Deashing and desulfurization of subbituminous coal from the East field (Bogovina Basin, Serbia) – Insights from chemical leaching

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Abstract: The study is focused on the determination of the most effective chemical leaching process for the simultaneous demineralization/deashing and desulfurization of subbituminous coal from the Bogovina Basin. Coal was treated for 30 min, at different temperatures, using variable concentrations of hydrochloric, nitric, acetic and citric acids; hydrogen peroxide, mixture of hydrogen peroxide and nitric acid (pH 2), as well as by the stepwise leaching process (nitric acid + mixture of hydrogen peroxide and nitric acid, pH 2). The changes in mineral composition, caused by the chemical leaching, are followed using X-ray diffraction, whereas alterations of coal organic matter are tracked by Fourier-transform infrared spectroscopy and the content of fixed carbon. Inorganic acid leaching, regardless of the temperature and acid concentration, enabled the successful deashing of coal, whereas the percent of desulfurization was insufficient. The organic acid leaching was not satisfactory for both, deashing and desulfurization. Leaching by H_2O_2 and H_2O_2/HNO_3 mixture (pH 2) resulted in moderate desulfurization, but the ash reduction was low. The most suitable method for the simultaneous effective ash (78 wt.%) and the sulfur (66 wt. %) removal from Bogovina coal is the two-step leaching, combining 10 vol. % HNO_3 and mixture of 35 vol. % H_2O_2/10 vol. % HNO_3 of pH 2 at 60 °C.

Keywords: Bogovina coal; stepwise leaching; acidic leaching; oxidizing agents leaching; ash removal; sulfur removal.

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INTRODUCTION

Coal is fossil fuel and an important source of power generation all over the world.[1] However, the coal combustion is associated with the release of a large quantity of pollutants that have negative impact on ecosystem and human health, agricultural products and also causes corrosion of metal in stokeholes.[2–4] The major coal components that cause problems with combustion are sulfur/its compounds and mineral matter (MM), which is transformed into ash.[4] Sulfur in coal is present in the elemental form, as well as in inorganic compounds and organic matter (OM). The latter includes "free" sulfur compounds in bitumen, but are also part of sulfur bounded in kerogen. The inorganic sulfur forms comprise sulfides (*e.g.*, pyrite, marcasite) and sulfates (gypsum, barite, *etc*).[4] The organic sulfur compounds in bitumen are represented by: thiols, sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophenes, benzo[*b*]naphtho[*d*]thiophenes, *etc*. In the addition to ash formation by combustion, MM in coal decreases the calorific value and increases transport costs.[1]

Therefore, the processes of demineralization/deashing and desulfurization of coal may prevent the serious environmental problems caused by the coal combustion.[1] Methods for deashing and desulfurization can be conducted using chemical treatments, physical processing and microbial treatments.[1,5–7] Some of physical methods like dry fluidization, jigging, dense media/heavy media separation, hydrocyclone washing, magnetic separation, oil agglomeration, float and sink, air dense medium separation *etc.* can remove ash to a limited extent.[8] The combination of physical and chemical methods (*e.g.*, flotation and leaching with potassium hydroxide/methanol) applied on Mezino coal is shown to achieve the reduction of ash content of up to 83 wt. % and total sulfur up to 82 wt. %.[9] Treatment of Mezino coal by froth flotation and nitric/hydrochloric acid leaching process resulted in ash reduction of 54.7 wt. %, whereas sulfur reduction was 74.1 wt. %.[10]

Numerous chemical leaching processes, single acid leaching,[11,12] stepwise acid leaching,[13–15] leaching with oxidizing and chelating agents,[16–19] alkali treatments[20] and combined alkali-acid leaching[3,21] was applied to decrease the ash and the sulfur content in coal, with relatively high efficiency. The percentage of ash reduction was between 38.9 and 90.0 wt. %, whereas the degree of desulfurization ranged from 52.7 to 89.7 wt. % for different alkali–acid leaching of diverse coal under variable conditions.[1,21]

The microbial treatment of coal under mild conditions (25–75 °C) is also reported in literature,[1,7] but this process is time consuming, with long incubation period. The biodesulfurization study of Colombian coal sample, using the native mixture of microorganisms showed 30–50 wt. % of total sulfur removal. Out of the total sulfur removed, 85–96 wt. % was pyritic sulfur.[22]

Concerning that coals have very different and complex chemical composition, depending on biomass sources, depositional and post-depositional factors

and maturity,[4] there is no single and unique reagent for the efficient demineralization/deashing and desulfurization.[1] Furthermore, since the calorific value of coal depends on content of organic matter (primarily on the amount of fixed carbon, C_{fix}),[4] it is important that the applied of demineralization/desulfurization process does not alter coal OM.

Considering the above-mentioned problems regarding pollution, and the significance of coal as the main source for energy production in Serbia,[23] designing of cheap and efficient methods for removal of MM and sulfur from coal is of essential importance. Hence, the manuscript is focused on the determination of the cost and time effective chemical leaching process for simultaneous demineralization/deashing and desulfurization of subbituminous coal from the Bogovina Basin (Eastern Serbia). For that purpose, the coal was treated by: hydrochloric acid, nitric acid, acetic acid, citric acid, hydrogen peroxide, mixture of hydrogen peroxide and nitric acid (pH 2), as well as by the stepwise leaching process (nitric acid + mixture of hydrogen peroxide and nitric acid, pH 2). Variable concentrations of mentioned reagents were used (with exception of hydrogen peroxide, 35 vol. %) and the leaching experiments were performed at different temperatures. The changes in mineral composition and alterations in structure of coal OM, caused by chemical leaching, were followed using X-ray diffraction (XRD) analysis and Fourier-transform infrared spectroscopy (FTIR), respectively. Furthermore, C_{fix} was determined in solid residues obtained by chemical leaching, since the coal calorific value mostly depends on this parameter.

EXPERIMENTAL

Coal sample, proximate analysis and determination of sulfur content

The subbituminous coal sample was collected from the Bogovina East field (Lower Miocene ≈ 20–16 million years ago) of the Bogovina Basin (Eastern Serbia). According to an average huminite reflectance, R_r, which equals 0.42±0.04 %,[24] the coal from this deposit belongs to bright brown coal group (Low-Rank A).[4] The sample was selected based on the previous studies of Bogovina East Field,[24,25] which indicated the high amount of sulfur, the relatively high percent of mineral matter and the considerable amount of liptinites for humic coal, that represent the most reactive maceral group.[4,25] Therefore, it serves as good substrate for checking the efficiency of demineralization and desulfurization, as well as the influence of applied chemical leaching treatments on OM structure.

The air-dried sample was crushed using Fritsch mortar grinder pulverisette 2 and sieved through a 200 μm sieve. Proximate analysis (determination of analytical moisture, volatile matter, ash and fixed carbon) of the coal was performed according to the ASTM D3172 standard,[26] whereas total sulfur content was determined by the Eschka method.[27] Bogovina coal sample, used in this study, contains 16.82 wt. % moisture, 38.44 wt. % of volatile matter, 17.52 wt. % of ash, 27.22 wt. % of fixed carbon and 6.03 wt. % of total sulfur.

Leaching procedure

Chemical leaching of coal was conducted with inorganic acids (hydrochloric and nitric), organic acids (acetic and citric), oxidizing agent (hydrogen peroxide), and the combination of

acid/oxidizing agent (nitric acid/hydrogen peroxide) in a single and two-step process. The acid-leaching treatment was chosen concerning the geological settings which are such that the coal from the Bogovina East field was formed in a slightly alkaline depositional environment generated by bentonite from the basement of the Main coal seam.[24] It was further confirmed by our preliminary leaching experiments using diverse concentrations of sodium hydroxide solution at different temperatures, which showed low efficiency of both deashing and desulfurization, attaining maximally 11.94 and 8.95 wt. %, respectively.

For each test, 600 cm^3 of leaching reagent was added to 30 g of coal sample and the mixture was heated and shaken on magnetic stirrer for 30 minutes at the constant mixing speed of 250 rpm. After the leaching, the hot leached residue was cooled, filtered by vacuum pump and rinsed with hot distilled water until the neutral reaction (pH 7) of filtrate. Finally, the leached residue was dried in the oven (Memmert UNE 400 drying oven) at 105 °C to the constant mass. The ash and sulfur contents, as well as of C_{fix}, in the obtained leached residues were determined using the same methods as the in initial coal sample.[26,27] For determining the optimal temperature of leaching treatment, the first set of experiments (I) was performed at temperatures 30, 60 and 90 °C using the 10 vol. % water solution of inorganic acids (hydrochloric and nitric), whereas treatment with organic acids (acetic and citric) of the same concentration (10 vol. %), hydrogen peroxide (35 vol. %), mixture of 35 vol. % hydrogen peroxide/10 vol. % nitric acid (pH 2), as well as 10 vol. % nitric acid + 35 vol. % hydrogen peroxide/10 vol. % nitric acid mixture at pH 2 (two-step leaching process) was carried out at 20, 40 and 60 °C. For establishing the influence of acids concentration on deashing and desulfurization, the second set of experiments (II) was conducted in the same way as previous one using the following concentrations of acids: 5, 10 and 15 vol. % at optimal temperature, which was determined in the first set of experiments. This range of concentrations was selected based on the data from literature, since it was shown that higher concentrations of acids (*e.g.*, 30 vol. % HNO$_3$) could alter the coal structure.[1] Considering literature data[5] which states that the desulfurization of coal by 20 vol. % hydrogen peroxide is unsuitable for removing organic sulfur and that 30 vol. % H$_2$O$_2$ could remove it up to 36 wt. % of sulfur from coal having similar content of total sulfur (5.8 wt. %) as here studied Bogovina coal sample, all experiments were done using 35 vol. % H$_2$O$_2$ and mixture of 35 vol. % hydrogen peroxide/10 vol. % nitric acid (pH 2). The performed leaching experiments are summarized in Table I. All experiments were repeated three times and mean values are reported here with standard deviation less than 0.5 %.

RESULTS AND DISCUSSION

Coal leaching with inorganic acids

The treatment with 10 vol. % HCl at all temperatures (30, 60 and 90 °C) resulted in ash reduction from 17.52 wt. % in the initial coal to about 3.65 wt. % in leached samples (Table I), indicating the deashing efficiency of about 79 wt. % (Table II). The sulfur reduction was also very similar at all temperatures, however, slightly better results were obtained at 60 and 90 °C (8.62 and 8.29 wt. %, respectively) than at 30 °C (7.46 wt. %; Table II). Independently of temperature, the amount of C_{fix} increases uniformly from 27.22 wt. % in initial coal to ~39.5 wt. % in all samples treated by HCl (Table I), due to the considerable removal of MM. This has a positive impact on calorific value. Although, the data from

Tables I and II clearly show that temperature plays insignificant role in coal treatment by 10 vol. % HCl, but the best results are obtained at 60 °C. Therefore, this temperature was chosen as optimal leaching temperature.

TABLE I. Summary of the performed experiments and contents of ash, total sulfur and fixed carbon (C_{fix}) in initial coal sample and solid residues obtained by chemical leaching

Exp. set	Leaching reagent	t / °C	Leaching reagent concentration, vol. %	Reaction time, min	Amount, wt.%		
					Ash	Sulfur	C_{fix}
Initial coal sample					17.52	6.03	27.22
I	HCl	30	10	30	3.65	5.58	39.57
		60			3.62	5.51	39.64
		90			3.68	5.53	39.34
	HNO$_3$	30	10	30	3.62	5.64	41.17
		60			3.16	4.9	38.25
		90			3.29	4.77	35.76
	CH$_3$COOH	20	10	30	6.78	5.37	38.17
		40			6.21	5.33	39.11
		60			5.80	5.32	38.92
	Citric acid	20	10	30	11.26	5.56	32.08
		40			9.59	5.39	35.87
		60			8.93	5.37	35.93
	H$_2$O$_2$	20	35	30	11.01	4.90	33.00
		40			8.60	4.14	34.24
		60			13.08	4.94	35.80
	H$_2$O$_2$/HNO$_3$ pH 2	20	35 (H$_2$O$_2$)/10 (HNO$_3$)	30	13.73	5.40	31.70
		40			8.81	4.64	35.25
		60			7.12	4.04	36.57
	HNO$_3$ followed by H$_2$O$_2$/HNO$_3$, pH 2 (two-step process)	20	10 (HNO$_3$) followed by 35 (H$_2$O$_2$)/10 (HNO$_3$)	15 followed by 15	4.09	5.05	40.96
		40			4.08	4.25	38.82
		60			3.86	2.03	37.59
II	HCl	60	5	30	3.35	5.69	40.84
		60	10		3.62	5.51	39.64
		60	15		3.33	5.49	43.45
	HNO$_3$	60	5	30	3.47	5.13	36.02
		60	10		3.16	4.90	38.25
		60	15		3.41	4.45	34.99
	CH$_3$COOH	40	5	30	8.51	5.50	36.28
		40	10		6.21	5.33	39.11
		40	15		7.04	5.47	37.44
	CH$_3$COOH	60	5	30	5.79	4.72	39.45
		60	10		5.80	5.32	38.92
		60	15		5.27	5.22	39.12
	Citric acid	60	5	30	8.08	5.35	35.95
		60	10		8.93	5.37	35.93
		60	15		10.18	5.38	34.85

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TABLE II. Ash and sulfur reduction in solid residues obtained by chemical leaching; the results for optimal concentrations and temperatures are marked by bolded text

Exp. set	Leaching reagent	t / °C	Leaching reagent concentration; vol.%;	Reaction time, min	Amount reduction, %	
					Ash[a]	Sulfur[b]
I	HCl	30	10	30	79.17	7.46
		60			79.34	8.62
		90			79.00	8.29
	HNO₃	30	10	30	79.34	6.47
		60			81.96	18.74
		90			81.22	20.90
	CH₃COOH	20	10	30	61.30	10.95
		40			64.55	11.61
		60			66.89	11.77
	Citric acid	20	10	30	35.73	7.79
		40			45.26	10.61
		60			49.03	10.95
	H₂O₂	20	35	30	37.16	18.74
		40			**50.91**	**31.34**
		60			25.34	18.08
	H₂O₂/HNO₃ pH 2	20	35 (H₂O₂)/10 (HNO₃)	30	21.63	10.45
		40			49.71	23.05
		60			**59.36**	**33.00**
	HNO₃ followed by H₂O₂/HNO₃, pH 2 (two-step process)	20	10 (HNO₃) followed by 35 (H₂O₂)/10 (HNO₃)	15 followed by 15	76.66	16.25
		40			76.71	29.52
		60			77.97	66.33
II	HCl	60	5	30	80.88	5.64
		60	10		79.34	8.62
		60	**15**		**80.99**	**8.96**
	HNO₃	60	5	30	80.19	14.93
		60	10		81.96	18.74
		60	**15**		**80.54**	**26.20**
	CH₃COOH	40	5	30	51.43	8.79
		40	**10**		**64.55**	**11.61**
		40	15		59.82	9.29
	CH₃COOH	**60**	**5**	30	**66.95**	**21.72**
		60	10		66.89	11.77
		60	15		69.92	13.43
	Citric acid	**60**	**5**	30	**53.88**	**11.28**
		60	10		49.03	10.95
		60	15		41.89	10.78

[a]Ash reduction = 100(Ash content in initial coal – Ash content in leached coal)/Ash content in initial coal; [b]bulfur reduction = 100(Sulfur content in initial coal – Sulfur content in leached coal)/Sulfur content in initial coa

The results from Table II indicate that the HCl concentration (5–15 vol. %) does not considerably affect deashing of Bogovina coal (being in range from

79.34 to 80.99 wt. %), whereas the influence on desulfurization is obvious. The percentage of desulfurization increases from 5.64 wt. % for 5 vol. % HCl to 8.62 wt. % for 10 vol. % HCl, being similar to 15 vol. % HCl (8.96 wt. %). The contents of C_{fix} in leached residues are also comparable for all studied concentrations of HCl (39.64–43.45 wt. %), however the highest abundance is observed for 15 vol. % HCl. Considering all data related to HCl treatment, it can be noted that the best results are achieved using 15 vol. % acid concentration at 60 °C.

Leaching with 10 vol. % HNO_3 at 30 °C resulted in almost identical deashing efficiency as leaching with 10 vol. % HCl at all temperatures (the ash content in leached residue was 3.62 wt. %; the ash reduction was 79.34 %; Tables I and II). At 60 and 90 °C slightly greater ash reduction is achieved using 10 vol. % HNO_3 (81.96 and 81.22 wt. %, respectively) than by 10 vol. % HCl (Table II). In difference to deashing, the influence of temperature on desulfurization by leaching with 10 vol. % HNO_3 is more evident.

The percent of sulfur reduction was 6.47 wt. % at 30 °C, 18.74 wt. % at 60 °C and 20.90 wt. % at 90 °C. The contents of C_{fix} in residues after leaching by 10 vol. % HNO_3 are higher than in the initial coal (Table I), as expected. However, the continuous decrease of C_{fix} content from 41.17 to 35.76 wt. % with the temperature rise was observed (Table I). This can be attributed to the oxidizing effect of HNO_3, which becomes more pronounced with the increase of temperature. The aforementioned data indicate the diverse efficiency of leaching by 10 vol. % HNO_3 depending on temperature. Since the highest efficiency for deashing by 10 vol. % HNO_3 is observed at 60 °C and considering that heating of HNO_3 from 60 to 90 °C reduces the sulfur content for 0.13 wt. %, only, but also decreases C_{fix} for 2.5 % (Table I), as well as, the energy consumption (that is lower at 60 °C than at 90 °C), the temperature of 60 °C was chosen as optimal.

The results from Table II indicate that HNO_3 concentration (5–15 vol. %) does not considerably affect the deashing of Bogovina coal (80.19–81.96 wt. %), with the highest ash reduction for 10 vol. % HNO_3 treatment. Different from the deashing efficiency, the increase of HNO_3 concentration showed significant impact on desulfurization and C_{fix} content. The percentage of desulfurization increased from 14.93 wt. % for 5 vol. % HNO_3 to 18.74 wt. % for 10 vol. % HNO_3, being the highest for 15 vol. % HNO_3 (26.20 wt. %). C_{fix} rose in leached residues from 36.02 wt. % for leaching by 5 vol. % HNO_3 to 38.25 wt. % for treatment with 10 vol. % HNO_3 and then decreased to 34.99 wt. % by leaching with 15 vol. % HNO_3. The results of leaching experiments with HNO_3 indicated that the highest efficiency of deashing and desulfurization can be obtained using the concentration of 15 vol.% at 60 °C. However, for coal utilization processes where C_{fix} content plays a more significant role than content of sulfur, leaching by 10 vol. % HNO_3 at 60 °C can be also considered.

The results from Tables I and II show that deashing has rather high and almost constant values for both HCl and HNO$_3$, regardless of temperature and acid concentration, while desulfurization process is more influenced by these leaching parameters, particularly for HNO$_3$. Comparing the results obtained by leaching with 5 vol. % acids at 60 °C, and 10 vol. % acids at 30 °C it can be noticed that desulfurization efficiency of HCl depends more on concentration, whereas in the case of HNO$_3$ temperature has a more pronounced impact. The optimal chemical leaching of Bogovina coal with both acids can be obtained using the concentration of 15 vol. % at 60 °C. However, it is evident that both single acid leaching treatments enable successful deashing of Bogovina coal, whereas percent of desulfurization is insufficient. The better efficiency of HNO$_3$ than HCl in desulfurization can be attributed to the fact that nitric acid in difference to hydrochloric acid has oxidizing properties. On the other hand, similar efficiency of both acids in deashing indicates that mineral part of Bogovina coal is relatively resistant to oxidizing agents. This suggests a low amount of sulfides (*e.g.*, pyrite), pointing out that sulfur in Bogovina coal is mostly present in OM as well as the inorganic sulfates (anhydrite), which is also documented by XRD data. The changes in qualitative composition of MM, caused by chemical leaching, are followed by XRD after subjecting the initial coal and the leached solid residues to the LTA process (Fig. S-1 of the Supplementary material to this paper), as explained in more detail in Supplementary material.

Since the content of OM, particularly C$_{fix}$ controls heating value of coal, C$_{fix}$ is determined (Table I) and the FTIR spectra of the initial and the leached coal are recorded (Fig. S-2). The FTIR spectra were done for all experiments, however, due to their great congruence for the same reagent they were done independently on concentration and temperature; those corresponding to the optimal conditions are explained in more detail in Supplementary material and shown in Fig. S-2.

Coal leaching with organic acids

The possibility of Bogovina coal deashing and desulfurization using organic acids (acetic and citric), that are generally less hazardous than HCl and HNO$_3$, was investigated as well.

Deashing by leaching with 10 vol.% acetic acid increases from 61.30 to 64.55 wt. % with temperature rise from 20 to 40 °C, being the highest (66.89 wt. %) at 60 °C. In difference to inorganic acid treatments, the temperature showed less impact on desulfurization ranged between 10.95 wt. % at 20 °C and 11.77 wt. % at 60 °C. The same is related to C$_{fix}$ content, which slightly increases from 38.17 wt. % at 20 °C to 39.11 wt. % at 40 °C, being similar at 60 °C (38.92 wt. %). Since the results at 40 and 60 °C were rather uniform and considering lower energy con-

sumption at 40 °C, the influence of acetic acid concentration on leaching efficiency was tested at both temperatures.

The obtained data indicate greater impact of CH_3COOH concentration on coal deashing at 40 °C than at 60 °C, where results are similar. The sulfur reduction generally diminishes with the increase of acid concentration at both temperatures. Contents of C_{fix} are uniform; the highest values are detected for CH_3COOH concentration of 10 and 5 vol. % CH_3COOH at 40 and 60 °C, respectively. The greatest efficiency at 40 °C is recorded for 10 vol. % acid concentration, whereas at 60 °C it is achieved with 5 vol. %. Comparison of the data from the experiments with 10 vol. % acid at 40 °C and 5 vol. % acid at 60 °C, clearly shows better efficiency of the latter, that can be considered as optimal for leaching with CH_3COOH (Tables I and II). This also led to the conclusion that temperature plays more important role in the leaching treatment than acid concentration.

The leaching with citric acid demonstrated a steady increase of deashing (35.73–49.03 wt. %) and desulfurization (7.79–10.95 wt. %) with the temperature rise from 20 to 60 °C. The content of C_{fix} also increases from 20 to 40 °C (32.08–35.87 wt. %), being almost identical to the latter (35.93 wt. %) at 60 °C. Therefore, it is evident that optimal temperature for citric acid leaching is 60 °C (Tables I and II). The coal leaching using different concentrations of citric acid at 60 °C showed greater influence on ash removal, ranged from 41.89 to 53.88 wt. %., in comparison with percent of desulfurization (10.78–11.27 wt. %) and C_{fix} (34.85–35.95 wt. %). The data from Table II clearly indicate that the highest efficiency by leaching with citric acid could be obtained using 5 vol. % concentration at 60 °C.

The most efficient leaching with both tested organic acids is achieved using the concentration of 5 vol. % at 60 °C. Better efficiency of acetic than citric acid is obvious (Tables I and II). This can be attributed to the more pronounced interactions of citric acid with coal OM and complexation with metal ions from MM, since it contains three carboxylic groups, in difference to monocarboxylic CH_3COOH that favours incorporation (capturing) of the former into coal structure. These interactions are most probably responsible for the decreasing of leaching efficiency with the increasing of acids concentration, the exception being deashing by CH_3COOH, which is slightly greater using 15 vol. % in comparison to 5 vol. %. However, it is obvious that the single step organic acid leaching is not satisfactory method for both, deashing and desulfurization (up to 67 and 22 wt. %, respectively) of Bogovina coal (Table II).

The results of inorganic and organic acids treatments under optimal conditions (concentration and temperature) clearly indicate that organic acids are much less effective in deashing, whereas leaching by both, CH_3COOH and citric acid enabled greater sulfur reduction than those by HCl. However, the leaching by organic acids cannot compete to the treatment with HNO_3 (Table II).

Coal leaching with oxidizing reagents

It was shown that oxidizing reagents (*e.g.*, hydrogen peroxide) are able to decrease the content of sulfur in coal, oxidizing both organic and pyritic sulfur to sulfonic acids and sulfates.[16,18] Therefore, some oxidizing agents were also tested on Bogovina coal.

The results from Tables I and II indicate that temperature plays significant role in deashing and desulfurization of Bogovina coal by leaching with 35 vol. % H_2O_2, due to the partial thermal decomposition of hydrogen peroxide at temperatures > 40 °C. Deashing increases from 37.16 wt. % at 20 °C to 50.91 wt. % at 40 °C, and falls back to 25.34 wt. % at 60 °C. The same stands for desulfurization, having maximum value of 31.34 wt. % at 40 °C, whereas at 20 and 60 °C sulfur the removal was very similar ~18 wt. %. The content of C_{fix} was uniform (33.00––35.80 wt. %); however the highest percent is recorded at 60 °C, consistent with partial thermal decomposition of hydrogen peroxide at > 40 °C. Since the coal leaching with 35 vol. % H_2O_2 resulted in the highest degree of desulfurization among the tested reagents (31.34 wt. %), whereas deashing was low (up to 50.91 wt. %; Table II), in order to improve the latter, as well as thermal stability, H_2O_2 was mixed with 10 vol. % HNO_3 at pH 2. 10 vol. % HNO_3 was chosen, since it showed the greatest deashing efficiency among the tested reagents (Table II).

Leaching of coal with this mixture resulted in deashing varied from 21.63 wt. % at 20 °C to 59.36 wt. % at 60 °C, whereas desulfurization raised from 10.45 to 33.00 wt. % in the same temperature range, indicating considerable impact of temperature. Percent of C_{fix} was higher in leached residues obtained by acidified H_2O_2 than H_2O_2 treatment at 40 and 60 °C, resulting from more effective deashing. The sulfur reduction by leaching with acidified H_2O_2 was apparently lower in comparison to treatment with pure H_2O_2 at 40 °C (23.05 *vs.* 31.34 wt. %), whereas at 60 °C application of H_2O_2/HNO_3 mixture resulted in greater desulfurization efficiency of 33.00 wt. % (Table II). This signifies that H_2O_2 plays a major role in desulfurization process and confirms improved thermal performances of acidified reagent. On the other hand, H_2O_2/HNO_3 mixture (pH 2) demonstrated more effective deashing (59.36 wt. %) than H_2O_2 solely (50.91 wt. %), implying that HNO_3 has dominant role in ash reducing, however at higher temperature (60 *vs.* 40 °C). Data from Table II clearly indicate that optimal temperatures for H_2O_2 and H_2O_2/HNO_3 mixture (pH 2) leaching are 40 and 60 °C respectively. Although, treatment with H_2O_2/HNO_3 mixture (pH 2) resulted in the most effective desulfurization (33 wt. %) comparing with all previous leaching treatments, the ash reduction was low, attaining maximally 59.36 wt. % (Table II). Therefore, Bogovina coal was further treated firstly by 10 vol. % HNO_3 (15 min) and then by H_2O_2/HNO_3 mixture (pH 2, 15 min) in the two-step process, maintaining the total leaching time of 30 min, as in all previous experiments (Table I).

Temperature does not have significant impact on the deashing efficiency in the two-step leaching process ranged from 76.66 wt. % at 20 °C to 77.97 wt. % at 60 °C. The result is in accordance with those of leaching by inorganic acids. The two--step process showed slightly lower deashing efficiency (77.97 wt. %) than the treatment with 10 vol. % HNO_3 solely (81.96 wt. %, Table II). Since, former experiments indicated that 10 vol. % HNO_3 plays the dominant role in deashing in comparison to H_2O_2/HNO_3 mixture (pH 2) and this result can be attributed to shorter duration of the acidic leaching in the two-step process than by pure HNO_3 (15 *vs*. 30 min). On the other hand, desulfurization by the two-step process considerably increases from 20 °C (16.25 wt. %) to 60 °C (66.33 wt. %) which is evidently the most efficient result among all performed leaching experiments (Table II). Furthermore, greater percent of desulfurization of 66.33 wt. % by the two-step leaching process at 60 °C that exceeds the sum of desulfurization percents by each treatment alone (18.74 wt. % for 10 vol. % HNO_3 + 33.00 wt. % for H_2O_2/HNO_3 mixture of pH 2, 51.74 %), under the same temperature, indicates certain synergetic effect resulted from combining of above mentioned reagents. The percent of C_{fix} after the two-step leaching process at 60 °C was 37.59 wt. % which is higher than after treatment with 35 vol. % H_2O_2/10 vol. % HNO_3 mixture (pH 2, 36.57 wt.%) and insignificantly lower than after 10 vol. % HNO_3 treatment (38.25 wt. %).

Taking into consideration results of all the performed experiments it can be concluded that the two-step leaching process combining 10 vol. % HNO_3 and mixture of 35 vol. % H_2O_2/10 vol. % HNO_3 of pH 2 is the most suitable single method for the simultaneous effective ash (~78 wt. %) and sulfur (~ 66 wt. %) removal from Bogovina coal, increasing in the same time C_{fix} from 27 wt. % in the initial sample to 38 wt. % in leached residue (Tables I and II). The obtained results are comparable or even better than those of deashing and desulfurization by chemical leaching reported in literature.[1,28]

Our further research would be addressed to the investigation of possible reuse of HNO_3 after adjusting the concentration to 10 vol. % and cost effective recovering of accumulated metals from filtrates, aimed to prevent the negative environmental impact of applied leaching reagent.

CONCLUSIONS

The study is aimed to determine the most effective chemical leaching process for the simultaneous demineralization/deashing and desulfurization of subbituminous coal from the Bogovina Basin. The sample is selected based on the high amount of sulfur, the relatively high percent of MM and the considerable amount of liptinites for humic coal, which represent the most reactive OM maceral group.

The leaching with HCl or HNO$_3$, regardless of temperature and acid concentration, enabled the successful deashing of coal (~80 wt. %), confirmed also by XRD, whereas the percent of desulfurization (up to 26 wt. %) was insufficient. The best results for both the inorganic acids are observed for the concentration of 15 vol. % at 60 °C. Nitric acid demonstrated better efficiency than hydrochloric acid, particularly for the sulfur removal, due to the oxidation properties.

The single step organic acid leaching was not satisfactory for both, deashing and desulfurization (up to 67 and 22 wt. %, respectively) of Bogovina coal. The most efficient leaching with organic acids is achieved using the concentration of 5 vol. % at 60 °C. Acetic acid showed greater efficiency than citric acid. The comparison of inorganic and organic acids treatments under optimal conditions indicated that organic acids are less effective in deashing, whereas the leaching by both, CH$_3$COOH and citric acid enabled greater sulfur reduction than those by HCl. However, the leaching by organic acids cannot compete to the treatment with HNO$_3$.

The leaching of coal by oxidizing reagents 35 % H$_2$O$_2$, and the mixture of 35 vol. % H$_2$O$_2$ and 10 vol. % HNO$_3$ (pH 2) resulted in better desulfurization (31–33 wt. %) than single step acidic treatments, whereas the percent of deashing was low (up to 60 wt. %). The optimal temperatures for H$_2$O$_2$ and H$_2$O$_2$/HNO$_3$ mixture (pH 2) leaching were 40 and 60 °C, respectively.

The most suitable method for simultaneous effective ash (78 wt. %) and sulfur (66 wt. %) removal from Bogovina coal is the two-step leaching, combining 10 vol. % HNO$_3$ and mixture of 35 vol. % H$_2$O$_2$/10 vol. % HNO$_3$ of pH 2 at 60 °C. XRD data showed the removal of all minerals with the exception of quartz and olivine, the content of C$_{fix}$ increased for 11 wt. % in relation to initial coal, whereas FTIR implied no significant alteration in the structure of coal OM by the treatment. Furthermore, greater percent of desulfurization by the two-step leaching process which exceeds the sum of desulfurization percents by each the treatment alone (10 vol. % HNO$_3$ and H$_2$O$_2$/HNO$_3$ mixture of pH 2), indicates the synergetic effect resulted from the combination of above-mentioned reagents.

SUPPLEMENTARY MATERIAL

И З В О Д

ОТПЕПЕЉАВАЊЕ И ОДСУМПОРАВАЊЕ МРКОГ УГЉА ИЗ ИСТОЧНОГ ПОЉА БАСЕНА БОГОВИНА (СРБИЈА) ХЕМИЈСКИМ ТРЕТМАНОМ

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Циљ рада је одређивање најефикаснијег хемијског третмана за истовремену деминерализацију/отпепељавање и одсумпоравање мрког угља из басена Боговина. Угаљ је третиран 30 min, на различитим температурама, користећи различите концентрације хлороводоничне, азотне, сирћетне и лимунске киселине; водоник-пероксид, смешу водоник-пероксида и азотне киселине (pH 2), као и двостепено испирање (азотна киселина + смеша водоник-пероксида и азотне киселине, pH 2). Промене у минералном саставу, проузроковане хемијским третманом, праћене су дифракцијом рендгентских зрака, док су промене органске супстанце угља праћене помоћу инфрацрвене спектроскопије са Фуријеовом трансформацијом и садржаја фиксног угљеника. Третман неорганским киселинама, независно од температуре и концентрације реагенса, омогућио је успешно отпепељавање угља, док је проценат одсумпоравања био недовољан. Третман органским киселинама није био задовољавајући, ни за отпепељавање, ни за одсумпоравање. Третман угља са H_2O_2 и смешом H_2O_2/HNO_3 (pH 2) резултовао је умереним одсумпоравањем, али је смањење садржаја пепела било мало. Најприкладнија метода за истовремено ефикасно уклањање пепела (78 мас. %) и сумпора (66 мас. %) из боговинског угља је двостепено испирање, комбинацијом 10 запр. % HNO_3 и смеше 35 запр. % $H_2O_2/10$ запр. % HNO_3 (pH 2) на 60 °C.

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