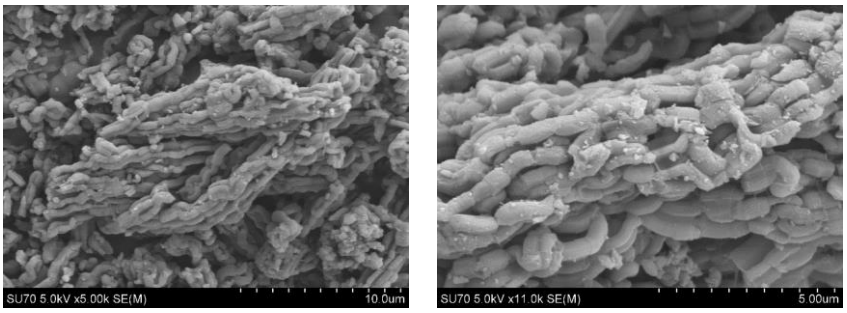


Fig. 2. X-ray diffractogram of R4 structure

The hexagonal array of the matrix shown in the XRD profiles for both R2 and R4 was identified at low angles (2θ = 0-5°). The two low intensity peaks at 2θ = 1-2° and the high intensity peak at 2θ = 0.8-0.9° are specific for the ordered hexagonal structure of SiO_2. This behavior is similar to the one reported in literature [9], [10], when it was obtained a modified mesoporous silica material SBA-15 with amino functional group ($–NH_2$) for adsorbing heavy metal ions from aqueous solutions.

The SEM micrographs for the two developed materials (R2 and R4) put in evidence that following the complete hydrolysis of the silica precursor (TEOS), occurred the micelles' transition from spheres to bars, forming short, cylindrical micelles. They continued to lengthen and form long, filamentous micelles. During condensation, they have become more and more straight-lined and less flexible. The long filamentous micelles have grown unidirectional, determining a specific structure for obtained mesoporous silica.



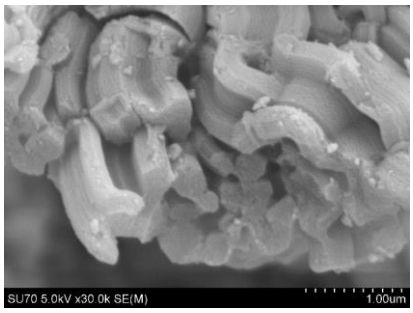


Fig. 3. SEM images for SiO_2 nanoparticles - R2

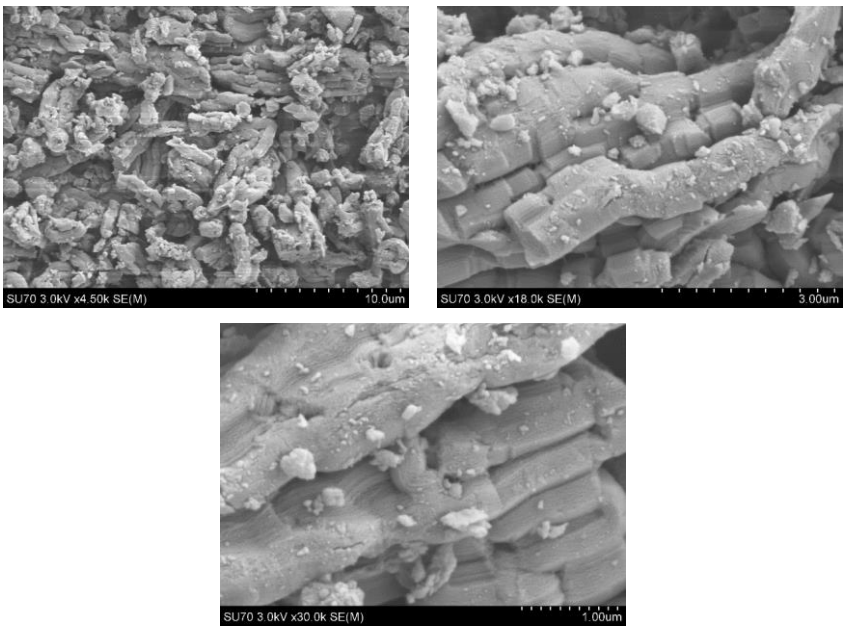


Fig. 4. SEM images for SiO_2 nanoparticles - R4

In order to perform the testing of the previously synthesized SiO_2 nanoparticles by determining the removal efficiency of heavy metals from wastewater, a synthetic wastewater was used. This water was obtained in the laboratory by enriching samples from the Danube River with various concentrations of Cu, Ni, Pb and Zn, at weak basic pH, about 8.

In order to determine the functionality of the two different nano-SiO_2 obtained in terms of heavy metals adsorption capacity, a series of preliminary tests were carried out using the pressed pills. The results of the first set of tests are introduced in Table 3. The experimental data have been determined through AAS method.

In Fig. 5 it could be followed the retention efficacy for R2 and R4. It can be observed that for the R2, the retention efficiency was over 99% for Pb and Zn (below the detection limit), 94.9% for Cu and 54.42% for Ni. For the R4, the

retention efficiency was 98.06% for Pb, 92.76%for Zn, 76.36% for Cu and 25.2% for Ni.

Table 3

Preliminary results of the heavy metals retention for R2 and R4

Heavy metals	***Cu, mg/L***	***Ni, mg/L***	***Pb, mg/L***	***Zn, mg/L***
Wastewater	**0,1844**	**0,9441**	**0,2571**	**1,1250**
R2	0,0094	0,4303	bdl*	bdl*
R4	0,0436	0,7062	0,0050	0,0814

*below the detection limit

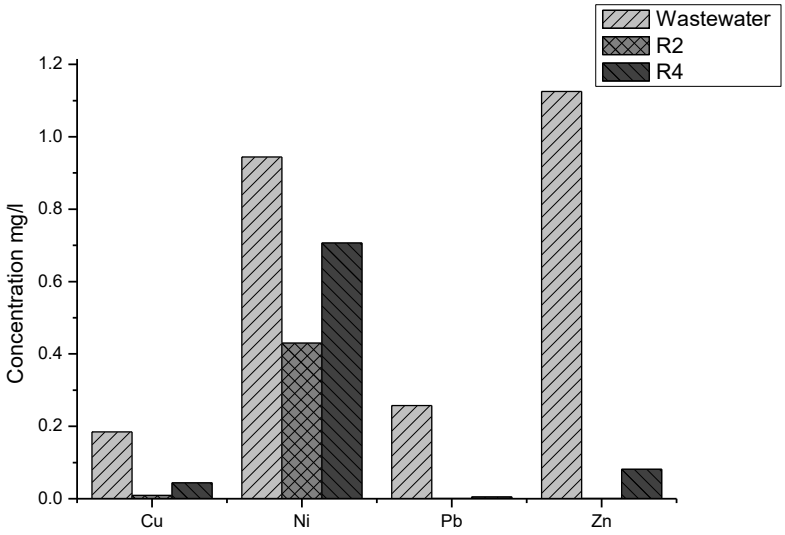


Fig. 5. Variation of the heavy metal retention efficiency for R2 and R4

In order to establish the repeatability of the results as well as to determine the retention efficiency after several passes of heavy metal loaded water, a set of tests were performed on the two nano-SiO_2 obtained for three consecutive passes of the wastewater. The results are presented in Table 4.

Table 4

The results of heavy metals retention for R2 and R4 for three passes of the heavy metal loaded water

Heavy metals	***Cu, mg/L***	***Ni, mg/ L***	***Pb, mg/ L***	***Zn, mg/ L***
Wastewater	**0,0854**	**0,8094**	**0,0446**	**0,4853**
R2-1pass	0,0218	0,6157	0,0208	0,1778
R2-2passes	0,0157	0,6427	0,0033	0,0010

R2-3passes	0,0115	0,7085	0,0019	0,0007
R4-1pass	***0,0164***	***0,4438***	***0,0065***	***0,0167***
R4-2passes	***0,0114***	***0,6984***	***0,0024***	***0,0011***
R4-3passes	***0,0110***	***0,7005***	***0,0002***	***0,0011***

In Figs. 6 to 9 are presented the retention efficiencies recorded for each of the obtained SiO_2 structures, R2 and R4, for three passes of the wastewater containing loads of heavy metals.

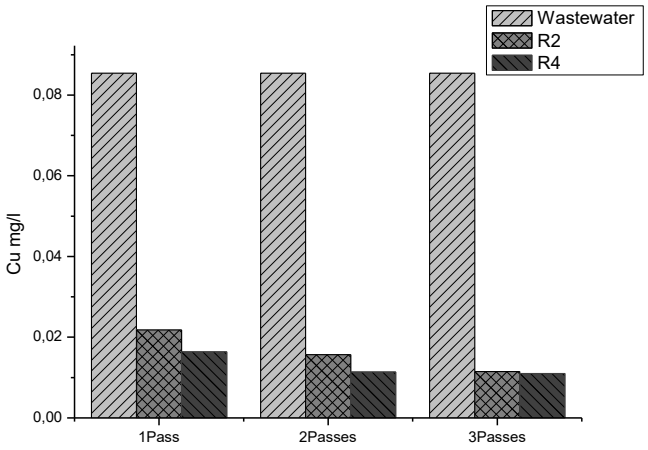


Fig. 6. Variation of Cu retention efficiency for R2 and R4 for three passes

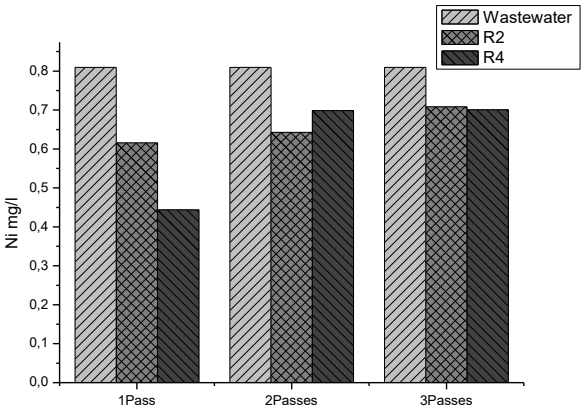


Fig. 7. Variation of Ni retention efficiency for R2 and R4 for three passes

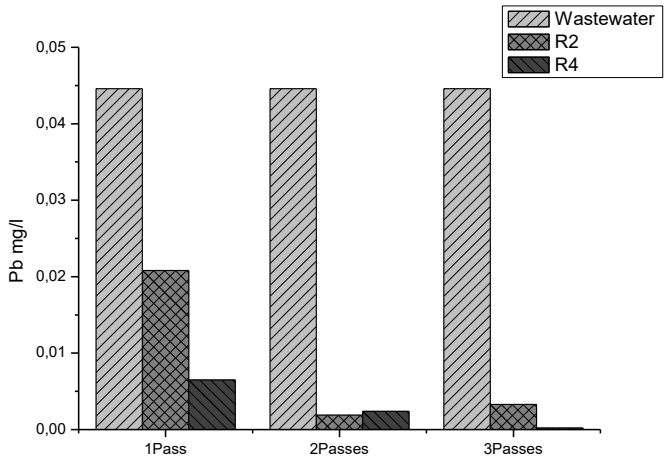


Fig. 8. Variation of Pb retention efficiency for R2 and R4 for three passes

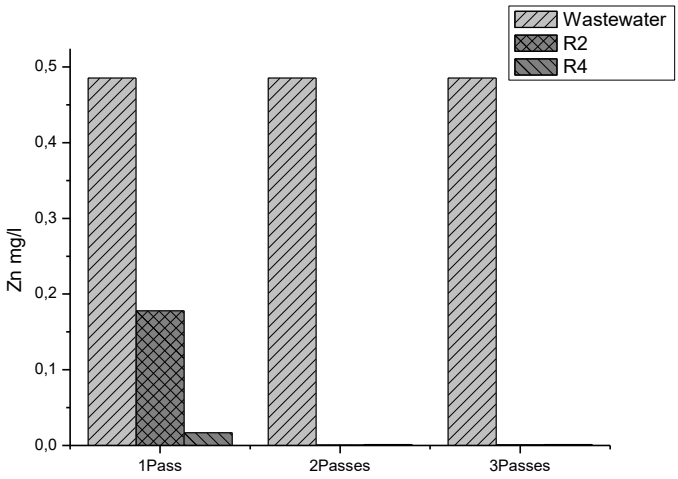


Fig. 9. Variation of Zn retention efficiency for R2 and R4 for three passes

It can be observed that for both SiO_2 nanoparticles obtained, R2 and R4, the filtration efficiency for Zn and Pb after three passes is over 99% (below the detection limit), for Cu about 87%, while for Ni, similar to the preliminary tests, the retention efficiency is lower, 24% for R2 and 45% for R4. Compared to other heavy metals (Zn, Pb and Cu), Ni retention efficiency decreases with each passing of wastewater because of the gradual coverage of the adsorbent silica surface with the tested heavy metal ions.

6. Conclusions

In this work it was successfully synthetized the hexagonal ordered mesoporous silica by hydrothermal method. Considering the resulted filtration efficiencies, it is highlighted that the two SiO_2 nanopowders obtained through the two paths presented were conducted in optimal synthesis conditions. In addition, their hexagonal structure, highlighted by SEM and XRD analysis, proves high adsorption properties for three out of four tested metals (Cu, Pb and Zn) in slight basic medium. There have been recorded unsatisfactory results for Ni removal from waste waters - retention efficiency for Ni for both R2 and R4 was 24%. Therefore, it is recommended the usage of a different absorbent material system [11].

R E F E R E N C E S

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