Utilization of nanosize spent oil shale for water treatment: application of top-down nanonization technology for solid residues

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Received: 15 March 2022 / Accepted: 4 June 2022 / Published online: 11 June 2022
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Abstract
Since the dawn of nanoscience, producing nanomaterials in a simple, low-cost, and high-yield manner has been a major issue. For the commercial manufacturing of nanomaterials, various bottom-up and top-down methodologies have been established. High-energy dry ball milling is widely used for the production of diverse nanomaterials, nanograins, nanoalloys, and nanocomposites. Physical grinding of inorganic solid waste into nanosize (1–100 nm) has improved their industrial applications particularly as water adsorbent. Application of nanosize spent oil shale by top-down methodology as adsorbent for phenol is addressed in the current research. The collected spent oil shale (SiO2 and Al2O3 making 45% of the material) has microstructure with average particle size of 56.6 μm. The dry grinding was performed in a vibrating ball mill at various grinding time (5–150 min) while keeping the grinding parameters constant including number of balls, ball size, total mass, vibration frequency, and amplitude. Upon grinding, the mean particle diameter of the bulk material was reduced to 191.8 and 85.2 nm using 0.5 and 0.1 mm grinding balls, respectively. The effect of grinding time on particle size and surface area was investigated; both particle size and surface area were not affected after 60 min of grinding. Physical grinding by 0.1 mm balls has notably improved surface area and total pore volume by 52% and 62%, respectively. Although nanosize particles (85.2 nm) perform better than bulk material for phenol uptake, they underwent serious aggregation at pH > 2 and ionic strength > 1.0 mM. Hence, the 191.8-nm size is selected to assess the effect of mechanical grinding on adsorption rate and equilibrium capacity for phenol as a common pollutant. Upon nanonization, adsorption rate of phenol was highly increased from 0.39 to 4.43 mg g⁻¹ min⁻¹ as analyzed by pseudo-second-order model. Adsorption isotherms were adequately presented by Sips model (prediction error 5.4–7.2%) with a maximum phenol retention capacity of 39.29 mg/g after nanonization compared to 10.71 mg/g for the raw material. The performance of the nanosize spent oil shale for phenol retention was promising when compared with advanced adsorbents like multiwalled carbon nanotube.

Keywords Top-down nanonization · Spent oil shale · Microsize · Nanosize · Textural analysis · Sorption

Introduction
Nanomaterials have emerged as an exciting class of materials that are in high demand for a range of practical applications. Materials are defined as nanomaterials if their size or one of their dimensions is in the range of 1 to 100 nm (Baig et al., 2022; Kreyling et al. 2010; Marques et al. 2021; Sharifi et al. 2012; Trotta and Mele 2019). Currently, nanotechnology is rapidly evolving and becoming part of almost every field related to materials chemistry (Marques et al. 2021; Sharifi et al. 2012). The field of nanotechnology is growing every day, and now powerful characterization and synthesis tools are available for producing nanomaterials with better-controlled dimensions (Trotta and Mele 2019). Nanotechnology is a superb example of an emerging technology since it offers tailored nanoparticles with a lot of potential for generating goods with significantly better performance. Currently, nanomaterials find many promising applications including biosensors, Li-ion batteries, paints, surface coatings by physical/chemical vapor deposition, cosmetics, H2 storage devices, CO2 capture/conversion, dielectrics, and water purification (Abu-Surrah et al. 2015; Sharifi et al. 2012; Trotta and Mele 2019).
El-Ghanem et al. 2014; Jian et al. 2019; Lu et al. 2016a, 2016b; Trotta and Mele 2019).

Bottom-up and top-down techniques are two commonly utilized experimental approaches for nanomaterial synthesis (Trotta and Mele 2019). Bottom-up techniques, which frequently result in homogeneous nanoscale materials, organize fundamental units (atoms and molecules) into larger structures or particles using chemical or physical forces operating at the nanoscale (Cao et al. 2017; Trotta and Mele 2019; Wu et al. 2011). Chemical vapor deposition, solvothermal/hydrothermal, sol–gel, and soft/hard templating are the main bottom-up approaches (Cao et al. 2017; Wu et al. 2011). In top-down approaches, the bulk or the large size materials are reduced into nanostructured materials, and this is accomplished by mechanical milling, etching, electro-explosion, and sputtering (Cao et al. 2017; Trotta and Mele 2019). Among the earlier methods, mechanical grinding is an effective process for producing materials at the nanoscale level (<100 nm) from bulk materials (Cho et al., 2009; Moys 2015; Yadav et al. 2012). Moreover, mechanical milling is effective to produce blends of different phases and production of nanocomposites (Cho et al., 2009; Yadav et al. 2012). In fact, mechanical grinding is often used to produce oxide- and carbide-strengthened aluminum alloys, wear-resistant spray coatings, aluminum/nickel/magnesium/copper-based nanoalloys, and many other nanocomposite materials (Yadav et al. 2012). In addition to ball milling, sputtering is an effective process to produce nanomaterials via bombarding solid surfaces with high-energy particles such as plasma or gas. There is no single nano grinding mill; at the same time, not all milling techniques can produce nanoparticles. Ball wet/dry media and jet mills are often used to reduce large particles to nanosize range 1–100 nm (Cho et al. 2009). Wet or dry milling methods would be used to make nanoparticles, and each approach has its own set of benefits and drawbacks (Moys 2015). Wet milling can handle particle agglomeration by encapsulating each nanoparticle in the liquid slurry, making it difficult to distribute them during grinding (Cho et al. 2009; Moys 2015; Trotta and Mele 2019; Zhuang et al. 2016). Moreover, wet milling was more stable and efficient for producing nanosize materials from solid residues (Cho et al. 2009). Dry methods, such as jet milling, can achieve the desired particle size without using milling media but consume more energy (Bilgili et al. 2006, 2004; Cho et al. 2009; He and Forssberg 2007). When comparing top-down versus bottom-up methods, the latter produces high-quality nanoparticles at a higher cost and frequently requires advanced and specialized equipment (Trotta and Mele 2019). There are many analytical methods can be applied to identify the size of nanomaterial in their solid state including scanning electron micrograph SEM, N2-adsorption method, laser diffractometer, scanning tunneling microscopy, and atomic force microscopy (Al-Ajji and Al-Ghouti 2021; Kyzas and Matis 2015; Sadegh et al. 2017). However, zeta potential, rate of aggregation, and hydrodynamic particle size in solution (under different conditions) can be studied using dynamic light-scattering spectroscopy (Jian et al. 2019).

Removal of organic and inorganic pollutants by engineered nanosize materials was studied using TiO2, Al2O3, and different nanoshapes of nanotubes activated/graphene was evaluated (He and Forssberg 2007; Sadegh et al. 2017). In fact, removal of pollutants by nanosize adsorbents is complicated due to possible aggregation of particles which may reduce the intrinsic sorption ability of the original nanomaterial (Trotta and Mele 2019). For instance, removal of organic compounds by nanosize Al2O3 was highly dependent on pH and ionic strength due to their influence on particle aggregation (Lu et al. 2016b). However, sorption capacity of nanomaterial would be higher (compared to the bulk material) apparently due to large surface area and surface charge (Trotta and Mele 2019). It should be noted here that many research articles investigated the adsorption affinity of engineered nanomaterials (TiO2, Al2O3, Fe3O4, MnO2, MgO, ZnO, carbon nanotubes, and graphite oxide) of different pollutants (Kyzas and Matis 2015; Sadegh et al. 2017), however, very limited research on using nanomaterial, prepared by top-down, as water adsorbent is addressed (Al-Ajji and Al-Ghouti 2021). Commercially activated carbon, natural, waste-based, polymeric, and nanosize adsorbents were all examined for removal of phenol and other derivatives from water. Among tested materials, activated carbon and nanosize iron oxides showed excellent affinities for phenol, 350 and 950 mg/g, respectively (Sulaymon and Ahmed 1997; Yoon et al. 2016). All tested nanosize adsorbents were prepared using bottom-up technology (Yoon et al. 2016).

To our knowledge, no published research has looked at top-down technology for preparing nanosize adsorbent from spent oil shale, which will add to the value of this study. In the current research, ball dry milling, as a common top-down technology, will be tested to generate nanosize spent oil shale and testing the generated nanosize particles to sequester phenol from solution under different conditions of pH and ionic strength. The “as-received” spent oil shale has an average particle diameter of 56.6 μm which is suitable for direct dry milling and generating nanosize materials of potential industrial applications. Nanonization of spent oil shale is carried out using dry-milling methodology which consumed lower energy compared to other methods and producing particles close to typical nanosize (1–100 nm). Effect of physical grinding of spent oil shale is evaluated by measuring specific surface area and particle size of the generated nanosize particles. Effect of aggregation on nanosize particles (<100 nm) is assessed using light dynamic scattering method. As a model pollutant, phenol uptake by
nanosize spent oil shale is tested and compared with bulk or microsize material.

**Methodology**

**Materials**

JOSCO, a Jordanian oil shale company, supplied about 3.0 kg of spent oil shale. JOSCO is a well-known oil shale extraction company with a lot of experience (Al-Saqarat et al. 2017). Analytical standard of phenol (C₆H₅OH 94.11 g/mol) with purity 99.9% was purchased from Sigma-Aldrich® (USA). Analytical grades of HCl, NaOH, NaNO₃, KCl, and NaCl were purchased from DBH® chemicals (UK). Double distilled water was used in all preparations. A 500 mg/L phenol solution was prepared using distilled water. Diluted solutions of phenol were prepared by mixing suitable volumes of standard solution and diluting with distilled water.

**Spent oil shale and grinding into nanosize material**

Due to the large proportion of calcium carbonate in local oil shale, the material was reacted with 0.1 M HCl for 5.0 h to remove carbonates and concentrate of other components such as Si and Al oxides. The residue was washed multiple times with water and dried at 130 °C after acid treatment. Spent oil shale was crushed and mechanically sieved into the following ranges: >106, 63–106, 45–63, and <45 μm, and the mass percentages of the collected fractions were 11.4, 55.8, 21.7, and 11.1%, respectively. Each fraction was analyzed for particle size distribution. Nanonization of the material was carried using 45–63 μm fraction following dry-milling methodology. A commercial beads mill instrument (Planetary Mill PULVERISETTE 7 premium line) was used to grind spent oil shale using 0.1- and 0.5-mm size zirconium balls. Initially, A 5.0 mL of dried spent oil shale (D₅₀ = 45 μm) was placed inside the grinding bowl (20 mL) along with the grinding balls. The bowl was fastened onto the sundial before the start of grinding operation. By crushing and grinding at extremely high speed, the sample was comminuted in small size particles. The maximum rotational speed of grinding using this technology would reach up to 1100 rpm which result in a high increase of the kinetic energy of grinding particles. The nanoscale grinding time ranged from 60 to 180 min. Grinding of wasted oil shale was done in this study using 0.1 and 0.5 mm zirconium oxide balls during a 60-min period. Nanonization by 0.1 mm balls was carried out after grinding with 0.5 mm which is necessary to get ultrafine particles by increasing contact area upon grinding process. At the end of grinding, the content of the bowl was removed and stored in glass container in preparation for adsorption and physiochemical tests.

**Surface characterization**

Scanning electron microscopy SEM (FEIINSPECT-F50-SEM, the Netherlands) was used to view the surfaces of the samples. Chemical composition was determined with X-ray fluorescence XRF (Shimadzu XRF-1800 Sequential X-ray Fluorescence Spectrometer, Japan). The textural characteristics (specific surface area, pore volume, and pore-size distribution) of the spent oil shale nanosize forms were determined using standard N₂-adsorption techniques (Nova 4200e, Surface Area and Pore Size Analyzer). The specific surface area was estimated with the multipoint BET method. The total pore volume was calculated from the N₂ gas adsorbed at P/Pₒ 0.95, while micropore volume was estimated with the Dubinin-Radushkevich method. The average pore diameter (APD) was obtained with the Barrett-Joynere-Hanlendra BJH approach. A laser diffractometer was used to measure particle size distribution of solid particles (Microtrac Zetatrac, Microtrac, Particle Size Analyzer, USA). The pHₑₚₑ (pH at zero point of charge) of adsorbents was estimated using potentiometric titration as outlined in the literature (Davranche et al. 2003). Two suspensions were prepared by adding 1.0 g of adsorbent in CO₂-free 300 mL of 0.1 M NaNO₃ as the supporting electrolyte. One suspension is directly titrated with 0.1 M HNO₃ while the other with 0.1 M NaOH. After 5 min of stirring, titrations were performed over the 3–11 to avoid any solid solubilization, and this was necessary due to alkaline nature of spent oil shale.

**Aggregation studies of nanosize spent oil shale**

Dynamic light scattering DLS was used to study the aggregation behavior of nanosize particles by measuring hydrodynamic particle diameter. A Nano ZS90 (Malvern Instruments) was used to monitor particle size distributions at different pH and ionic strength (KCl) conditions. The experimental conditions in DLS tests were kept consistent with adsorption experiment before the DLS analysis. Each sample (with different solution chemistry) was measured in duplicate.

**Adsorption tests of phenol by nanonized spent oil shale**

Initially, effect of pH and ionic strength on phenol uptake by nanonized materials was investigated by contacting 50 mg adsorbent with 50 mL solution containing 100 mg/L phenol.
In general, the ratio 40–50 mg/50 mL is recommended to get stable nano-suspension and avoid aggregation at higher dosages (Jian et al. 2019; Lu et al. 2016b). pH was adjusted by adding 0.1 M HCl or NaOH before adding adsorbent to cover the range (2.0–12.0), while ionic strength was adjusted by adding NaCl to final range 0–15 mM. pH measurements were made using Toledo Mettler (Switzerland). All mixtures were agitated at 25 °C in a thermostated shaker (GFL, Germany) for 240 min to attain equilibrium. The particles of oil shale were separated by centrifugation at 15,000 g for min, and the clean supernatant was measured at 270 nm using spectrophotometer. Spectral measurements were carried out with a UV–Vis spectrophotometer (Cary 3E UV–Vis spectrophotometer, Varian, USA). The equilibrium concentration of phenol was estimated from the following calibration equation: 

$$A = 0.0167C + 0.0004 \left( R^2 = 0.9988 \right)$$

which derived from Beer’s law by plotting $A_{270\text{nm}} (\lambda_{\text{max}} \text{ of phenol is } 270 \text{ nm})$ against concentration (0.1–55.0 mg/L). Adsorption rate of phenol was carried out at 25 °C, pH 6.0, initial concentration 100 mg/L, and solid-to-liquid ratio of 30 mg/50 mL. The samples were removed at preselected time spacing and analyzed as outlined above, and phenol uptake at time $t$ was estimated as follows: 

$$q_t = \frac{tk_2q_e^2}{1 + tk_2q_e}$$

where $q_t$ and $q_e$ are the amounts of dye removed at time $t$ and equilibrium time, respectively. The parameters $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the first-order and the second-order rate constants (g mg$^{-1}$ min$^{-1}$). Using the common intraparticle diffusion model, the potential of intraparticle diffusion of phenol within the pores of adsorbent was investigated (Akar et al. 2014):

$$q_t = k_p t^{1/2} + C$$

where $k_p$ is the intraparticle diffusion rate constant (mg g$^{-1}$ min$^{1/2}$) and $C$ is the intercept (mg g$^{-1}$).

### Adsorption isotherms

Among known models, Langmuir, Freundlich, and Sips were used to present phenol isotherms. Langmuir isotherm is as follows (Al-Degeis et al. 2008, 2003; Al-Zawahreh et al. 2021; Issa et al. 2014):

$$q_e = \frac{Q_L K_e C_e}{1 + K_e C_e}$$

where $Q_L$ (mg/g) and $K_e$ (L/mg) are the maximum sorption capacity (9 mg/g) and the affinity constant. Freundlich isotherm expression defines the heterogeneity of the surface as well as the exponential distribution of the active sites on the surface (Al-Zawahreh et al. 2021; Issa et al. 2014):

$$q_e = K_F C_e^{1/n_F}$$

where $K_F$ is the Freundlich constant and can indicate uptake capacity, while $1/n_F$ measures favorability of the process, and both are system-specific constants. Temkin isotherm is derived using the assumption that the drop of sorption heat as a function of temperature is linear rather than logarithmic, as implied by the Freundlich equation (Rangabhashiyam et al. 2014). The following equation describes the model:

$$q_e = \frac{RT}{B} \ln(A_T C_e)$$

where $A_T$ is Temkin isotherm equilibrium binding constant (L/mg). $R$ stands for the universal gas constant (8.314 J/mol K), $T$ for temperature (K), and $B$ for the heat of sorption constant (J/mol) (Rangabhashiyam et al. 2014). Sips model is a three-parameter model that often applied to present sorption isotherm data over a wide concentration range. Sips model has the validity in localizing the adsorption without the adsorbate–adsorbate interaction (Al-Zawahreh et al. 2021):

### Mathematical models

#### Adsorption kinetics

Kinetics of phenol uptake was presented by pseudo-first- (Eq. 1) and second-order (Eq. 2) models (Akar et al. 2014; Al-Zawahreh et al. 2021):

$$q_t = q_e \left(1 - e^{-k_1t}\right)$$

$$q_t = \frac{tk_2q_e^2}{1 + tk_2q_e}$$

$$q_t = k_p t^{1/2} + C$$

$$q_e = \frac{Q_L K_e C_e}{1 + K_e C_e}$$

$$q_e = K_F C_e^{1/n_F}$$

$$q_e = \frac{RT}{B} \ln(A_T C_e)$$
\[ q_e = \frac{Q_s K_s C_e^{n_s}}{1 + K_s C_e^{n_s}} \]  

(7)

where \( Q_s \) (mg/g), \( K_s \) (L/mg), and \( n_s \) are Sips maximum adsorption capacity (mg/g), Sips equilibrium constant, and the model exponent. The relative error of prediction (\( REP\% \)) was used as a criterion to select the optimum model as equilibrium data was fitted by more than one model. \( REP\% \) is estimated as follows (Al-Zawahreh et al. 2021):

\[ REP\% = 100 \times \left( \frac{\sum_{i=1}^{n} (q_{i,\text{pred}} - q_{i,\text{act}})^2}{\sum_{i=1}^{n} q_{i,\text{act}}^2} \right)^{1/2} \]  

(8)

where \( q_{i,\text{pred}} \), \( q_{i,\text{act}} \), and \( n \) are predicted sorption value, actual sorption value, and the number of experimental points, respectively. Lower \( REP\% \) indicates better model fitting to the data.

Results and discussion

Physicochemical characterization of spent oil shale: solid-state characterization

Before discussing the activity of nanosize particles in solution, physicochemical characterization results were discussed for different sizes of spent oil shale. SEM, XRF, FTIR, textural qualities (SSA and porosity), particle size distribution, size influence of grinding balls, and effect of grinding duration on nanostructure of the final materials were among the tests conducted. Figure 1 depicts the electron micrographs of bulk SOS and other nanosize form, which make it possible to qualitatively estimate the size range and shape of these particles.

As viewed in Fig. 1A, the particles of SOS have nonhomogenous and irregular shapes which resulted upon heating the oil shale up to 500 °C while extracting kerogen. In general, the image shows particles smaller than 40 μm in diameter and particles much larger than 40 μm in diameter. The SEM image of the tiniest particles (85.2 nm as determined by laser technology) clearly shows the effect of nano-grinding, which created reasonably uniform particles (compared to the raw material) with a diameter of 100 nm or less.

XRF and FTIR

In fact, the raw material has large amount of CaCO₃ along with Si and Al oxides. Hence, removal of carbonate mineral by acid dissolution was necessary to concentrate Si and Al improve mechanical properties. For raw sample, XRF indicated that CaO, SiO₂, Al₂O₃, and Fe₂O₃ were the main oxides with mass content of 41.14, 16.41, 2.56, and 1.24%, respectively. Upon acid treatment, SiO₂, Al₂O₃, and Fe₂O₃ were notably increased to 33.4, 12.5, and 5.62%, respectively. Both XRF and TGA for the examined spent oil shale
can be found elsewhere (Mashaal et al. 2022). The high increase in the earlier oxides was attributed to the elimination of carbonates from the solid matrix. The dissolution of carbonate mineral by acid treatment (Mashaal et al. 2022) and detection of polar surface functional groups (like Si–OH and Al–OH) which contributed to the surface charge of the adsorbent and removal of phenol can be detected by FTIR as shown in Fig. 2.

In fact, IR analysis was limited to SOS 191.8 nm as this adsorbent showed high sorption for phenol; hence, detection of adsorbed solute is possible. The following IR bands were noticed in the spectrum of SOS 191.8 nm before and after phenol uptake: 1011–1105, 879–881, 798–802, 709–710, and 478–480 cm$^{-1}$. None of the earlier bands evidenced the presence of organic phenol on the surface but related to the structure of the material which mainly composed of Si, Al, and Fe as confirmed by XRF. The strong and broad IR band located at 1011 and 1105 cm$^{-1}$ (Fig. 2A and B) with shoulders at 1161 and 1164 cm$^{-1}$ is assigned to the TO and LO modes of the Si–O–Si asymmetric stretching vibrations (Darmakkolla et al. 2016). The strong band of Si–O–Si reflected the high concentration of SiO$_2$ in the sample which in agreement with XRF analysis. The IR bands at 881 (Fig. 2A) and 879 (Fig. 2B) cm$^{-1}$ are assigned to silanol groups. The IR bands at 798 and 802 cm$^{-1}$ were assigned to Si–O–Si symmetric stretching vibrations, while the bands (478 and 480 cm$^{-1}$) are attributed to O–Si–O bending vibrations. The bands appeared at 710 (Fig. 1A) and 709 cm$^{-1}$ (Fig. 2B) are attributed Al–O vibrations. The new IR bands that appeared upon phenol uptake (Fig. 1B) are 2530 and 2869 cm$^{-1}$ were attributed to C–H starching in the organic solute. The bands appeared at 3620 and 3697 cm$^{-1}$ (Fig. 2A) are attributed to the intense –OH stretching (in Si–OH or Al–OH) (Darmakkolla et al. 2016). The involvement of the earlier –OH groups in phenol uptake is evidenced by reduction in their intensity in the IR spectrum of used adsorbent (Fig. 2B).

Influence of grinding ball size on nanonization of spent oil shale

The development of ultrafine processing forms has lately been advanced in response to the need to manage low-grade finely dispersed solid wastes (Moys 2015). Blended media or centrifugal mills, which use progressively fine media and tactics of increasing control input that are not governed by gravity, are displacing ball grinders or mills. For ultrafine processing (i.e., down to item sizes of less than 1–10 μm), these tactics proved to be basic, increasing grinding rate while also demonstrating increased power productivity (Bilgili et al. 2004). Vertical blended mills such as the Met-ProTech and Deswik plants are potential competitors in the industry, and flat or horizontal grinders such as the IsaMill have been built with 3 MW control requirements. He and Forssberg investigated the impact of slurry rheology on blended processing kinetics with molecule intermediate sizes as small as 4 μm as part of their research (He and Forssberg 2007). At the same time, Bilgili and colleagues have achieved a nanoscale size of 30 nm, which is well within the normal nanoscale range (Bilgili et al. 2006). In the current work, nanonization of spent oil shale was accomplished using dry milling using Planetary Mill PULVERISSETTE 7. The mass ratio of wasted oil shale to zirconium beads, the rotor speed, and the bead size were the experimental parameters for the grinding process. The earlier factors can be adjusted by the instrument to achieve the optimum results, i.e., fine particle of size less than 100 nm. One of the main dry grinding parameters is the ratio ($V_{\text{grinding zone}}/ V_{\text{voids}}$), and the efficiency of grinding is incensed by increasing the earlier ration (Moys 2015). A graphical presentation of mechanical milling by zirconia balls is depicted in Fig. 3.

In fact, the grinding rate in a mill is limited by the volume of the grinding zones in the mill (area $b$ in Fig. 1). The beads are assumed to be a distance $f$ apart, due to the presence

![Fig. 2 FTIR of SOS 191.8 nm before (A) and after phenol retention (B)](image)
of fine particles in the gap. Hence, the grinding zone (b) is then the circular biconcave segment as shown in Fig. 3. The volume between the beads (d as shown in Fig. 1) is also important as it affects the final grinding efficiency. Particles outside this zone cannot be compressed by zirconia balls and hence will not be ground. It has been shown that the ratio $V_{\text{Grinding Zone}}/V_{\text{voids}}$ (b and d in Fig. 3) can be correlated with the diameter of particles to be grinded and beads diameter as follows (Moys 2015):

$$\frac{V_{\text{Grinding Zone}}}{V_{\text{voids}}} = 13.4 \left( \frac{d_{\text{particle}}}{d_{\text{beads}}} \right)^2$$

(9)

In fact, Eq. 9 indicated that fine particles can be generated at low size of grinding balls, and this factor should be carefully selected. Hence, the size of grinding balls used for nanonization has high influence on the size of the final product. Balls of smaller size can produce finer particles due to the high contact with solid particles. $D_{10}$, $D_{50}$, and $D_{90}$ values obtained from particle size distribution profiles are provided in Table 1 and Fig. 4.

As indicated in Table 1, spent oil shale has average particle diameter of 56.6 µm where 90% of particles has diameter less than 68.1 µm. It should be recall that laser analysis was performed for the 45–63 µm fraction which presents 22% of the examined sample. The formation of fine particles of spent oil shale was attributed the exposure of high temperature (550 °C) and pressure during retorting process (Al-Saqarat et al. 2017). As a result, two bell-shaped distribution curves are formed instead of a regular bell-shaped distribution curve for the particle size distribution of SOS (Fig. 4A). As indicated in Fig. 4A, the first maxima occurs at a relatively smaller range (70–140 µm) of particle diameters, while the second one positioned between 160 and 240 µm. The presence of two peaks would indicate the unequal thermal distribution during grinding. In general, industrial composition of organic matters often generated restudies of diameter 0.2–90 µm. Upon mechanical crushing, the mean particle diameter was significantly reduced, and nanosize material was produced. Moreover, sample grinding by smaller beads (0.1 mm) has been significantly reduce particle diameter to 85.2 nm, which typically fall with nanosize range 1–100 nm (Moys 2015). The interesting point was the normal bell-shaped distribution curve of the particles (Fig. 4B) that resulted upon nanonization. The normal distribution curve was expected due to the uniform grinding of the particles of spent oil shale. The best nanonization result was obtained using 0.1 mm balls with $D_{10}$, $D_{50}$, and $D_{90}$ values of 68.3, 77.5, and 109.9 nm, respectively. The substantial rise in the grading zone volume, as shown in Eq. 9, is responsible for the generation of nanosize particles utilizing 0.1 mm balls. According to Eq. 9, lowering the size of the balls from 0.5 to 0.1 mm increased the grading zone 25 times, resulting in the generation of finer particles (85.2 nm). The apparent density of the material appears to have been affected by nanonization of the original material, as shown in Fig. 5.

As indicated in Fig. 5, the same mass of the material (Fig. 5A) has occupied double size after nanonization (Fig. 5B) which can reflect the high increase in surface charge upon nanonization.

### Textural measurements of nanosize adsorbents and effect of grinding time

The main factors that can affect the particle size-distribution of the material is grinding time (Arsoy et al. 2017). Hence, effect of grinding time on and particle size distribution and specific surface area was investigated for the particles

| Table 1 Estimated $D$-values of spent oil shale after nanonization at different sizes of grinding balls.a |
|-----------------|-----------------|-----------------|
| Spent oil shale | Grinding— 0.5 mm balls^a | Grinding— 0.1 mm balls^a |
| $D$-value | Particle diameter (µm) | $D$-value | Particle diameter (nm) | $D$ value | Particle diameter (nm) |
| $D_{10}$ | 43.6 | $D_{10}$ | 147.3 | $D_{10}$ | 68.3 |
| $D_{50}$ | 58.1 | $D_{50}$ | 189.4 | $D_{50}$ | 77.5 |
| $D_{90}$ | 68.1 | $D_{90}$ | 238.7 | $D_{90}$ | 109.9 |
| Arithmetic mean diameter | 56.6 µm | 191.8 nm | 85.2 nm |

a. Grinding time 60 min. b, $D_{10}$=43.6 indicated that 10% of particles have diameter ≤43.6 µm. c, The size of zirconium balls is 0.5-mm diameter. d, The size of zirconium balls is 0.1-mm diameter.

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**Fig. 3** Grinding zone (b) for particle (a) of size d, between two balls (c) which are a distance f apart and are approaching each other at a velocity u.
obtained using 0.1 mm zirconia balls (Table 1). Particle size distribution including D10, D50, and D90 and specific surface area as a function with grinding time are shown in Fig. 6. Before starting the discussion, it is important to note that effect of grinding time on the particle size distribution and surface area of the resulting particles was performed on the initial particle size of 191.8 nm (Table 1). The reason for this selection is that the particles produced using 0.1 mm balls were in the nanosize range (85.2 nm), which is important in this research. The results (Fig. 6A) showed that D10, D50, and D90 fractions were notably reduced with grinding time and over the period 20–60 min. The particle size distribution did not change much after 60 min of grinding. D90 was the most heavily reduced fraction, with size reductions of 50%, 37%, and 33% for D90, D50, and D10, respectively, within the first milling hour. The considerable drop in D90, i.e., the region of Table 1 that contains the largest particles, can be attributed to coarser particles grinding easier than smaller ones. Moreover, grinding coarser particles would insure higher grinding zone volume compared to voids area as anticipated in Eq. 9. Similar results were also obtained in literature (Arsoy et al. 2017; Liao and Senna 1992). The influence of grinding time on average particle diameter and specific surface area is depicted in Fig. 6B. In fact, specific surface area is a physical parameter which depends on particle size, density, and porosity of the solid material. Since the available surface area increases with decreasing particle size, an increase in surface area was observed upon grinding. As can be seen in Fig. 6B, the decrease in average particle size has been resulted in increase in the surface area of material. Highest surface area (38 m²/g) was reported at the lowest particle size (80 nm). With altering particle size, the specific surface area of aluminosilicate minerals was observed to grow from 9.0 to 24.0 m²/g (a twofold increase) (Arsoy et al. 2017; Zbik and Smart 2005). Even while there was no significant reduction in particle size as grinding time increased, the surface area of the grinded material increased, which was attributable to the nanosize structure of the grinded material. Moreover, this also be explained by conversion of closed pores into open pores and a consequent increase in the total pore volume during the grinding process (Arsoy et al. 2017; Zbik and Smart 2005). The influence of nanonization on specific surface area and porosity was studied using N₂-adsorption methodology. N₂-adsorption/desorption isotherms and BJH plots for SOS and 85.2 nm
Fig. 6 Effect of grinding time on particle size distribution (A) and specific surface area of nanosize particles (B)

Fig. 7 $N_2$ adsorption–desorption isotherms and BJH plots of SOS (A and B) and nanonized SOS using 0.1 mm balls (C and D)
Surface area is a physical property which depends on particle size and porosity of material. Since the available surface would increase with decreasing particle size, an increase in surface area was observed upon grinding. The increase in surface area upon grinding is attributed to the conversion of closed pores into open pores and a consequent increase in the total pore volume during the grinding process. As indicated in Fig. 7 A and C, typical type-2 isotherms were reported for micro- and nanosize materials. Filling of micropores in both materials was achieved at low pressure $P/P_o \approx 0.2$. It seems that grinding particles to nanosize has relatively increased the mesoporous structure of the material as indicated from the higher adsorbed amount of N$_2$ within the region $(P/P_o, 0.4–0.6)$ with values 9.0 and 23.0 cm$^3$/g for SOS and 85.2-nm size particles. In fact, the flatter region in the middle of the isotherm indicates the formation of a monolayer. Micropores fill with nitrogen gas at very low pressure. Monolayer formation is starting at the knee, while multilayer formation is happening at medium pressure. Capillary condensation happens when pressures are high. Type-2 isotherms are frequently observed on nonporous solids or solids with diameters greater than micropores, as was the case in this study (Al-Zawahreh et al. 2021). As shown in Table 2, specific surface area of the raw material has been improved upon nanonization; more than twofold increase was reported upon grinding with 0.1 mm balls. Moreover, nanonization has increased external surface area, total pore volume, and little increase in mesoporosity of 0.1-mm-nanonized material. It seems that crushing the material has improved the physical surface area of the material with slight effect on the microstructure of the solid material. As indicated in Table 2 and Fig. 7 B and D, the materials have microporous structure with average pore diameter of 2.41, 2.73, and 2.85 nm for SOS, 191.8-nm size, and 85.2-nm size, respectively. The slight increase in pore diameter of 85.2-nm size adsorbent would be attributed to the pores opening upon crushing. It is necessary to mention that adsorption performance of nanosize material in solution would be affected by many factors.

### Sorption and aggregation behavior of SOS particles under different conditions

In fact, sorption behavior of phenol by different sizes of SOS was tested at different pHs and ionic strengths. Moreover, the results indicated that particle size has high influence on phenol retention especially for nanosize range ($<100$ nm); hence, aggregation of particles was checked by measuring hydrodynamic particle size using dynamic light scattering.

### Effect of pH on phenol uptake and particles aggregation

Removal of phenol was tested at wide pH range 2.0–12.0, 120 mg/L concentration, ionic strength 0–15 mM, and S/L ratio of 40 mg/50 mL, and this is necessary to minimize aggregation of nanosize particles at adsorbent dosage (Jian et al. 2019; Lu et al. 2016b). Moreover, surface charge was measured for different particle sizes. The results are shown in Fig. 8. For nanosize materials, S/L ratio should be maintained as low as possible to prevent particles aggregation (Baalousha et al. 2016), and most studies conducted sorption test over the range (10–250 mg)/50 mL (Jian et al. 2019; Lu et al. 2016b; Wang et al. 2015; Wang and Shih 2011). In this work, phenol uptake was tested at S/L 10–60 mg/50 mL.

### Table 2: Textural parameters estimated N$_2$ isotherms for spent oil shale and other nanonized versions

| Parameter                  | Adsorbent                  |
|-----------------------------|----------------------------|
|                            | Spent oil shale | Grinding — 0.5 mm balls | Grinding — 0.1 mm balls |
| $S_{BET}^a$                 | 16.7                      | 23.5                      | 36.4                      |
| $S_{ext}^b$                 | -                         | 6.41                      | 14.2                      |
| $S_{mic}^c$                 | 16.7                      | 21.8                      | 25.3                      |
| $V_t^d$                     | 0.010                     | 0.016                     | 0.026                     |
| $V_{mic}^e$                 | 0.010                     | 0.015                     | 0.018                     |
| $V_{mes}^f$                 | -                         | -                         | 0.008                     |
| Average pore diameter$^g$ (nm) | 2.41                      | 2.73                      | 2.85                      |
| Arithmetic mean particle diameter | 56.6 μm                  | 191.8 nm                  | 85.2 nm                   |

$^a$Specific surface area (m$^2$/g), multipoint BET method (El-Barghouthi et al. 2007). $^b$External surface area (m$^2$/g), $t$-plot method (El-Barghouthi et al. 2007). $^c$Micropore surface area, $t$-plot method (Al-Degs et al. 2008; El-Barghouthi et al. 2007). $^d$Total pore volume (cm$^3$/g) estimated at $P/P_o=0.95$ (El-Barghouthi et al. 2007). $^e$Micropore volume (diameter <2 nm) (cm$^3$/g) estimated from Dubinin-Radushkevich method (Al-Degs et al. 2008). $^f$Mesopore volume (diameter: 2–50 nm) (cm$^3$/g) estimated at $P/P_o$ range 0.40–0.95 (Al-Degs et al. 2008). $^g$Barrett-Joyner-Halenda (BJH) method (El-Barghouthi et al. 2007)
and at 60 mg/L pollutant. In general, phenol uptake was increased and stabilized at S/L ratio of 50 mg/50 mL. Hence, all sorption tests were performed at S/L ratio 50 mg/50 mL.

Although particle grinding ended up with nanosize particles (Table 1), high phenol uptake was achieved at 191.8 nm but not 85.2 nm particles, and this was attributed to aggregation of the later particles. However, the interesting point in Fig. 8A is that both 85.2 and 191.8 nm outperformed bulk SOS, and this was attributed to the higher surface area and pore volume of the former adsorbents (Table 2). At pH 6.0, the best removal (35 mg/g) was attained by 191.8-nm size particles. In fact, nanoparticles agglomerate at a considerably higher rate than other sizes, reducing phenol absorption from solution (Baalousha 2017). In reality, pH, ionic strength, adsorbate chemistry, and complexing agents all influence nanomaterial aggregation behavior (Jian et al. 2019). Hence, aggregation behavior of SOS 85.2 nm was examined at the same sorption conditions as shown in Fig. 8B. As indicated in Fig. 8, the particles involved high aggregation with pH and are also reported in the literature (Jian et al. 2019; Raza et al. 2016). At pH 2.0, the nanosize material has been aggregated to generate aggregates of hydrodynamic diameters H–d of 1000 nm (33%) and 3000 nm (3%). In fact, the nanosize particles encountered high aggregation in solution as H–d was increased from 85.2 to around 1000 nm at pH 2. At pH 4.5, more aggregation was observed, and the average H–d was increased to 2000 nm with intensity of 60%. Because pH 4.5 is so close to pH_{ZPC}, the significant aggregation can be attributed to a large drop in surface charge. At basic medium (pH 10), the particles underwent intense aggregation with H–d of 2500 and 5000 of intensities 55 and 12%, respectively; this large increment on H–d would be attributed to the reduction in dielectric layer at high ionic solution as predicted from DELVO theory (Baalousha 2017). SOS (85.2 nm) nanoparticles exhibited high aggregation with pH in general, and specific nanomaterials exhibited comparable behavior (Jian et al. 2019). As a result, the steady decrease in phenol absorption (Fig. 8A) with pH was attributed to particle aggregation, which was thought to limit surface area and pore volume, as well as adsorbent-adsorbate repulsion, as stated later. The fate of nanomaterial in adsorption medium is dependent on particle shape, pH, ionic strength, and chemistry of adsorbate (Raza et al. 2016). Hence, the aggregation behavior of nanomaterials was tested at different pH, ionic strength, and complexing agents (Jian et al. 2019; Lu et al. 2016b; Raza et al. 2016). For instance, TiO₂ nanomaterial has high stability (i.e., do not strongly aggregate) at acidic pH and over a wide salt level but aggregate at neutral pH and low concentration of salt (Lu et al. 2016b). In the same line, aggregation kinetics of different nanomaterials were tested using dynamic light scattering of UV spectroscopy and published data indicating that increasing ionic strength increases the rate of aggregation of nanomaterial (Baalousha et al. 2013). Aggregation kinetics of nanomaterials is often controlled by the following: (a) electrostatic forces among particles (diameter 1–100 nm) and (b) electrostatic interferences which depend on ionic strength, solution pH, stabilizing agent of nanoparticle, and coating thickness (Baalousha et al. 2013; Raza et al. 2016). The results provided in Fig. 8A indicated that both pH and particle size have significant influence on phenol uptake. For the examined pH range, the bulk material and SOS 191.8 nm manifested the same adsorption trend, and the best uptake was reported over the range (4–8) and a high reduction observed at pH > 10.0. Moreover, phenol uptake at pH 2.0 was not high. Both electrostatic interaction and H-bonding were involved in solute uptake from solution. As indicated from IR spectra, both Si–OH and Si–O–Si were the main surface functional groups and the ionization of the particles with pH shown in Fig. 8C. As shown in Fig. 8C, the point of zero charge pH_{ZPC} was 4.3, and above this point, the surface ionizes to carry negative charge (Si–O⁻) and positive
charge (Si-OH$_2^+$) at pH < 4.3. pH$_{pzc}$ was close to pure SiO$_2$ (4.0), and this was expected as silica making a large fraction of the material. As SOS and SOS 191.8 nm did not encounter serious aggregation at tested pHs, then the mechanism of phenol retention is explained as the following: (a) at pH 4–8, the H-bonding between neutral phenol (pK$_a$ = 10) and polar Si–OH (especially in the range 3.5–4.5) is the dominating mechanism, while above 4.5, another mechanism like van der Waals forces will dominate the process; (b) at pH < 4.0, surface protonation is started, and this will reduce phenol uptake via H-bonding keeping van der Waals forces the controlling mechanism; and (c) at pH > 10.0, surface ionization is strengthened leading to electrostatic repulsion between phenolate ions and the surface (Fig. 8). The best retention for SOS and SOS 191.8 nm was at pH 6, and hence, van der Waals forces were more dominate than H-bonding. Despite the similarity in the adsorption behavior, SOS 191.8 nm removed 3.7-folds phenol from solution (Fig. 8, pH 6.0) than SOS and this thank to its finer particle size and high surface area (Table 2). In fact, in mechanical grinding leading to finer particles and maximize surface charge as shown in Fig. 8, the maximum surface charge was reported for 191.8 nm at pH 7.3 with a value of 150 μmol(−)/m$^2$ which was 4 times higher than the bulk material. In summary, SOS 191.8 nm was the winner adsorbent to remove phenol as it has higher surface area compared to bulk and did not encounter serious aggregation like nanosize form (85.2 nm).

**Effect of ionic strength on phenol uptake and particles aggregation**

Removal of phenol was tested at different ionic strengths 0–15 mM and S/L ratio at 50 mg/50 mL. The results are shown in Fig. 9.

Particle size has an inconsistent effect on phenol absorption, as shown in Fig. 9A. Adding KCl to bulk SOS and 191.8-nm size increased phenol removal, but there was no significant effect at concentrations higher than 10 mM. The most noteworthy finding was with nanosize particles (85.2 nm), which showed a significant reduction with KCl, with phenol absorption dropping to 15 mg/g at 15.0 mM NaCl. Another important factor that affects aggregation of nanosize particles was ionic strength as shown in Fig. 9B. Undoubtedly, the nanosize particles (56.6 nm) underwent intense aggregation in solution which increased H–d to 6000 nm at 15.0 mM, and this negatively affected phenol uptake from solution (Fig. 9B). The results of dynamic light scattering (not provided) that reported for bulk and 191.8 nm did not show serious aggregation with ionic strength, and this can explain their comparable behavior toward phenol uptake (Fig. 9A). In fact, the effect of ionic strength on phenol elimination was investigated without changing the pH of the solution. The equilibrium pH of the solutions was between 3.9 and 4.3, and at this pH, both phenol (pK$_a$ 10.0) and solid particles (pH$_{pzc}$ 4.2) are neutral forms; therefore, electrostatic attraction was not a significant factor. The previous discovery is consistent with literature in that nanomaterial aggregation increases dramatically with the addition of salt (Baalousha et al. 2013). For the bulk material (56.6 μm) and 191.8 nm particle size, the increase in phenol uptake would be attributed to the salt effect as the salt will reduce phenol solubility and hence improve its uptake (Wang et al. 2016). The high affinity of 191.8 nm compared to the bulk one is attributed to the higher surface area/porosity (Table 1) which attracts more phenol from solution.

**Adsorption kinetic and isotherm**

As indicated in Figs. 8B and 9B, nanosize particles, although perform better than bulk material, they underwent serious aggregation at pH > 2 and ionic strength > 1.0 mM. Hence, the 191.8-nm size was selected to assess the effect of mechanical grinding on sorption kinetics and equilibrium sorption capacity against bulk material. Sorption kinetics and isotherms were measured to get a better picture on phenol uptake by bulk and 191.8-nm size. The results are depicted in Fig. 10, while parameters of the tested models are summarized in Tables 3 and 4.

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**Fig. 9** Effect of ionic strength on phenol uptake. A. Intensity-based particle size distribution of SOS-85.2 nm at different NaCl concentrations using dynamic light scattering. B.
As indicated in Fig. 10A, phenol uptake was higher for SOS 191.8 nm as indicated from its steeper slope over the initial time of interaction (10 min). Moreover, the higher surface area of SOS 191.8 nm (Table 2) offers more contact with solution which ended up with faster equilibrium time, 60 against 180 min for the bulk material.

As indicated in Table 3, kinetic curves of phenol were fairly presented by pseudo-second-order model which was more flexibility compared to pseudo-first-order model as indicated from the lower REP% values. The magnitudes of sorption rate \( h \), which estimated from second-order model, were 0.39 and 4.43 mg g\(^{-1}\) min\(^{-1}\) for SOS and SOS 191.8 nm, respectively, and this jump is equivalent to an 11-fold increase in the rate of phenol sorption. Rate constants \( k_1 \), estimated by pseudo-first-order model, also indicated faster uptake of phenol by SOS 191.8 nm (Table 3). It seems that the contribution of intraparticle diffusion for phenol uptake was limited as indicated the poor fit of this model (REP 12.1–19.7%). Upon nanonization, the surface was notably increase, and this will speed up external interaction with phenol over intraparticle diffusion.

As shown in Fig. 10B, typical L-type isotherm was obtained. In solution, L-type isotherms are most typically encountered in solute sorption. The initial shape of the equilibrium curve follows the basic premise that the higher the solute concentration, the greater the adsorption capacity.
until the number of possible adsorption sites is occupied. Comparable isotherm shapes were reported for phenol uptake by carbon nanomaterials (de la Luz-Asunción et al. 2015). The parameters of examined models are summarized in Table 4.

Among tested models, Sips was the more suitable to present phenol uptake by both adsorbents with REP% 5.4–7.4. In fact, Sips model is a combination of both Langmuir and Freundlich isotherms, which is often applied to predict the heterogeneity of the adsorption systems as well as to circumvent the limitations associated with the increased concentrations of the adsorbate of Freundlich model. This, in turn, leads to the production of an expression that has a finite limit at high concentration (Al-Zawahreh et al. 2021). However, both Langmuir and Sips models were fairly predicated in the maximum retention of phenol from solution. The maximum saturation values, as predicted from Sips model, were 10.71 and 39.29 mg/g for SOS and SOS 191.8 nm, respectively. For comparison purposes, the maximum adsorption capacities of only nano adsorbents for phenol uptake from solution were compiled in Table 5.

As indicated in Table 5, only advanced materials of nanosize structure were included. The reported capacities were ranged from 1.1 for carbon nanotube up to 123.0 mg/g for magnetic nanoparticles. It should be reminded that examined adsorbents were fabricated using bottom-up rather than top-down technology that employed in this work. The performance of SOS 191.8 nm for phenol uptake (39.29 mg/g) was rather comparable to nanomaterial that derived from carbon with maximum retention of 31 mg/g. The comparison study (Table 6) reveals that SOS 191.8 nm examined and studied in this work exhibited capacity affinity generally higher than many of the reported sorbents (Table 6).

In addition, the exponents of Freundlich model (4.37 and 4.92, Table 4) indicated the favorability of sorption process over the concentration range and heterogeneity of adsorbents (Al-Zawahreh et al. 2021; Al-Degs et al. 2008). Temkin model was shown to have limited utility for presenting phenol isotherms with notably high REP values 16.4–22.3% among the examined isotherms (Table 4). Although the Temkin model is more accurate in presenting gas phase equilibrium, it falls short of precisely capturing the equilibrium data in the case of liquid phase adsorption, particularly of organic molecules (Rangabhashiyam et al. 2014).

Conclusions

Mechanical grinding of wasted oil shale solid leftovers reduced the bulk material (56.6 m) to two small particles, one in the nanosize range (85.2 nm) and the other near nanoscale (191.8 nm). Mechanical grinding increased surface area and pore volume significantly, allowing researchers to investigate the adsorption capacity of these compounds in water. Although nanosize particles (85.2 nm) performed better than bulk material to remove phenol, they exhibited significant aggregation at pH > 2 and ionic strength > 1.0 mM. Because it has a larger surface area than bulk and does not experience substantial aggregation like nanosize form, adsorbent with a particle size of 191.8 nm won the competition to remove phenol (85.2 nm). In fact, nanomaterial (1–100 nm) undergoes serious aggregation in solution, and this may limit their application as adsorbent. However, particle sizes more than 100 nm can perform better in solution due to modest aggregation.

Acknowledgements Dr. Al-Degs thanks Mr. Bassem Nasrallah (Chemistry Department, Hashemite University, Jordan) for the continuous technical support represented by the spectroscopic analyses as well as the compositional analysis of spent oil shale.

Author contribution ASAS, conceptualization, methodology, and writing — review and editing. YSAID, methodology and writing — review and editing.

Data availability The datasets used and/or analyzed during the current study are available from the corresponding author (Y.S. Al-Degs) upon request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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Table 5 Adsorption capacities of some nanosize adsorbents for phenol as collected from the literature

| Nano adsorbent                              | Adsorption value (mg/g) |
|--------------------------------------------|-------------------------|
| Carbon nanotube — Al2O3 (Ihsanullah et al. 2015) | 1.1                     |
| Carbon nanotube (Ihsanullah et al. 2015)     | 3.0                     |
| Activated carbon nanosize (de la Luz-Asunción et al. 2015) | 31.0                   |
| Multiwalled carbon nanotubes (Abdel-Ghani et al. 2015) | 32.2                   |
| Multiwalled carbon nanotubes (Dehghani et al. 2016) | 65.4                   |
| Magnetic nanoparticles (Kakavandi et al. 2016) | 123.0                   |
| Spent oil shale SOS — nanosize              | 39.3                   |
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