

Conversion of Low-Rank Kilyos Coal to Nitrogenous Fertilizers

Journal:	<i>Energy Sources, Part A: Recovery, Utilization, and Environmental Effects</i>
Manuscript ID:	UESO-2009-0054.R1
Manuscript Type:	Original Article
Date Submitted by the Author:	
Complete List of Authors:	Hakli-Birel, Ozgöl; Celal Bayar University, Chemistry Dumanli, Ahu; Sabanci University Nalbant, Asli; Sabanci University Okyay, Firuze; Sabanci University Yurum, Yuda; Sabanci University, Faculty of Engineering and Natural Sciences
Keywords:	humic acid, nitro-coal, oxy-ammoniated coal, nitrogenous fertilizer, trace elements



Conversion of Low-Rank Kilyos Coal to Nitrogeous Fertilizers

Özgül Hakli[§], Ahu Gümrah Dumanli, Asli Nalbant, Firuze Okyay and Yuda Yürüm*

Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, 34956 Istanbul, Turkey

[§]Department of Chemistry, Celal Bayar University, Muradiye, 45100 Manisa, Turkey

*Author to whom all correspondence should be addressed:

Yuda Yürüm
Faculty of Engineering and Natural Sciences
Sabanci University
Tuzla, 34956 Istanbul
Turkey

Phone: 90 216 483 9512
E-mail: yyurum@sabanciuniv.edu

Conversion of Low-Rank Kilyos Coal to Nitrogenous Fertilizers

Özgül Hakli[§], Ahu Gümrah Dumanli, Asli Nalbant, Firuze Okyay and Yuda Yürüm^{*}

Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, 34956 Istanbul, Turkey

[§]Department of Chemistry, Celal Bayar University, Muradiye, 45100 Manisa, Turkey

Abstract

The aim of this work is to convert the low-rank Kilyos coal to a material that could be used as a nitrogenous fertilizer. Incorporation of nitrogen into this Kilyos coal was accomplished by oxidative ammoniation, which was a two-step process involving oxidation with nitric acid followed by a treatment by ammonia. The nitrogen content of the raw coal increased from 0.8% to 8.3-9.3% after ammoniation process. Trace element concentrations in the nitro-coal, HA and OAC samples were within the acceptable ranges to be used as nitrogenous fertilizer. Therefore the oxy-ammoniated products could be considered as high-value fertilizers.

Keywords humic acid, nitro-coal, oxy-ammoniated coal, nitrogenous fertilizer, trace elements

Introduction

Low-rank coals contain high ash and moisture. Their calorific value are low and they are not favored as good fuels (Yan et al., 2001). Use of these low-rank coals for power generation produces environmental problems due to surface mining, and emission of gaseous pollutants during combustion. Boiler fouling and corrosion are additional problems that should be mentioned. Unusual uses of low-rank coals such as organic, organomineral fertilizers and soil conditioners give them more hopeful opportunities (Patti et al., 1992; Dick et al., 2002). There are many principles for the agronomic value of low-rank coals (Ivanov, 2007). Primarily, the quality and quantity of organic matter contained is the most essential issue to decide about the end use of a low-rank coal; humic substance content, especially, is

1
2
3 the most important factor in using these coals as fertilizers. Humic substances improve the
4 productiveness of soils by developing their physical properties and also upgrade the transport
5 of water and nutrient, consequently making possible the availability of nutrient elements,
6 especially trace metals (Piccolo et al., 1997).
7
8
9

10 Thus, humic acids (HA) present in soils, natural waters, river and sea sediments
11 (Novak et al. 2001; Kurkova et al. 2004) and the alkali-soluble fraction of so-called humic
12 substances are extremely important agronomically (Peuravuori et al. 2006; Skhonde et al.
13 2006). It has been recognized for many years that fertilizers could be obtained from low-rank
14 coals by reaction with ammonia combine the properties of both humus or organic manure and
15 the chemical nitrogen fertilizers. Several studies were carried out in order to produce coal-
16 based fertilizers by processes that involved the oxidation of coal followed by treatment with
17 ammonia (Gürüz, 1980; Coca et al. 1984; Awad et al. 1989; Patti et al. 1992; Yildirim and
18 Ozbayoglu, 1997). Elbistan lignite has been found to contain 50.1 wt% (daf) humic acid. The
19 IR spectrum of this lignite, however, indicates the absence of free carboxyl groups. Treatment
20 with mineral acids, however, regenerates the carboxyl groups. A product containing 18.8 wt%
21 N (daf) has been obtained by treatment of HNO₃-treated Elbistan lignite in aqueous ammonia
22 for 4 h at 165 °C and under oxygen pressure. Water-soluble and active nitrogen tests indicate
23 that such products may have the properties of slow release nitrogenous fertilizers (Gürüz,
24 1980). Sorption of ammonia on conditioned Yallourn brown coal was studied from the point
25 of view of increasing its nitrogen content to produce nitrogenous fertilizer (Awad et al. 1989).
26 Nitrohumic acids from a Victorian brown coal, produced by nitric acid oxidation of low rank
27 coals have been advocated for a variety of applications including nitrogenous humic
28 fertilizers, fertilizer additives to enhance plant yields, plant growth stimulators and a variety
29 of non-agricultural uses (Patti et al. 1992). Two of the most important features of nitrogenous
30 humic fertilizers are good control and conditioning of the soil properties (mechanic properties,
31 pH, retention of nutrient ions, microorganism activity and heat capacity of the soil) and
32 controlled release of nitrogen, avoiding losses by run-off water as it occurs with synthetic
33 fertilizers, in which more than 50-60% of the in put nitrogen is lost. Nitrogen-rich coal humic
34 acids have good value as a fertilizer. Their effects depend on the amount of added nutritional
35 matter (Yildirim and Ozbayoglu, 1997).
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

56 The aim of this work is to convert the low-rank Kilyos coal to a material that could be
57 used as a nitrogenous fertilizer. Incorporation of nitrogen into this Kilyos coal was
58 accomplished by oxidative ammoniation, which was a two-step process involving oxidation
59 with nitric acid followed by a treatment by ammonia.
60

Experimental

Coal

The coal sample used in the present study was from Kilyos, Istanbul and elemental analysis (dmmf) of the coal is, C%: 62.2, H% : 6.6, N%: 0.8, S%: 0.8, O%: 29.6 (by diff.). The moisture and mineral matter contents of the raw sample were 15.0% and 52.4%, respectively. The coal used was crushed to a particle size of 1 mm for all the subsequent experiments.

Chemical Treatment of Coal

The oxidation step was carried out by making a slurry with 10 g of coal and 10 mL distilled water in the three-neck flask provided with a thermometer, a stirrer, and a graduated dropping funnel. 15 mL of nitric acid (20% w/w) in a dropping funnel was added to the coal slurry at 75°C. The content of the flask was kept stirred at 75°C for 2 h. After this period, the reaction mixture was cooled, filtered and the nitrated coal (nitro-coal) was washed up to neutralization with distilled water and dried under a nitrogen atmosphere.

Humic acids (HA) were then extracted from the resulting nitro-coal, using extraction methods that are capable of extracting only humic acids (Skhonde et al. 2006). The extraction was carried out on 2.5 g of oxidized coal, using an aqueous sodium hydroxide solution (2.5 g NaOH/100 mL water). The mixture was refluxed for 5 h. The reaction mixture was cooled and filtered to separate the residue. The pH of extracted solution was neutralized with HCl to precipitate the HA. The HA was filtered, washed with water and dried under a nitrogen atmosphere.

The ammoniation experiments were carried out using 20 mL of ammonium hydroxide solutions of different concentrations (5%, 10%, 15%, and 20%) with 5 g of nitro-coal in a two-neck flask equipped with a thermometer and a stirrer. The mixture was refluxed for 2 h. After this period, the reaction mixture was cooled; the oxy-ammoniated coal (OAC) was filtered and dried under a nitrogen atmosphere.

Elemental Analyses

Elemental analyses (C, H, N, S, O by difference) was conducted at the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Center, Gebze using a standard C-H-N-S analyzer.

FTIR Spectra

FTIR spectra of the raw and treated coal samples were obtained using a Bruker Equinox 55 FTIR spectrometer equipped with an ATR system by co-adding 20 scans over the range 600–4000 cm^{-1} performed at 1 cm^{-1} of digital resolution.

ICP Analysis

Concentrations of some inorganic elements in the ashes of raw and treated coal samples were determined with a Vista-Pro Axial; Varian Pty Ltd, Mulgrave, Australia, inductively coupled plasma optical emission spectrometer (ICP-OES).

Results and Discussion

The yield of nitric acid oxidation experiment in the production of nitro-coal was 86%. 33% of nitro-coal could be extracted as HA by aqueous sodium hydroxide solution. Elemental analysis results for the raw, nitro-coal, OAC and HA are presented in Table 1. Due to the nitration reactions nitrogen percentage of the coal increased from 0.8% to 4.6%. After ammoniation process, the OAC which contained ammonium nitrohumates were found to have nitrogen contents ranging between 8.3 and 9.3%. Using increasing concentrations of ammonium hydroxide solutions (from 5% to 20%) in ammoniation reactions increased the nitrogen content. Table 1 also contained the atomic H/C, O/C and N/C ratios. All the chemical treatments increased the values of H/C, O/C and N/C ratios from the raw coal to AC. Increase of the O/C and N/C values indicated formation of higher concentrations of nitro groups in the treated coal samples. Therefore the oxy-ammoniated products could be considered as high-value fertilizers.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The raw coal, nitro-coal, residue after NaOH extraction and HA were examined by FTIR spectroscopy, Figures 1 and 2. The FTIR spectrum of the raw coal is presented in Figure 1a. The spectrum is very typical for a low-rank coal. The bands in different regions are assigned to the functionalities indicated in the parentheses: 3700-3300 cm^{-1} (free and bonded $-\text{OH}$ stretch vibration), 2900 cm^{-1} ($-\text{CH}_3$ symmetric stretch), 2850 cm^{-1} ($-\text{CH}_3$ asymmetric stretch), 1580 cm^{-1} (aromatics ring vibration), 1420 cm^{-1} ($-\text{CH}_3$ symmetric bending), 1240 cm^{-1} ($-\text{CH}_3$ rocking vibration), 1085 cm^{-1} ($-\text{C}-\text{OH}$ stretch vibration), 1016 cm^{-1} (ring vibration), 900 cm^{-1} ($-\text{C}=\text{C}-\text{H}$ out-of-plane vibration), 800-650 cm^{-1} ($\text{C}-\text{H}$ bending vibrations) (Shevla, 1976).

The nitration of coal seemed to add new peaks to the spectrum of the raw coal, Figure 1b. The nitro-coal indicated new peaks near 1650 cm^{-1} due to $-\text{N}=\text{O}$ stretching and asymmetric NO_2 stretching vibrations, 1530 cm^{-1} of asymmetric NO_2 vibrations, two shoulders near 1300 cm^{-1} and 1140 cm^{-1} because of NO vibrations, and a sharp peak at 680 cm^{-1} due to $-\text{N}=\text{O}$ stretching and $\text{O}-\text{N}=\text{O}$ deformation vibrations. Absorption bands in the region of 1440-1650 cm^{-1} confirmed the aromatic character of the oxidized coal. Treatment of coal with nitric acid formed polycarboxylic acids, nitro-hydroxy, quinonoid acids in the coal structure (Pehlivan and Arslan, 2006) as these were also observed in the present study. Nitrogen was introduced into the coal molecules as nitro (1510-1550 cm^{-1} , 1335-1365 cm^{-1} , 840-860 cm^{-1}) and nitroso groups (ca. 1500 cm^{-1}).

FTIR spectra of the residue and HA are presented in Figure 2a and 2b, respectively. Both of the spectra looked similar to each other, but the peaks in the spectrum of HA are sharper. Both spectra contained the following peaks indicating the presence of similar structures: 3500-3300 cm^{-1} (free and bonded $-\text{OH}$ stretch vibration), 2900 cm^{-1} ($-\text{CH}_3$ symmetric stretch), 2850 cm^{-1} ($-\text{CH}_3$ asymmetric stretch), 2535 cm^{-1} ($>\text{NH}_2^+$ and $-\text{NH}_3^+$ amine hydrochloride), 2155 cm^{-1} ($-\text{C}-\text{N}$ and $-\text{C}-\text{O}$ stretching vibrations), 2026 cm^{-1} ($>\text{C}=\text{O}$ and $-\text{C}=\text{O}$ stretching vibrations), 1950 cm^{-1} ($-\text{C}=\text{C}$ asymmetric stretching vibrations), 1564 cm^{-1} (aromatics ring vibration), 1390 cm^{-1} ($-\text{CH}_3$ symmetric bending), 1306 cm^{-1} ($>\text{CH}_2$ wag), 1250 cm^{-1} ($-\text{C}-\text{N}$ - stretching vibrations), 1139 cm^{-1} (methyl rocking vibrations), 1029 cm^{-1} (ring vibration).

Concentrations of some inorganic elements in the ashes of raw coal, nitro-coal, HA and OAC samples determined by inductively coupled plasma optical emission spectrometry are given in the Table 2. As can be seen, the raw coal and treated coal samples contained mainly of Ca, Al, Mg and Fe species. Compounds of Na (252 ppm), B (145 ppm), K (121 ppm), S (67 ppm), Mn (55 ppm), P (21 ppm) were the inorganic constituents present in

1
2
3 moderate amounts. Na content of the HA was very high, 4482 ppm, this was due to NaOH
4 extraction of the HA from the nitro-coal. Raw coal contained also contained some elements
5 in minor quantities: Cu (7 ppm), Cr (6 ppm), Co (6 ppm), Ni (4 ppm), Pb (3 ppm) and Zn (2
6 ppm). were also present in minor quantities. Concentration of all of the elements mentioned
7 in the raw coal seemed to decrease in nitro-coal, the reason for this reduction was probably
8 dissolution of the inorganic species during nitric acid treatment of the raw coal. Na content of
9 the HA was observed to be very high: 4482 ppm, this was due to NaOH treatment to extract
10 the HA from the nitro-coal. Although the precipitate obtained after acid neutralization of the
11 NaOH extract was filtered and washed with water, it seemed that Na ions remained in the
12 precipitate probably forming stable compounds. Ammoniation experiments conducted with
13 increasing concentrations of ammonium hydroxide reduced the concentrations of the
14 inorganic elements (except for Na and B) in the OAC samples to values slightly lower than
15 those in nitro-coal. The reason for the reduction of the concentrations of the inorganic
16 constituents were probably again solubility of these inorganics in the ammonium hydroxide
17 solutions. Average concentrations of trace elements in silty and loamy soils reported in the
18 literature are as follow (Kabata-Pendias and Pendias, 2001): B (40 ppm), Mn (525 ppm), Cu
19 (23 ppm), Cr (51 ppm), Co (10 ppm), Ni (26 ppm), Pb (28 ppm), and Zn (60 ppm).
20 Concentrations of trace elements in the nitro-coal, HA and OAC samples were within the
21 acceptable ranges given by Kabata-Pendias and Pendias (2001). The results obtained in the
22 ICP analysis of the treated coal samples obtained in the present study indicated that these
23 could be used as nitrogenous fertilizers for plants since the inorganic material content would
24 not harm the crop.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

43 44 Conclusions

45
46
47 The low-rank Kilyos coal was converted to a material that could be used as a
48 nitrogenous fertilizer. Incorporation of nitrogen into this Kilyos coal was accomplished by
49 oxidative ammoniation, which was a two-step process involving oxidation with nitric acid
50 followed by a treatment by ammonia.
51

52
53
54 The nitrogen content of the raw coal was 0.8%. After ammoniation process, the
55 products which contained ammonium nitrohumates were found to have nitrogen contents
56 ranging between 8.3 and 9.3%. Therefore the oxy-ammoniated products could be considered
57 as high-value fertilizers.
58
59
60

1
2
3 The nitration of coal seemed to introduce nitro and nitroso groups into the coal
4 structure. HA contained aromatic structures attached with groups of free and bonded $-\text{OH}$, $-\text{CH}_3$, $>\text{CH}_2$, $>\text{NH}_2^+$, $-\text{NH}_3^+$, $-\text{C}-\text{N}$, $>\text{C}=\text{O}$.
5
6
7

8 Trace element concentrations in the nitro-coal, HA and OAC samples were within the
9 acceptable ranges to be used as nitrogenous fertilizer.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

Oussa, A.R. and Evans D.G. 1989. The interaction of ammonia with brown coal : 1. Physical interaction, *Fuel*, 68: 1363-1367.

Coca, J., Alvarez, R. and Fuertes, A.B. 1984. Production of a nitrogenous humic fertilizer by the oxidation-ammoniation of lignite, *Ind. Eng. Chem. Prod. Res. Dev.*, 23: 620-624.

Gürüz, K. 1980. Oxy-ammoniation of Elbistan lignite to produce a nitrogenous fertilizer, *Fuel*, 59, 772-776.

Dick, D.P., Mangrich, A.S., Menezes, S.M.C. and Pereira, B.F. 2002. Chemical and spectroscopical characterization of humic acids from two south Brazilian coals of different Ranks, *J. Braz. Chem. Soc.*, 13: 177-182.

Ivanov, I.P. 2007. Main trends in the biotechnological processing of coals: a review. *Solid Fuel Chem.* 41: 3-10.

Kabata-Pendias, A. and Pendias, H. 2001. Trace Elements in Soils and Plants, 3rd Edition, CRC Press, Boca Raton. p.31.

Kurkova, M., Klika, Z., Klikova, C. and Havel, J. 2004. Humic acids from oxidized coals I. Elemental composition, titration curves, heavy metals in HA samples, nuclear magnetic resonance spectra of has and infrared spectroscopy, *Chemosphere* 54: 1237-1245.

Novak, J., Kozler, J., Janos, P., Cesikova, J., Tokarova, V. and Madronova, L. 2001. Humic acids from coals of the North-Bohemian coal field I. Preparation and characterisation” *Reactive and Functional Polymers* 47: 101-109.

Patti, A.F., Verheyen, T.V., Douglas, L. and Wang, X. 1992. Nitrohumic acids from Victorian brown coal. *Sci. Total Environ.* 113: 49-65.

Pehlivan, E. and Arslan, G. 2006. Comparison of adsorption capacity of young brown coals and humic acids prepared from different coal mines in Anatolia, *J. Hazardous Mat.* B138: 401-408.

Peuravuori, J., Zbankova, P. and Pihlaja, K. 2006. Aspect of structural features in lignite and lignite humic acids, *Fuel Proc. Technol.* 87: 829-839.

Piccolo, A., Pietramellara, G. and Mbagwu, J.S.C. 1997. Use of humic substances as soil conditioners to increase aggregate stability, *Geoderma* 75: 267-277.

Shevla, G., 1976. Comprehensive Analytical Chemistry, Volume VI, Analytical Infrared Spectroscopy, Elsevier, Amsterdam, p. 333.

Skhonde, M.P., Herod, A.A, Walt T.J., Tsatsi W.L. and Mokoena, K. 2006. The effect of thermal treatment on the compositional structure of humic acids extracted from South African bituminous coal, *Int. J. Miner. Process.* 81: 51-57.

1
2
3
4 Yan, R., Gauthier, D. and Flamant, G. 2001. Volatility and chemistry of trace elements in a
5 coal combustor, *Fuel* 80: 2217–2226.
6
7

8 Yildirim, M. and Ozbayoglu, G. 1997. Production of ammonium nitrohumate from Elbistan
9 lignite and its use as a coal binder, *Fuel* 76: 385-389.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 **LIST OF TABLES**
5
6
7

8 **Table 1.** Elemental composition of coal, oxidized coal and oxy-ammoniated coal, %, dmmf.

9
10 **Table 2.** Concentration of inorganic elements in raw coal, nitro-coal, HA and OAC, ppm.
11
12
13

14
15 **LIST OF FIGURES**
16
17

18 **Figure 1.** FTIR spectra of a) raw coal and b) nitro-coal

19
20 **Figure 2.** FTIR spectra of a) residue after NaOH extraction and b) humic acid precipitate
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 1

Elemental composition of coal, oxidized coal and oxy-ammoniated coal, %, dmmf

	C	H	N	S	O, by diff.	H/C	O/C	N/C
coal	62.2	6.6	0.8	0.8	29.6	1.27	0.36	0.011
nitro-coal	64.0	4.7	4.6	0.7	26.0	0.88	0.31	0.062
HA	52.9	4.5	9.3	0.6	32.7	1.02	0.46	0.151
OAC (5%)	45.9	4.6	8.3	0.6	40.6	1.20	0.66	0.155
OAC (10%)	42.3	4.7	8.4	0.6	44.0	1.33	0.78	0.170
OAC (15%)	41.6	5.5	8.6	0.7	43.6	1.59	0.79	0.177
OAC (20%)	37.2	5.2	9.4	0.6	47.6	1.68	0.96	0.217

Table 2

Concentration of inorganic elements in raw coal, nitro-coal, HA and OAC, ppm

	Ca	Al	Mg	Fe	Na	B	K	S	Mn	P	Cu	Cr	Co	Ni	Pb	Zn
Raw coal	12898	2084	2029	1588	252	145	121	67	55	21	7	6	6	4	3	2
Nitro-coal	7401	1309	278	1037	25	38	81	58	11	5	10	5	5	3	3	2
HA	130	703	21	336	4482	18	71	58	2	4	11	20	7	11	0	4
OAC (5%)	5457	875	250	828	70	49	67	56	9	5	10	4	4	3	2	3
OAC (10%)	4769	926	254	1042	50	53	43	61	9	5	10	4	4	3	2	3
OAC (15%)	3456	651	310	621	50	46	45	56	10	4	9	4	5	3	1	2
OAC (20%)	5998	625	259	854	51	37	42	57	9	4	8	4	5	3	2	2

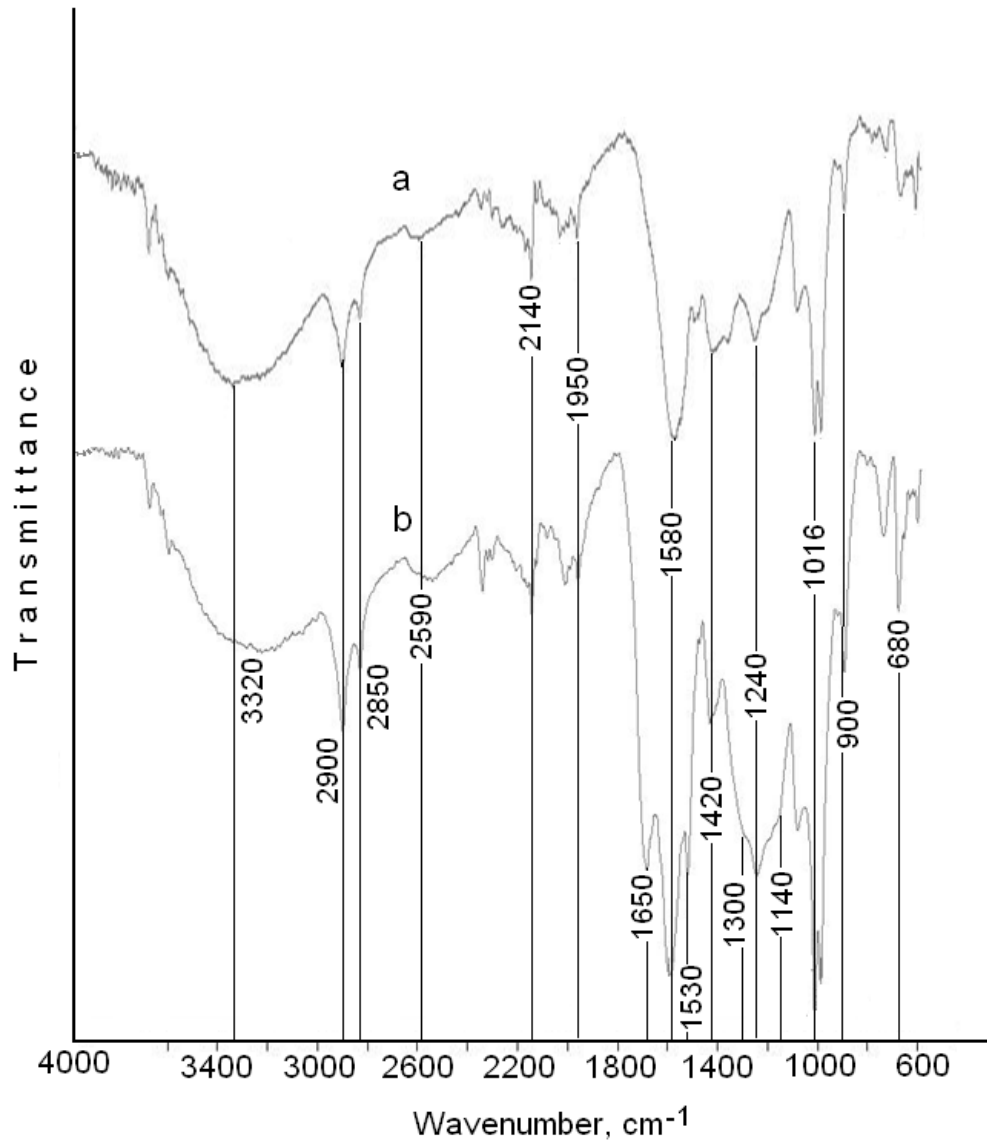


Figure 1. FTIR spectra of a) raw coal and b) nitro-coal

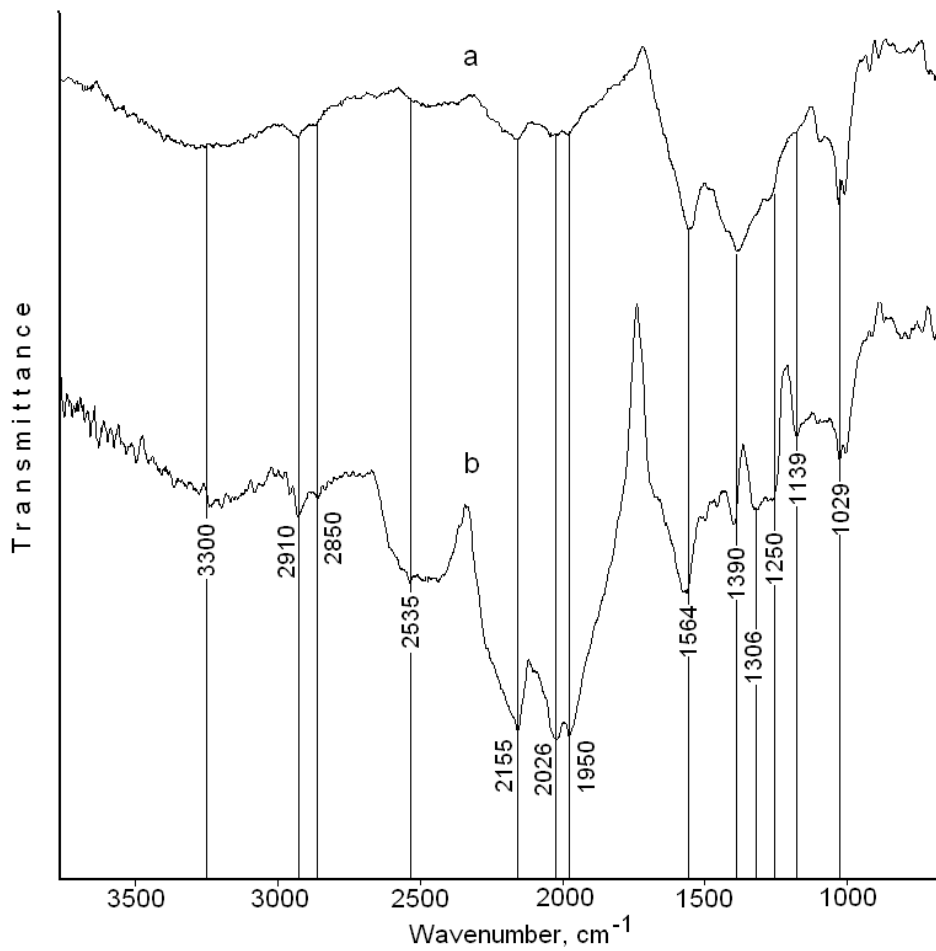


Figure 2. FTIR spectra of a) residue after NaOH extraction and b) humic acid precipitate