

GRANULATION OF OIL SHALE ASH WITH SODIUM ALGINATE FOR THE REMOVAL OF PHENOLS FROM SHALE OIL WASTEWATER

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Abstract. Oil shale ash (OSA) from the circulating fluidized bed (CFB) boiler was granulated and used as a sorbent for the removal of phenols from shale oil wastewater. The method for preparation of the sorbent involved washing of the ash, mixing with clay, gelling the mixture with sodium alginate solution, solidifying the granules in barium chloride solution, drying and calcination of the granules and modifying with a surfactant – hexadecyltrimethylammonium bromide (CTAB). The sorbent was characterized by specific surface area (BET_{N_2}), X-ray diffraction (XRD) and ^{29}Si Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR) analysis. Batch adsorption experiments were conducted to determine the phenol adsorption isotherm at 20 °C and removal of water-soluble phenols from phenolic shale oil processing wastewater. Removal of phenols from wastewater was found to be 50–65% under given conditions.

Keywords: oil shale ash, sodium alginate, granulation, phenolic wastewater, adsorption.

1. Introduction

Oil shale as one of the sources of energy has attracted increasing attention in recent years. It is a fine-grained sedimentary rock containing relatively large quantities of organic matter from which significant volumes of shale oil and combustible gas can be produced [1–7]. Among world reserves of fossil fuels, oil shale is seen to be the second largest after coal. Estonian oil shale kukersite is a low-grade fossil fuel, which is the country's dominant commercial fuel. It is utilized by thermal treatment to produce shale oil and

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combusted in power plants to produce energy [3, 6, 8]. The oil shale-to-energy company Eesti Energia AS uses kukersite to produce shale oil, electricity, and heat. For shale oil production, Eesti Energia operates Narva Oil Plant (Estonia), which uses a Galoter-type solid heat carrier (SHC) technology process [9]. In this case, fine-grained kukersite (particles smaller than 25 μm) with low calorific value (ca 9.0 MJ/kg) is used.

In the Galoter process the raw kukersite is heated by mixing it with the retorting residue at ca 800 °C before the horizontal retorting chamber. The retorting residue is burnt in the aero furnace at temperatures below 800 °C. The plant processes ca 2.5–3 million tons of oil shale per year and produces more than one million barrels of various shale oil fractions.

The thermal processing of oil shale and refining of the retorting products are accompanied by the formation of a large amount of wastewater containing alkyl resorcinols and phenols, which are heavily separable and represent a serious hazard to the environment [10, 11]. The phenol content in industrial phenolic wastewater may reach 2000 mg/L and pH about 5 [12, 13]. The treatment of phenolic effluents includes mainly oil separation, dephenolation and biological treatment together with municipal wastewater [12, 13]. Increase of industrial shale oil production and high environmental quality standards require finding an effective way to eliminate phenols from industrial wastewater before its treatment.

Oil shale ash (OSA) is the main by-product of oil shale combustion for electricity production. Due to its high mineral content the combustion of oil shale generates a huge amount of ash. The chemical composition of fresh OSA is characterized by a high concentration of free CaO, and it is classified as hazardous waste due to high alkalinity when contacted with water. OSA produced in the circulating fluidized bed (CFB) boiler at the Eesti Power Plant is highly alkaline and is characterized by a high percentage of the fine fraction (over 86% with a size < 0.045 mm), according to literature [14–16]. The ash also contains various carbonate and sandy-clay minerals and less than 0.5% of organic matter [8, 15]. There are problems related to the ash handling and landfilling because only a small portion of it is utilized in construction materials or in agriculture/forestry and as a filter material for wastewater treatment [8, 15, 17, 18].

Combustion fly ashes could be used as low-cost sorbents for the removal of various pollutants, including phenols from fluid streams. Several studies have demonstrated that fly ash may be used for removal of organic pollutants from wastewater [19–26, 27, 28]. However, utilization of OSA as an adsorbent to remove phenols from aqueous environments has not been studied. A complete recycling of OSA from CFB boiler to granulated material would be an economically useful and environmentally friendly approach.

Before utilizing OSA for wastewater treatment it is necessary to reduce its content of soluble components and increase adsorption capacity towards specific pollutant(s). These objectives can be achieved by washing OSA,

granulating it and modifying the granules with a surfactant [22, 29–37]. The granulation can be performed using a method developed by Charkhi et al. [30]. The said method includes washing of the material, mixing it with sodium alginate to form a gel, and granulating of the ash/alginate gel suspension in barium chloride solution. Alginate, which is a natural linear biopolymer, has found numerous applications in biomedical science and engineering due to its favorable properties as a gelling agent [30, 37–39]. This biopolymer is composed of two monomeric units: β -D-mannuronic acid and α -L-guluronic acid. In the presence of divalent cations (Ca^{2+} , Ba^{2+} , etc.) the alginate forms a hydrogel. The intermolecular cross-linking with divalent cations to form hydrogels is associated with the proportions and lengths of guluronic acid blocks [38].

The aim of the study was to prepare a sorbent from CFB OSA, characterize the sorbent and test its effect on removing water-soluble phenols from the phenolic retort wastewater of shale oil production.

2. Materials and methods

2.1. Oil shale ash

The OSA sample was collected at the gas flow duct at the first unit of electric precipitators of the CFB boiler at the Eesti Power Plant. OSA from the 1st electrostatic precipitator of CFB was a fine powder with 100% of particles less than 120 μm in diameter.

2.2. Retort wastewater

Two phenolic wastewater samples were collected from Narva Oil Plant of Eesti Energia. The concentration of water-soluble phenols exceeded 1500 mg/L in both cases.

The samples were immediately delivered to the laboratory and stored at 7 °C in dark conditions until adsorption experiments. The samples were dark green in color with a pungent odor and consisted of an oily phase, a water phase and a blackish insoluble fraction at the bottom.

2.3. Preparation of CTAB-modified adsorbent

The CFB OSA was used as a raw material for preparation of modified granulated adsorbent. The scheme for processing of hexadecyltrimethylammonium bromide-modified adsorbent (CTAB-G) is shown in Figure 1.

Prior to this process, the OSA sample was subjected to pretreatment to decrease the content of soluble components and the alkalinity of the OSA leachate. For this purpose, the sample (100 g) was repeatedly washed with tap water containing small amounts of 40% formic acid (CH_2O_2 , Sigma-Aldrich) until pH 8–9. The use of formic acid promoted the decrease of pH because in alkali conditions it formed formyl and hydroxy-formyl radicals, which reacted with silicates to form stable products [40, 41].

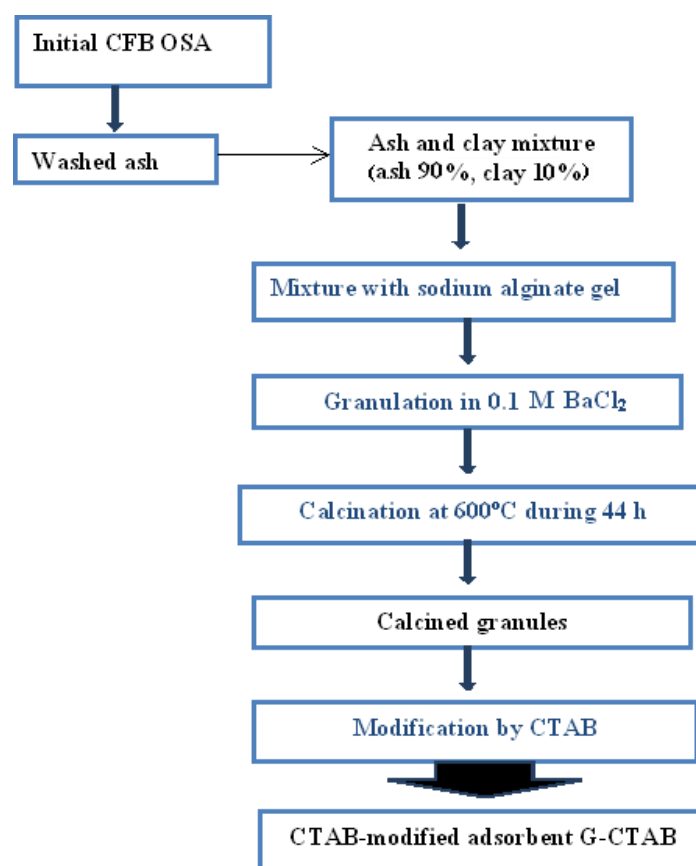


Fig. 1. Preparation of CTAB-modified adsorbent.

The washed ash particles (100 g) were gravimetrically separated and immersed in deionized water (Millipore SAS, France) for 24 h. The ash was then dried in an oven at 40 °C for 72 h and kept in a desiccator. The particles were mixed with dried and milled blue clay (Uninaks AS, Estonia) (ash:clay 9:1, wt/wt). The mixture was dispersed in 80 ml deionized water for 15–20 minutes, and then 150–200 ml of 2% sodium alginate gel was added. A commercial low-viscosity gelling agent sodium alginate (alginic acid sodium salt from brown algae, Sigma) was used.

The suspension was mixed for 1 h, retained for 30 minutes and then centrifuged at 2200 rpm for 8 minutes. The upper liquid layer was separated, and the residual slurry was used for tailoring the granules. The slurry was transferred to a 0.1 M solution of barium chloride under stirring. The formed raw granules were kept in solution overnight. Then the granules were separated, washed several times with deionized water, and dried by immersing the material in acetone for 1 h. Finally the granules were kept at room temperature for 24 h, and then calcined at 600 °C for 44 h to decompose the

residual alginate. The calcined granules were kept in a desiccator until reaching room temperature and then washed with deionized water, dried in an oven at 40 °C for 72 h, and kept in a desiccator until the modification process.

For the modification process a 10% suspension of calcined granules was agitated at 20 °C for 3 h in a CTAB solution (0.01 mol/L hexadecyltrimethylammonium bromide, Sigma). Then the solid matter was separated from the solution by filtration (Whatman paper No 40, 8 µm, Sigma-Aldrich), washed with deionized water, and dried at 40 °C for 72 h. The modified granules were kept in a desiccator at room temperature until use. The average diameter of the CTAB-modified adsorbent particles was 5.4 ± 0.6 mm.

2.4. Specific surface area

Specific surface area (BET_{N_2}) data were determined by the Brunauer–Emmett–Teller method using a KELVIN 1042 sorptometer (Costech Microanalytical SC, Estonia) with Kelvin 1042 V3.12 software. Helium was employed as the carrier gas and nitrogen as the adsorptive gas. The volume of gas adsorbed on the material surface was measured at liquid nitrogen temperature at four relative pressures: 0.05, 0.1, 0.15 and 0.2 p/p_0 .

2.5. X-ray diffraction and ^{29}Si MAS-NMR analysis

X-ray diffraction (XRD) patterns of the original and washed ash as well as CTAB-modified adsorbent samples were recorded with an X'Pert Powder diffractometer (PANalytical, Holland) equipped with a scintillation detector. Diffraction patterns of Cu K α were registered in the range of 5°–70° 2-theta. The mineral composition of the samples was quantitatively determined by the Rietveld analysis method using the HighScore Plus program (PANalytical).

^{29}Si MAS-NMR (Magic Angle Spinning-Nuclear Magnetic Resonance) spectra were recorded on a Bruker AVANCE-II-360 spectrometer at 8.5 T external magnetic field, using a bespoke MAS probe and 10 mm od zirconia rotors. A simple one pulse excitation (7 µs, 80-degree pulse), a relaxation delay of 60 s and a spinning speed of 5 kHz were used for all three spectra.

2.6. Phenol adsorption isotherm

Batch experiments were performed for determination of the equilibrium adsorption isotherm of phenol on the CTAB-modified adsorbent at 20 °C. The solute spiked water samples (100 ml) with a phenol concentration of 50 mg/L were agitated at 134 rpm at 8 °C during 24 h. The adsorbent dose was varied between 0 and 10.0 g per 100 ml. The pH of the solution was adjusted with HCl to 9 to avoid phenol dissociation at higher alkalinity levels. After 24 h contact time, the phenol concentration was determined using a UV-VIS-NIR-Spectrophotometer UV-36 00Plus (Shimadzu, Japan) at a wavelength of 269 nm. Before the analysis the liquid sample was filtrated through a 0.45 µm syringe filter (Sartorius, Germany). The experi-

mental data was subjected to regression analysis by using the Freundlich isotherm model.

2.7. Adsorption of phenols from phenolic wastewater

The efficiency of the CTAB-modified adsorbent on the removal of phenols from the real retort wastewater was studied on two samples at a temperature of 8 °C by using the batch method. In both cases 1 liter of the wastewater sample with the adsorbent (307.6 g/L) and 1 liter of the wastewater sample without the adsorbent in glass bottles were agitated at 100 rpm in dark conditions at 8 °C for 24 h. After the adsorption experiment the content of the bottles was separated by filtration using a 0.45 µm Whatman membrane filter. The content of water-soluble phenols in filtrated initial wastewater samples and filtrates was determined by a high performance liquid chromatograph (HPLC) (Shimadzu, detector DECADE; eluent 1% acetic acid: methanol 60:40 (v/v); isocratic elution with a flow rate of 1.4 ml/min).

Removal efficiency was calculated as follows:

$$\%R = \frac{C_i - C_e}{C_i} \times 100, \quad (1)$$

where C_i is the mean initial concentration of pollutant, C_e is the mean residual concentration of pollutant after 24 h contact with the CTAB-G adsorbent.

3. Results and discussion

3.1. Characteristics of solids

The results of BET_{N₂} specific surface area measurements are presented in Table 1.

Washing and granulation enhanced the specific surface area of the CFB ash over ten times when compared to the original sample (Table 1).

The XRD patterns of the original CFB ash, washed ash and CTAB-G adsorbent samples are shown in Figure 2.

The analysis showed that the composition of the original ash sample included mainly quartz, lime, anhydrite, calcite and smaller amounts of orthoclase, periclase, gehlenite, larnite, merwinite, pseudowollastonite, hematite, ettringite, melilite and dolomite (Table 2). As expected, the

Table 1. Specific surface area of ash samples

Sample	BET _{N₂} surface area, m ² /g	Micropore area, m ² /g	Non-microporous surface area, m ² /g
CFB OSA	3.2	0.7	2.5
Washed ash	44.0	4.2	39.8
CTAB-G	50.5	7.1	43.4

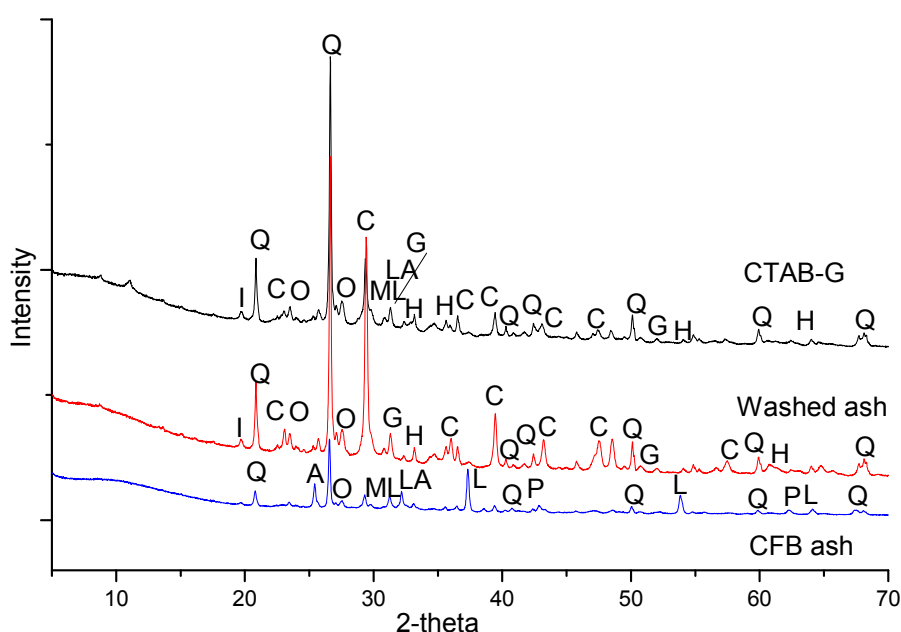


Fig. 2. XRD patterns of the original CFB ash, washed ash and CTAB-G adsorbent samples (washed CFB ash and 10% of added clay were granulated using sodium alginate gel; the granules were calcined and then modified by CTAB). (For abbreviations see Table 2.)

washed ash sample was characterized by the absence of lime and a decreased amount of anhydrite, merwinite and gehlenite compared to the original ash sample. The washed ash sample also contained a higher percentage of calcite, quartz and orthoclase than the original ash sample (Table 2). The main mineral composition of calcined CTAB-G granules included higher percentages of quartz and orthoclase. In addition to lime, merwinite, larnite, hematite, melilite, dolomite, illite-smectite, gehlenite, pseudowollastonite and periclase, the granules contained small amounts of calcite, ettringite and anhydrite. Furthermore, the composition of the granules was characterized by the presence of a minor amount of calcium aluminate hydrate. The original ash contained lime, whilst in the washed ash and CTAB-G samples, lime had been carbonized to calcite (Fig. 2). In addition, both the original ash and the adsorbent CTAB-G contained the mineral larnite (belite).

The ^{29}Si MAS-NMR analysis showed a broad resonance in the chemical shift range from -80 to -110 ppm in all three samples. This resonance can be assigned to the variety of silicon sites in amorphous fly ash glass. The resonance lines at -71.5 and -107.3 ppm arise from larnite (Ca_2SiO_4) and quartz, respectively [18]. The appearance, decay and reappearance of larnite in the original ash, washed ash and CTAB-modified adsorbent samples, respectively, are in accordance with both the X-ray and the ^{29}Si MAS NMR

analysis (Figs. 2 and 3) and are most probably caused by calcination of the intermediate product (washed ash + clay).

Table 2. Composition of the original CFB ash, washed ash and CTAB-G adsorbent samples, mass%

Compound	Abbreviation	Chemical formula	CFB ash	Washed ash	CTAB-G
Quartz	Q	SiO ₂	24.9	25.6	32.5
Lime	L	CaO	17.1	0	0
Anhydrite	A	CaSO ₄	10.7	0	0
Calcite	CT	CaCO ₃	9.2	46.4	19.5
Orthoclase	OR	KAlSi ₃ O ₈	8.3	19.7	23.1
Illite	I	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ , (H ₂ O)]	8.1	0.9	6.5
Larnite	LA	Ca ₂ SiO ₄	6.8	0	2.3
Melilite	ML	(Ca,Na) ₂ (Al,Mg,Fe ²⁺)[(Al,Si)SiO ₇]	6.8	0	0.3
Periclase	PR	MgO	4	0.4	1.3
Merwinite	M	Ca ₃ Mg(SiO ₄) ₂	1.2	0	0.9
Hematite	HM	Fe ₂ O ₃	1.2	1.5	2.3
Ettringite	E	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	1.1	0.3	0.7
Dolomite	D	CaMg(CO ₃) ₂	0.6	0.4	3
Gehlenite	G	Ca ₂ Al[AlSiO ₇]	0	3.3	6.3
Wollastonite	W	CaSiO ₃	0	1.5	1
Calcium aluminat hydrate	CAH	3CaO,Al ₂ O ₃	0	0	0.3

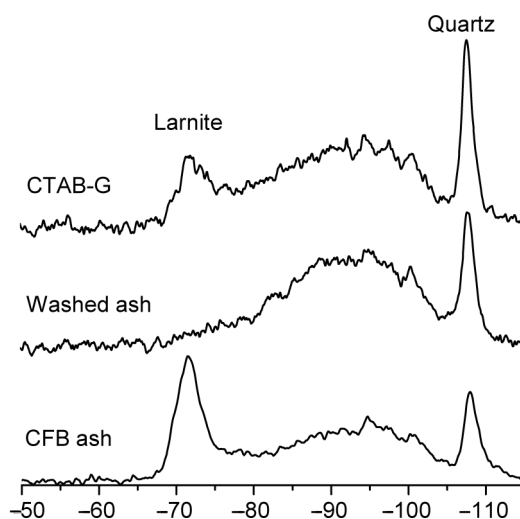


Fig. 3. ²⁹Si MAS-NMR spectra of the original CFB ash, washed ash and CTAB-G adsorbent samples.

3.2. Phenol adsorption isotherm

The phenol adsorption isotherm was satisfactorily described ($R^2 = 0.75$) by the Freundlich equation with $q_{\max} = 0.38$ mg/g at an initial phenol concentration of 50 mg/L (Fig. 4).

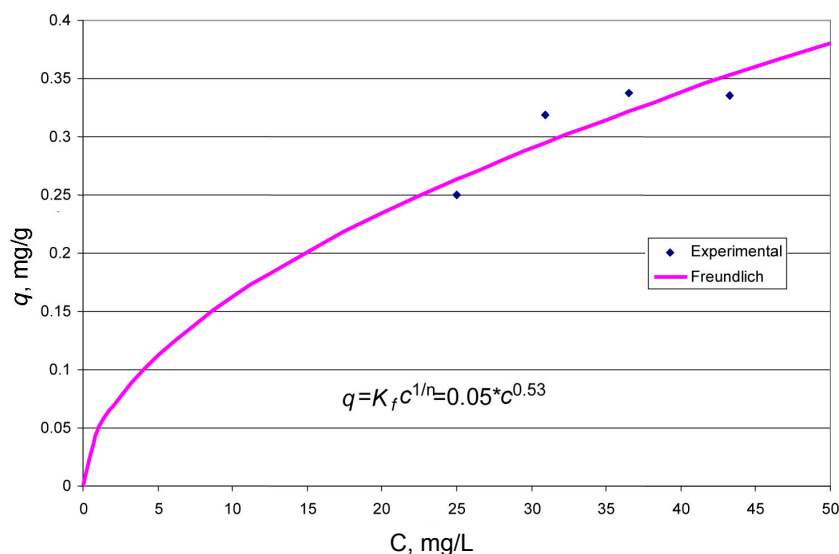


Fig. 4. Phenol adsorption isotherm.

3.2. Adsorption of phenols from phenolic wastewater

The efficiency of the CTAB-modified adsorbent towards phenols present in retort wastewater samples was studied using the batch method.

The results obtained are presented in Table 3. A significant decrease of the phenols content in the retort wastewater after contact with CTAB-modified granules was observed. The percent of removal was around 50% for phenol and 65% for cresols under given conditions. At the end of the experiment the solution was alkaline (pH about 10).

Table 3. Results of adsorption tests with retort wastewater samples

Compound	$C_i \pm$ range, mg/L	$C_e \pm$ range, mg/L	Removal efficiency and SD, %	Amount adsorbed onto CTAB-G, mg/g
Phenols	722 ± 156	375 ± 75	48 (50)	1.1 ± 0.6
<i>p</i> -, <i>m</i> -Cresols	609 ± 91	211 ± 31	65 (24)	1.3 ± 0.3
<i>o</i> -Cresol	403 ± 123	142 ± 43	64 (50)	0.8 ± 0.4

Note: SD – standard deviation.

Under given conditions, the capacity of CTAB-G to adsorb water-soluble phenols from wastewater was 3.2 ± 1.3 mg/g (Table 3). This is significantly less than indicated from the adsorption. At the same time, the retort wastewater contained also other contaminants, such as oil products and BTEX compounds (benzene, toluene, ethylbenzene, xylenes), which all compete with phenols for toxicity. Still, the capacity of CTAB-G OSA to adsorb phenol is similar to that of a number of industrial by-products and adsorbents [22, 23, 32, 42–47] (Table 4), for example, organo-modified clays at pH 10 [32] and wood fly ash [44].

Table 4. Capacity of some industrial by-products and adsorbents for phenols removal

Adsorbent	Capacity, mg/g	Reference
Bentonite	0.292	[32]
PTMA-bentonite	4.740	[32]
HDTMA-bentonite	10.3	[32]
Kaolinite	0.579	[32]
PTMA-kaolinite	0.818	[32]
HDTMA-kaolinite	2.60	[32]
Lignite coal fly ash	0.26	[42]
Bagasse fly ash	0.67	[43]
Wood fly ash	5.4	[44]
Blast furnace sludge	7.5	[45]
Coal fly ash	17.1	[46]
Carbonaceous adsorbent	17.2	[45]
Natural coal	18.8	[47]

Thus, the tests demonstrated that the CTAB-G adsorbent may be used for adsorption of water-soluble phenols from the retort wastewater. After the adsorption tests the adsorbent was covered with a blackish layer of bituminous matter. Future studies will address these issues. The adsorbent can be regenerated, remodified and reused for further removal of phenols from the retort wastewater.

4. Conclusions

Based on the results of the study, the following conclusions can be drawn:

1. The ash from the circulating fluidized bed oil shale combustion can be granulated using sodium alginate as a gelling agent. Addition of 10% of clay to the ash gives enough strength to the granules to be used in the adsorption process. Using hexadecyltrimethylammonium bromide the calcined ash granules can be modified for adsorbing specific pollutants.
2. The mineral composition of calcined granules organo-modified by CTAB-G consists mainly of quartz (32.5%), orthoclase (23.1%) and calcite (19.5%). In addition, illite (6.5%), gehlenite (6.3%), dolomite

(3.0%), larnite (2.3%), hematite (2.3%), periclase (1.3%), wollastonite (1.0%), merwinite (0.9%), ettringite (0.7%), melilite (0.3%) and calcium aluminate hydrate (0.3%) are present.

3. The appearance, decay and reappearance of larnite in the samples of original ash, washed ash and CTAB-G are most probably caused by calcination of the intermediate product (washed ash + clay).
4. The CTAB-G organo-modified OSA granules can be successfully used for adsorption of water-soluble phenols from shale oil processing phenolic water. Removal of phenols was found to be 50–65% under given adsorption conditions.
5. Hence, the industrial by-product of oil shale processing such as CFB oil shale ash could be considered as a promising material for producing low-cost adsorbent for removal of water-soluble phenols from the shale oil retort wastewater.
6. Granulation of CFB OSA also allows its use in other industrial applications and agriculture in the future.

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