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SCIENTIFIC PAPER

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RECYCLE OF GOLD MINE TAILINGS SLURRY INTO MCM-41 MESOPOROUS SILICA WITH HIGH SPECIFIC SURFACE AREA

Article Highlights

- MCM-41 was synthesized from tailings slurry from gold mine treatment plant for the first time
- Reaction time, temperature, and pH adjustments played a significant role in the synthesis
- The optimum condition was found to be at 30°C for 60 minutes with a pH of 11
- The sample synthesized at optimum condition had a high surface area
- The structural properties were found to be close to those obtained from a pure silica source

Abstract

In this study, MCM-41 was prepared from the gold mine tailings slurry as an alternative silica source. The effects of the reaction time, temperature, and pH adjustments on the synthesis of MCM-41 were investigated. The optimum condition for the synthesis process of pure and highly ordered MCM-41 from tailings slurry was found to be at 30 °C for 60 min with a pH of 11. In addition, MCM-41 was synthesized from a pure silica source, in order to compare the structural properties of the obtained sample from that of the slurry produced at optimum conditions. The samples synthesized from tailings slurry had a high surface area of 983 m^2/g and a pore volume of 0.74 cm^3/g. The structural properties of the samples produced from the slurry were closely related with those that were synthesized from a pure silica source. Results indicate that the tailings slurry has the potential to be used as a cheap, alternative silica source which can be used for the synthesis of a pure and ordered mesoporous silica MCM-41.

Keywords: MCM-41; synthesis; waste treatment; gold mine.

Since the new family of mesoporous molecular sieves, known as M41S, was discovered in 1992 by researchers at the Mobil Oil Corporation, mesoporous molecular sieves have attracted much attention by scientific research projects and for practical applications [1]. The main driving force for researchers' attention to M-41 has been the numerous potential applications for use in different fields, such as catalysis and adsorption [2].

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M41S family members have pore sizes that can vary within a range of 15-100 Å, and wide surface areas. The M41S family has three main members classified by their different structural features: 3-D cubic pore structured, MCM-48; 1-D hexagonal pore structured, MCM-41; and the unstable pore layer structured, MCM-50 [3]. Among all the M41S members, MCM-41 has been receiving much attention due to its peculiar characteristics of being unidirectional and having a hexagonal, honeycomb-like structure. Owing to this well-formed structure, which provides a high specific surface area and pore volume, uniformity and controllability of pore size, MCM-41 has become a remarkable member of the M41S family [2,4-7].

MCM-41 is produced in aqueous, alkaline conditions using three main components: structure-directing surfactants, a source of silica, and an acidic or

base catalyst [7]. Typical silica sources include sodium silicate, tetraethyl orthosilicate (TEOS) [8], tetramethylammonium silicate (TMA-silicate) [9], alkosilanes, alkylamines, sodium water glass, and fumed silica [10]. The high costs of synthesizing MCM-41 materials have mainly been attributed to the costliness of its templates which promote the need for using a cheap silica sources in lieu of more expensive ones for synthesis [10,11].

Scientists have considered waste products such as rice husk, bottom ash, fly ash, and iron ore tailings for the synthesis of MCM-41 [12-14]. Unbeknownst to this project group, no effort had previously been directed to introduce a synthesis of MCM-41 from tailings slurry. A tailings slurry with a high content of SiO_2 can be obtained from the treatment plant of a gold mine [15]. Every year, approximately 277.882 t of tailings slurry is produced during the extraction processes of gold at gold mine treatment facilities [16]. Thus, the conversion of the slurry into usable products is rather important for helping solve environmental and economic issues.

In this paper, the novel synthesis of MCM-41 from Bergama Ovacık Gold Mine's tailings slurry and the influences of synthesis parameters are reported for the first time. The reaction time, temperature, and pH were varied. The influences of these parameters on the synthesis of MCM-41 were investigated by XRD analysis. In addition, textural and morphological properties of synthesized MCM-41 at optimum reaction conditions were carried out. For the comparison of the structural properties of the obtained sample, MCM-41 was also synthesized from a pure silica source.

EXPERIMENTAL

Materials

For usage in this study, the tailings slurry was supplied from the Bergama Ovacık Gold Mine Treatment Plant in Turkey. The tailings slurry was composed of SiO_2 (77.70%), Al_2O_3 (12.10%) and small amounts of other metal oxides [17]. It was used in this study without any reduction or elimination of impurities. Hexadecyltrimethylammonium-bromide (HDTMA-Br, Merck) was used as a surfactant. Sulphuric acid and sodium hydroxide were purchased from Merck chemicals. All materials were used as received. Tetraethyl orthosilicate (TEOS, Merck, 99% pure) was used as a pure silica source.

Characterization

Powder X-ray diffractograms of samples were recorded on a Philips Panalytical X'Pert-Pro diffractometer using CuKα (λ = 0.15406 nm) radiation. The diffraction data were recorded in the scanning range of 2θ = 0.58–8° for small angle XRD (SAXRD) and 2θ = 5–80° for wide angle XRD (WAXRD) with a scanning speed of 1°/min. The concentrations of Si and Al of the synthesized sample from slurry at optimum conditions were analyzed using a Perkin Elmer Optima 2100 DV inductively coupled plasma optical emission spectrometry (ICP-OES) device. Nitrogen physisorption measurements of synthesized MCM-41 samples from slurry and pure silica sources were carried out at 77 K using a Micromeritics ASAP 2020 surface area and porosimetry analyzer. The pore size distributions and pore volumes were calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption isotherm. Prior to the experiments, samples were outgassed under vacuum at 300 °C. The morphology of products was observed using a CamScan Apollo 300 scanning electron microscope (SEM). High resolution transmission electron microscopy (HRTEM) observations were carried out by a JEOL-2100 HRTEM.

The extraction of silicon (Si)

Extraction of silica from tailings slurry. Tailings slurry used in this study was obtained from the Bergama Ovacık Gold Mine Treatment Plant in Turkey. The slurry was prepared according to the previous study [17]. Extraction of silica (Si) from tailings slurry was studied in fusion method [18]. The fusion process was performed by mixing slurry and sodium hydroxide at a ratio of 1:1. The extracted solution was examined with Perkin Elmer Optima 2100 DV ICP-OES. The amounts of Al, Si and Na in the solution were 1145, 28030 and 72800 mg L^{-1}, respectively. The Si/Al ratio of 24.48 in the extracted solution was close to the best quality MCM-41 obtained from the extracted solution of fly ash, which has the highest Si/Al ratio [19].

Synthesis of MCM-41 from tailings slurry and pure silica

HDTMA-Br surfactant was added into distilled water under ultrasonic irradiation at different temperatures (30, 40, 50, 60 and 70 °C) for determining the influence of temperature on the synthesis process of MCM-41. After the solution became clear, Si solutions obtained from a fusion process were added into the mixture. Stirring under ultrasonic irradiation was continued for different reaction times (15, 30, 60, 90 and 180 min) for determining the influence of time on the synthesis process. After reaction times were finished, the pH adjustments were carried out with sulphuric acid for different acidic and base pH values for determining the influence of pH on the synthesis process.

Precipitation was observed during the pH adjustment. Three different synthesis parameters were examined using a one-factor-at-a-time approach [20]. After the pH adjustments, the samples were stored for 24 h at room temperature and then the precipitated products were filtered. The filtered products were washed thoroughly with distilled water, dried in oven for a day, and calcined at 550 °C for 6 h for removal of residual surfactants.

After preparing MCM-41 from slurry at optimum conditions, the synthesis of MCM-41 was performed using a pure silica source for comparison. Firstly, HDTMA-Br was dispersed in distilled water under ultrasonic irradiation at 30 °C. The designated amount of 1 M of sodium hydroxide solution was added. Next, TEOS was added into the mixture drop by drop. After 60 min, the pH value of the sample was adjusted to 11. Finally, the solution was kept at room temperature for 24 h. The precipitated solid was separated by filtration and washed with distilled water and then dried at room temperature. The remaining surfactant was removed through calcination at 550 °C for 6 h. The synthesized samples obtained from slurry at optimum conditions and pure silica accordingly were hereafter labeled as M-41-S and M-41-PS, respectively.

RESULTS AND DISCUSSION

Effects of reaction parameters on the synthesis of MCM-41

In order to investigate the effects of the reaction parameters on the formation of the MCM-41 materials, different syntheses were conducted by individually changing and testing the parameters. The values of the reaction parameters were chosen according to which were related to the synthesis of mesoporous materials in the literature [12,21-23].

Effects of reaction time. In order to study the effects of the reaction time on the synthesis of MCM--41, the synthesis experiments with different reaction times (15, 30, 60, 90 and 180 min) were performed, whereas the other variables were held constant (temperature 50 °C and pH 11). Figure 1 reveals the XRD patterns of the samples that were produced at different reaction times. A strong intensity peak (100) directly indicates the presence of the MCM-41 structure, and the two weak intensity peaks (110) and (200) can be indexed on a hexagonal structure with 2-D hexagonal p6mm symmetry [24]. As shown in Figure 1, MCM-41 mesoporous material was obtained from samples synthesized at 30, 60, 90 and 180 min, whereas it was not obtained from sample synthesized at 15 min. Compared to other samples peaks, the diffraction peaks of the sample synthesized at 60 min

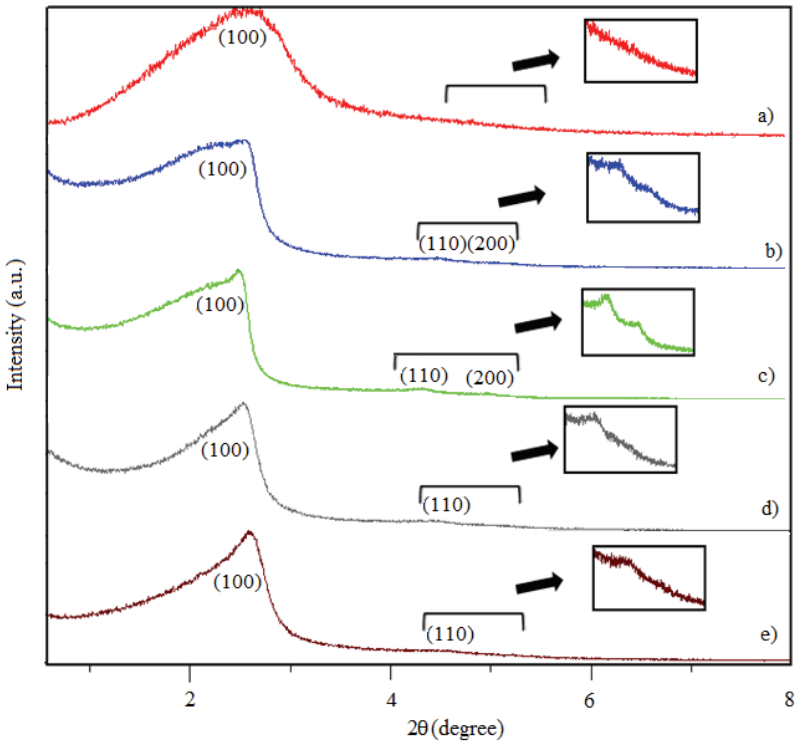


Figure 1. XRD patterns of the synthesized samples at different reaction times: a) 15, b) 30, c) 60, d) 90 and e) 180 min.

were sharp and well-resolved, which was interpreted as an indication of a higher ordering of the mesopore channels [22,25].

In order to verify such improvement in the degree of ordering, hexagonal unit cell parameters (a_0) values are calculated using the following equation [26]:

$$a_0 = 2d_{hkl}/\sqrt{3} \quad (1)$$

In this equation, d_{hkl} was obtained from the peak in the XRD pattern using Bragg's equation ($2\lambda d\sin\theta$, where $\lambda = 0.15406$ nm was used for the CuKα line. The value of a_0 was equal to internal pore diameter plus the wall thickness of one pore [6,21,26]. The sample with the highest a_0 value resulted in the best quality product. It should be noted, however, that according to Hui and Chao that there are no rules for the assertion of the incorporation of the metal ions within the MCM-41 structures, due to its amorphous structure in which the bond lengths and the angles of the metal ions on the silica surface is fluctuating. Furthermore, they also explain that the size of the cations and their coordination states play important roles for the possibility of their incorporation into the skeleton [11]. The a_0 values of the synthesized samples were given in Table 1. It was seen that the a_0 value of the synthesized sample started to decrease by time after 60 min, that is, longer reaction time made the pore size decrease [27]. The best quality product (with maximum a_0 values) was found as the sample synthesized at 60 min.

Effects of reaction temperature. In order to study the effects of the reaction temperature on the synthesis of MCM-41, synthesis experiments were carried out at different temperatures (30, 40, 50, 60 and 70 °C), whereas the other variables were held constant (time 60 min and pH 11). Figure 2 shows the XRD patterns of the samples that were produced at different reaction temperatures. As shown in the figure, MCM-41 mesoporous material was obtained from all samples. Compared to the other samples peaks, the diffraction peaks of the sample synthesized at 30 °C were sharp and well-resolved, which can be interpreted as an indication of a higher ordering of the mesopore channels [22]. The a_0 values of the synthesized sample at 30, 50 and 60 °C were calculated as 41.16, 40.12 and 37.59, respectively. Consequently, the best quality product (with maximum a_0 values) was found to be the sample synthesized at 30 °C.

Effects of pH value. Figure 3 shows the XRD patterns of the samples that were produced at low and high pH values whereas the other variables remained constant (time 60 min and temperature 30 °C). Only the samples at pH 2, 3 and 3.5 exhibited a diffraction peak relative to the (100) plane while diffractions corresponding to other peaks found at higher angles were not observed (Figure 3a). A poor crystallinity of the material and the distortion of the long range ordering of the mesoporous structure which may or may not include poorly structured hexagonal arrays are typically indicated by a broader and less intense main peak [25]. According to this, it was understood that ordered, hexagonally structured MCM-41 mesoporous material was not obtained under an acidic medium. On the other hand, it was successfully obtained from the samples that were synthesized at pH 10 and 11 which contained the three characteristic peaks with a better definition and higher intensity. Compared to other samples peaks, the diffraction peaks of sample synthesized at pH 11 were sharp and well-resolved, which can be interpreted as an indication of higher ordering of the mesopore channels [22]. The a_0 values of the synthesized sample at pH 10 and 11 were calculated as 39.94 and 41.16, respectively. Consequently, the best quality product (with maximum a_0 values) was found to be the sample synthesized at pH 11.

Characterization of M-41-S and M-41-PS

The SAXRD and WAXRD patterns of the synthesized samples are given in Figure 4. It was seen that all samples demonstrated three well-resolved characteristic diffraction peaks, which suggested that there are ordered hexagonal mesoporous structures in the SAXRD patterns. According to the WAXRD patterns of samples, only a broadened diffraction peak can be observed, which confirms the existence of amorphous silica, the samples are composed of only one phase.

The amounts of Si and Al of the M-41-S were found as 210380 and 15740 mg kg^{-1}, respectively. In our previous study, it was found that Si/Al ratio and Si content, thereby chemical composition of waste play

Table 1. Values of d_{100} peaks and a_0 of samples synthesized at different reaction times, temperatures, and pH

Parameter	Reaction time, min				Temperature, °C			pH		
	30	60	90	180	30	50	60	2	10	11
2θ / °	2.6010	2.5428	2.5446	2.6558	2.4787	2.5428	2.7143	2.8982	1.9815	2.4787
d_{100}	33.9678	34.7449	34.7208	33.2667	35.6466	34.7449	32.5504	30.4604	34.5855	35.6466
a_0	39.2226	40.1199	40.0921	38.4131	41.1611	40.1199	37.5860	35.1726	39.9359	41.1611

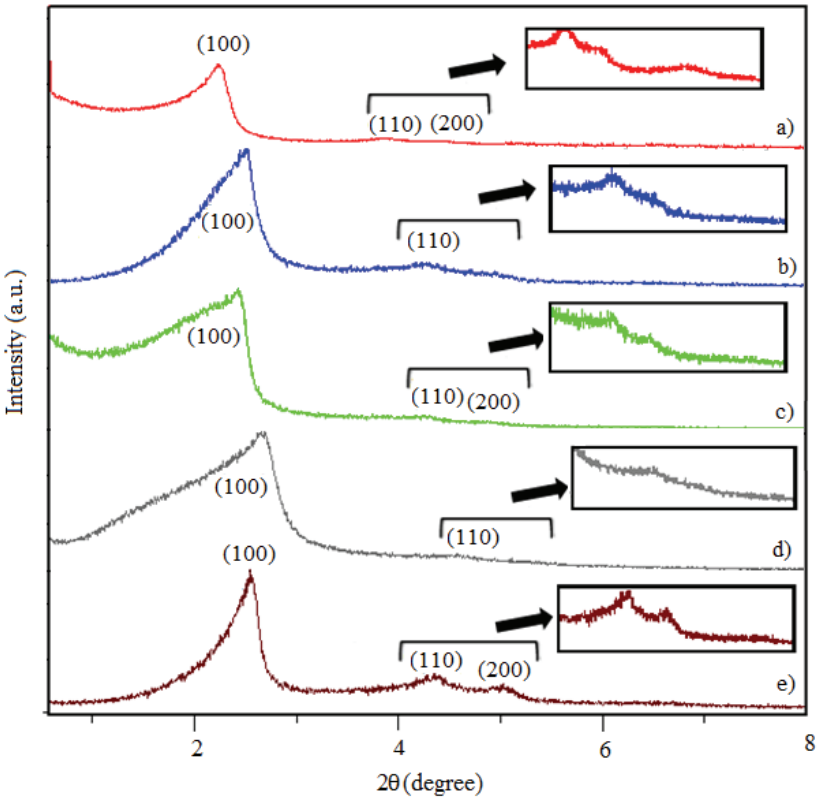


Figure 2. XRD patterns of the synthesized samples at different reaction temperatures: a) 30, b) 40, c) 50, d) 60 and e) 70 °C.

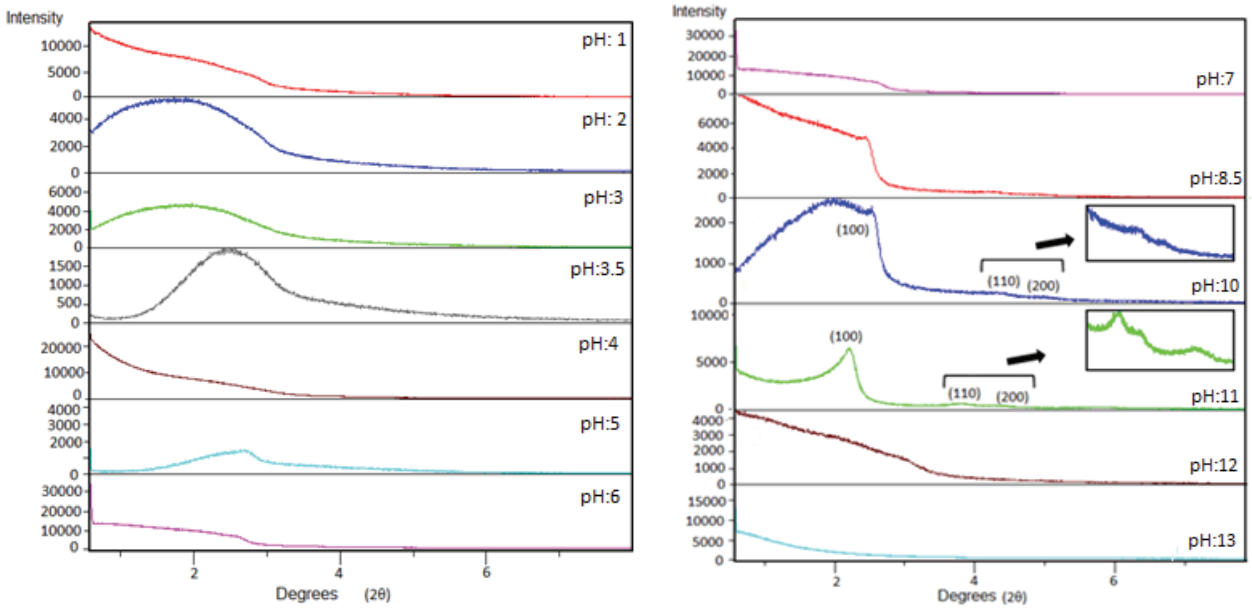


Figure 3. XRD patterns of the synthesized samples at a) low and b) high pH values.

a significant role in the synthesis of ordered MCM-41. The minimum Si/Al ratio was found as 10.30 to synthesize of highly ordered MCM-41 [19]. Chang *et al.* demonstrated that MCM-41 from fly ash can be synthesized with an Si/Al of 13.4 [28]. In the present study, it can be seen that highly ordered MCM-41 with an Si/Al ratio 13.37 was successfully synthesized from slurry.

The nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of

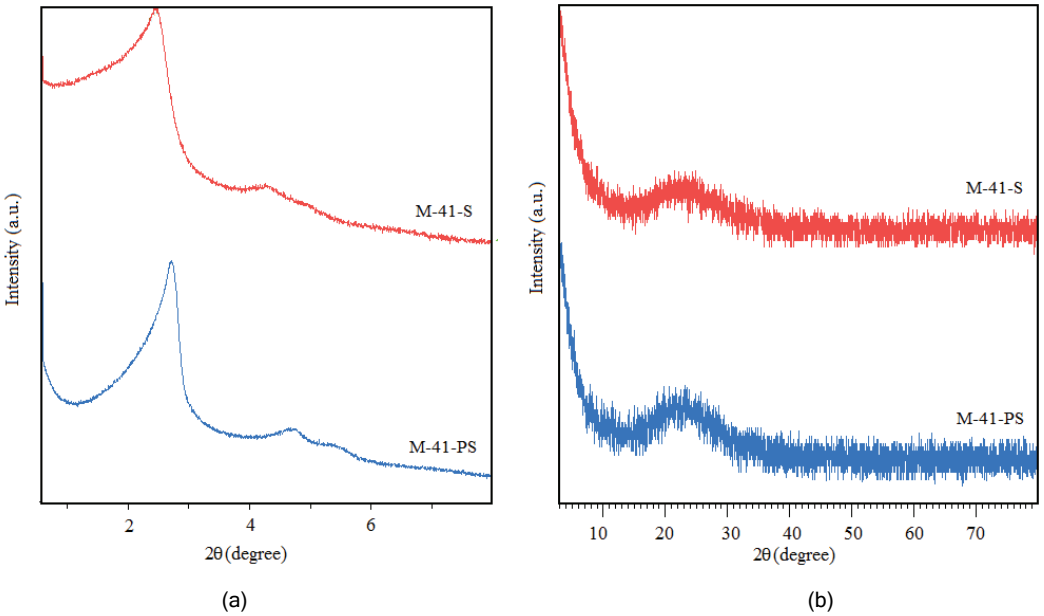


Figure 4. XRD patterns of the samples: a) small and b) wide angle.

M-41-S and M-41-PS are shown in Figure 5. The nitrogen sorption isotherm of M-41-S had the type IV shape, typical of a uniform mesoporous material. The sharp inflection between the relative pressures of 0.25-0.45 is attributed to the uniformity of pore size distribution. The adsorption isotherm for M-41-PS, with its S-shape, was similar to the previous studies [29,30]. It also displays a larger adsorbed volume than the M-41-S. The BJH pore diameter distributions of M-41-S and M-41-PS are relatively narrow with a maximum at 2.89 and 2.93 nm, respectively. The specific surface area and pore volume of samples were found as being 983 and 0.74 cm^3/g for the M-41-S, as 1223 and 0.83 cm^3/g for M-41-PS. Although, the textural properties of M-41-S were inferior to those of M--41-PS, to the best of the authors' knowledge, the surface area of M-41-S had the highest BET surface area obtained for MCM-41 samples synthesized from different wastes [12-14].

SEM and HRTEM images of the samples are shown in Figure 6a and b. It can be seen that the morphological features of the M-41-S were quite simi-

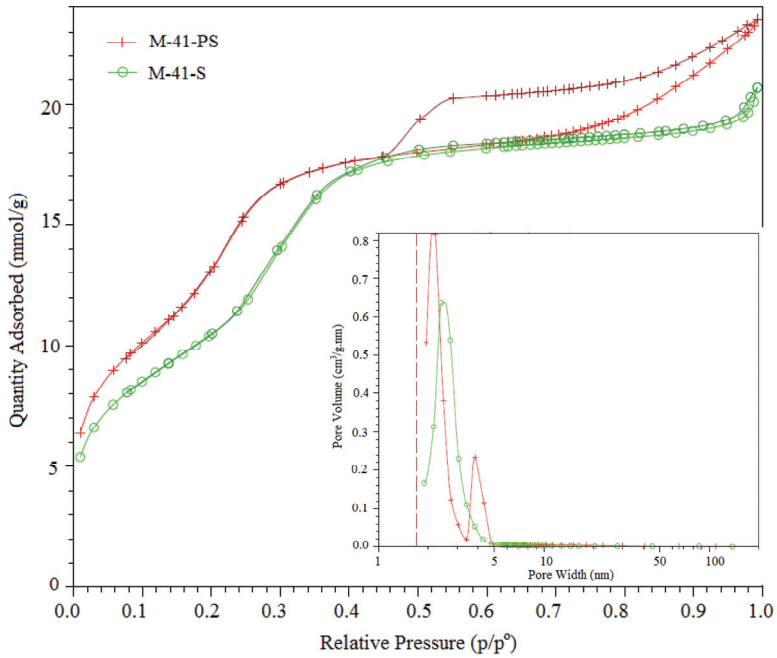
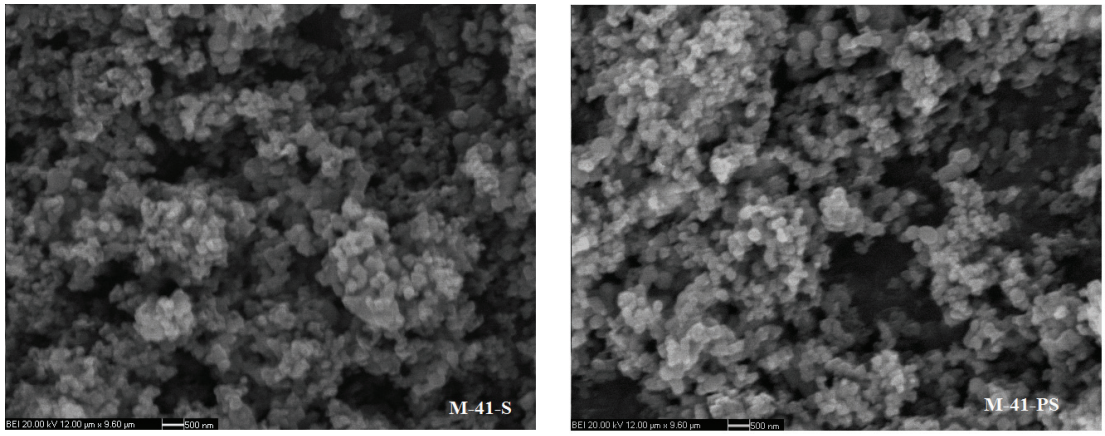
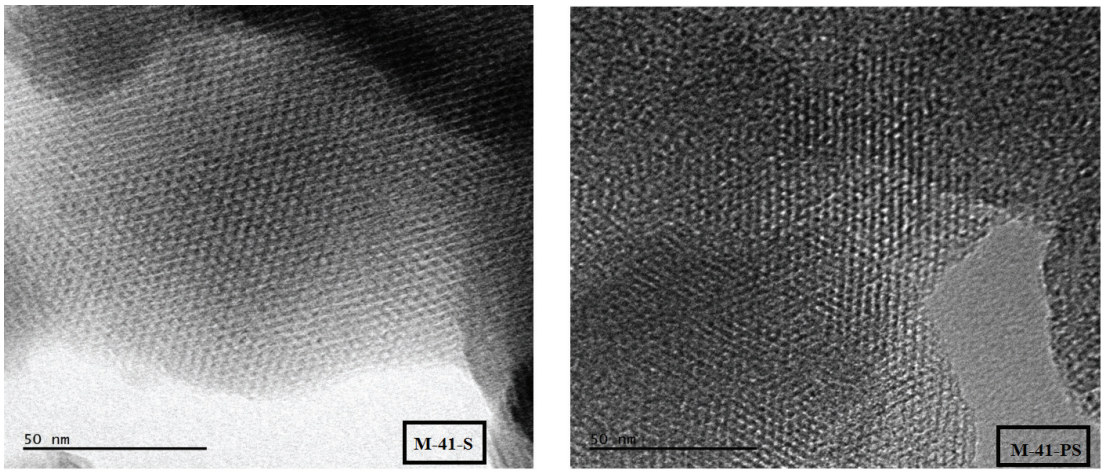


Figure 1. XRD patterns of the synthesized samples at different reaction times: a) 15, b) 30, c) 60, d) 90 and e) 180 min.



(a)



(b)

Figure 6. Images of the samples: a) SEM and b) HRTEM.

lar to M-41-PS. SEM images indicate that the samples displayed spherical shaped particles with a size of <0.4 μm and non-spherical, irregularly agglomerated particles which were similar to those reported in previous studies [31]. HRTEM images show the well--ordered hexagonal arrays of uniform channels. The pore size of the samples was determined as approximately 2.60 nm for the M-41-S and 2.75 nm for the M-41-PS, consistent with the result of nitrogen adsorption analysis.

CONCLUSIONS

Ordered MCM-41 molecular sieves were successfully synthesized from tailings slurry, as a source of silica. The results demonstrate that the reaction parameters (reaction time, temperature and pH value) played a significant role in the synthesis of the ordered mesoporous silica MCM-41. The best quality MCM-41 was obtained under the following conditions: a reaction time of 60 min at 30 °C and a synthesis pH of 11, which were confirmed by XRD analysis. The prepared MCM-41 at optimum reaction conditions has high specific surface area (983 m^2/g) and a total pore volume (0.74 cm^3/g). Structural properties of the samples obtained from slurry were found to be close to those obtained by pure silica source. In view of environmental and economic aspects, the synthesis of MCM-41 from tailings slurry may provide solutions to the disposal problem of slurry and recycle the waste into a useful material.

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NAUČNI RAD

RECIKLAŽA JALOVINE IZ RUDNIKA ZLATA U OBLIKU MEZOPOROZNE SILIKE MCM-41 SA VELIKOM SPECIFIČNOM POVRŠINOM

U ovom radu je pripremljena silika MCM-41 iz suspenzije jalovine rudnika zlata kao alternativnog izvora silicijum oksida. Proučavani su efekti vremena reakcije, temperature i pH sintezu silike MCM-41. Utvrđeni su sledeći optimalni uslovi sinteze čiste i visoko organizovane MCM-41 iz jalovine: vreme reakcije od 60 min, temperatura 30 °C i pH 11. Pored toga, silika MCM-41 je sintetisana iz čistog izvora silicijum oksida, kako bi se uporedile strukturna svojstva dobijenog uzorka sa uzorkom koji je sintetisan iz jalovine pod optimalnim uslovima. Uzorci sintetizovani iz jalovine imaju veliku specifičnu površinu od 983 m^2/g i zapreminu pora od 0,74 cm^3/g. Strukturna svojstva uzoraka proizvedenih iz jalovine su bila vrlo slični svojstvima uzoraka sintetisanih iz čistog silicijum-oksida. Rezultati pokazuju da jalovina može da se koristi kao jeftini, alternativni izvor silicijum oksida za sintezu čiste i organizovane mezoporozne silike MCM-41.

Ključne reči: MCM-41, sinteza, tretman otpada, rudnik zlata.