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Sorption of Neodymium from Nitrate Solutions by Humic Acids-Based Sorbent

A.G. Ismailova[1], G.Zh. Akanova[1]*, Kh.S. Tassibekov[1], D.Kh. Kamysbayev[1],
B.T. Yermagambet[2], M.K. Kazankapova[2], Zh.M. Kassenova[2]

[1]al-Farabi Kazakh National University, al-Farabi ave. 71, Almaty, Kazakhstan
[2]Institute of Coal Chemistry and Technology LLP, 26 Akzhol Str., Astana, Kazakhstan

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Abstract

This work obtained a sorbent based on humic acids (HA) isolated from oxidized brown coals of the Maikuben deposit. The study of humic acids by IR spectroscopy showed the presence of various functional groups (OH-, COOH-) in the sorbent, which can enter into ion-exchange reactions with metals. Humic acids have been tested as a sorbent for neodymium. Neodymium sorption was carried out under static conditions from nitrate solutions. It was found that with a sorption time of 30 min and a solution pH is 1.0, the sorption efficiency of neodymium is 95.5%. A sorbent based on humic acids was used to separate neodymium from a solution obtained by dissolving electronic waste (neodymium magnet). SEM-analysis and mapping of the sorbent surface after neodymium sorption showed that neodymium was absent on the sorbent surface.

1. Introduction

Rare earth elements (REE) are naturally found in the composition of various minerals and ores. Coal deposits are considered potential raw material sources of REE. There are several coal deposits containing REE in Kazakhstan [1]. In the technology of REE production, synthetic materials are widely used for their extraction and separation [2–11] and carbon-containing sorbents. It is noted that humic acids [12–16] have a good sorption capacity for various metals. Table 1 provides information on the sorption of some REEs by various carbon-containing sorbents. As follows from the above data, such materials are effective REE sorbents.

The elemental composition and functional groups will be required to study the sorption properties of humic acids. The comparative elemental and functional composition of humic acids were given below in Table 2.

The chemical composition of humic acids (HA) was very complex and consists of several functional groups, such as carboxyl, phenolic, sulfide and carbonyl. From these groups, carboxyl and phenolic groups were considered the most important, which affect the complexation of metals in the form of chelates [22–24].

Other authors had studied the adsorption properties of humic acids for different metals. Masoud et al. studied the adsorption properties of HA for heavy metals, such as Pb (II) and Cd (II) for removal from water. The adsorption capacity of the HA for Pb was 6.02 mg/g and Cd 0.66 mg/g. This proved that HA based sorbent is a perspective sorbent for separating metals [25].

In the following work, the authors studied the sorption of Hg (II) using HA, as well as with the sorbent vermiculite (VT) and a mixture of HA+VT. In comparison with VT, HA showed high sorption properties for mercury, the sorption capacity was 537±30 μmol/g [26].

In our work, the sorption properties of HA for neodymium have been studied.

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*Corresponding author.
E-mail: gulsaraakanova.kz@gmail.com

Table 1
REE sorption by various carbon-containing sorbents

Sorbent	REE	The main results of the experiments	References
Humic acid-based sorbent	Nd (III)	pH = 1; 30 min; 97.59%	In this work
Oxidized multi-walled carbon nanotubes	La(III) Dy(III)	pH = 4–6; 78 mg/g (Dy (III)) 99.01 mg/g (La (III))	[17]
Activated carbon	Dy(III)	pH = 4; 294 mg/g	[18]
Magnetic nanocomposite based on graphene (MNGO)	La (III)	pH = 4.0; 49,75 mg/g R = 93%	[19]

Table 2
Comparative elemental and functional composition of different humic acids

Humic acids	Elemental composition, %				Carboxyl groups, mmol/g	Phenolic groups, mmol/g	References
	C	H	N	O			
HA Maikuben	39.6	2.9	0.26	27.6	1.18	0.42	In this work
HA Zoo Giza	52.8	3.4	1.2	42.6	4.87	1.12	[20]
HA Aldrich	50.0	4.5	2.3	43.2	2.16	0.08	[20]
HA-2 Gurovskoe	71.0	5.3	3.6	19.1 (+S)	3.9	5.1	[21]

The purpose of this work was to obtain a sorbent based on humic acids from the coals of the Maikuben deposit [27], as well as to study the sorption of neodymium from nitrate solutions with the resulting sorbent.

2. Materials and methods

2.1. Materials

Maikuben humic acid sorbent was obtained from the Institute of Coal Chemistry and Technology. The stock solution of neodymium was prepared by dissolving its oxide (99.95%) in concentrated nitric acid (w = 67%) solutions and diluting them with distilled water to the required volume. For spectrophotometer analysis acid buffer solution (pH = 2.4) and Arsenazo III (0.1%) solution were used.

2.2. Equipment

The following equipment was used in this work: LEKI SS spectrophotometer (Russia), muffle furnace (SNOL 7,2/1300, Lithuania), rotary shaking apparatus (EKROS Model 6410 m), pH meter (I–160 with glass electrode ESL-63-07, Russia), X-Ray diffractometer (DRON-4-07, Russia), Scanning electron microscope with microanalysis capability (JEOL JSM-6610 LV), IR Fourier spectrometer (Nicolet iS 10), Sorbmeter (Katakon Sorbtometer M), SEM scanning electron microscope (Quanta 3D 200i).

2.3. Determination of metals in solutions

Determination of neodymium from model solutions before and after sorption was conducted by the spectrophotometric method with Arsenazo III. Characterization of this method showed in Savvin's work [28]. The concentration of metals in multicomponent solutions was determined by inductively coupled plasma mass spectrometry (ICP-MS).

2.4. Sorption of neodymium with a humic acids-based sorbent

The batch neodymium sorption experiments were performed in the static mode at room temperature. A solution of neodymium with a specific pH value was placed in a conical flask, and a suspension of the sorbent was added so that the ratio of solid to liquid was 1:100 and mixed with a shaking apparatus for a selected time. At the end of sorption, the phases were separated and the concentration of neodymium was determined spectrophotometrically in the aqueous phase. All experiments were carried out in three parallels.

2.5. Determination of static sorption capacity (q) and the adsorption percentage (R) of the metal

REs static sorption capacity onto sorbent was calculated by mass balance, according to:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \tag{1}$$

where q_t is the amount of adsorbed metals, mg/g, C_0 is the initial concentration of neodymium, mol/L; C_t is the equilibrium concentration of neodymium, mol/L; m is the sorbent dosage, g, V is the volume of the solution, mL.

The adsorption percentage was defined as:

$$R = \frac{C_0 - C_t}{C_0} \cdot 100\% \tag{2}$$

where, R is the adsorption percentage, %.

2.6. Obtaining a humic acid-based sorbent

Humic acids were obtained based on oxidized brown coal from the Maikuben deposit (Kazakhstan). The chemical composition of humic acid is shown in Table 2. The size of coal particles was: 2.95 microns – 10%, 63.8 microns – 50%, 452 microns – 90%. X-Ray phase analysis revealed that the composition of the coal sample includes galloisite ($Al_2Si_2O_5(OH)_4$), silicon dioxide and albite $Na(AlSi_3O_8)$.

A rotary pulsating apparatus with an ultrasonic reactor was used to prepare sorbent based on humic acids for making the size of coal particles 19.2 nm and 3.57 microns. Air was supplied for oxidizing coal and increasing the content of humic substances. In the dispersion and ultrasonic exposure process, the mixture's temperature was maintained in the range of 50–55 °C. This temperature was acceptable for the oxidation of coal with air oxygen and the extraction of the formed salts of humic and fulvic acids. In the oxidation process by air, a micelle-like dispersed system was formed in which humic acid particles were less than a micrometer in size. Further, humic acids were purified and determined in accordance with the recommendations of the International Humic Substances Society (IHSS).

Humic acids were obtained by acidifying them with a 5% acid solution to pH = 3.0–4.5. As a result of the reaction, humic acids fell out in the form of amorphous brown precipitation. All organic substances remaining in the acidic solution after the isolation of HA were treated as fulvic acids. HA was separated by centrifugation, transferred to a filter, washed with distilled water to a neutral pH value, and dried at 60–70 °C to a constant mass.

3. Results and discussions

3.1. Analysis of humic acids-based sorbent by IR spectroscopy

The IR spectrum of humic acids isolated from oxidized angles was shown in Fig. 1. A wide absorption peak was observed in the spectrum at 2923 cm^{-1}, which refers to asymmetric and symmetrical fluctuations of methylene ($-CH_2-$) groups characteristic of aliphatic and undeformed cyclic hydrocarbons. This peak, however, can also mask a wide signal of N–H/O–H groups. The absorption band of 1701 cm^{-1} was associated with the presence of free carboxyl groups in the composition of acids. The absorption band at 1590 cm^{-1} corresponds to the carboxyl ion. In the region of 1400–800 cm^{-1}, peaks corresponding to the deformation vibrations of C–O appear. Peaks of C–C oscillations were observed at 1005 cm^{-1} and 1226 cm^{-1}. Peaks in the range of 1000–800 cm^{-1} were responsible for the strong stretching of the C–O group. The peaks at 1565, 1363 and 995 cm^{-1} were attributed to the valence oscillations of the groups -COO- and -CH, -OH, etc. An increase in the peak intensity at 1565 cm^{-1} makes it possible to attribute this peak to fluctuations in the carboxylate ion.

The IR spectrum of humic acids showed that their structure is very complex [27]. The composition of humic acids includes many different functional groups. Metals react with functional groups OH- and COOH- for ionic reactions. Humic acids are formed complex compounds with metals [29].

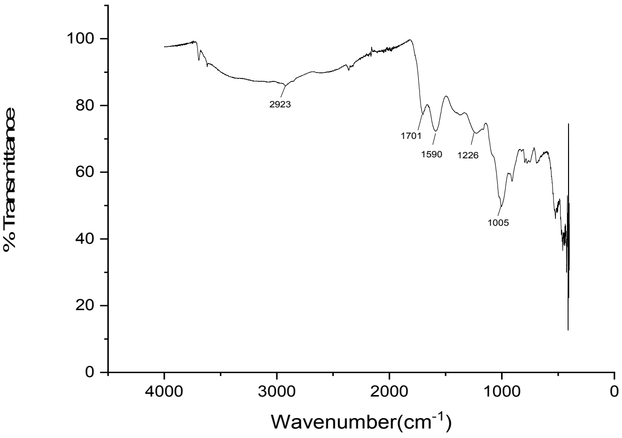
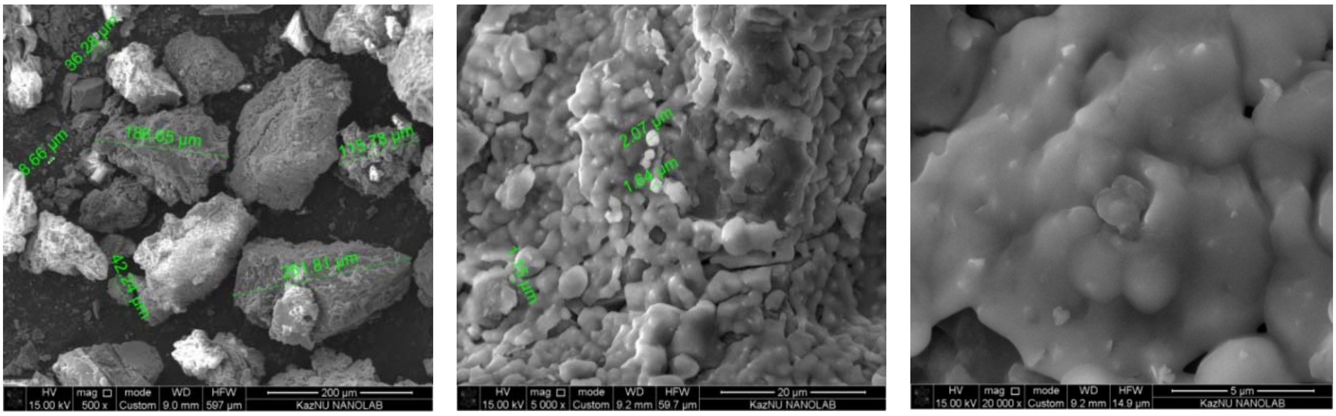


Fig. 1. IR spectrum of humic acids.



a) ×500 b) 5000 c) 20.000

Fig. 2. Electron micrographs of humic acid.

3.2. Analysis of humic acids-based sorbent by SEM analysis

An SEM image of the resulting structure, which enables the estimation of the grain size of the powder used in the experiment, is shown in Fig. 2.

Micrographs of samples were enlarged 500 times (a), 5000 times (b), and 20.000 times (c). When analyzing the morphology of the surface of the initial humic acids, it was found that the cleavage surface was represented by the heterogeneity of structure and has dense formations with strong agglomerates with particle sizes 1.15–10.47 microns.

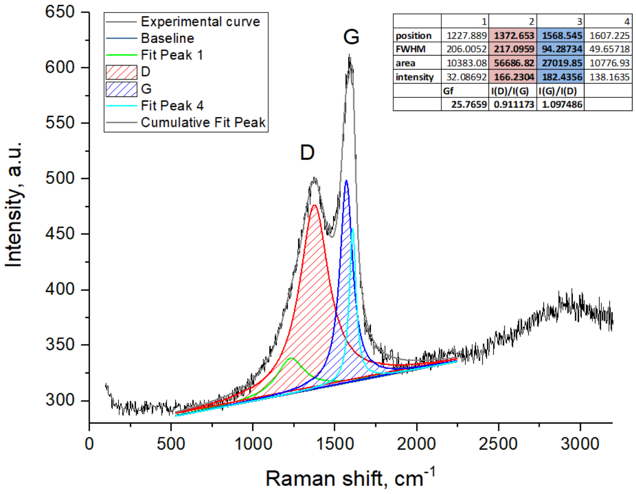
3.3. Raman Light scattering (RAMAN) method

The type of carbon modification was studied using Raman spectroscopy using the Raman light scattering (RAMAN) method. The RAMAN spectra of the samples were recorded on a probe scanning microscope Integra Spectra, using a laser with a wavelength of 473 nm.

Figure 3 shows the results of the humic acid signals with characteristic peaks D and G (1372.85 cm^{-1} and 1584.98 cm^{-1}). The ratio of the intensities of D and G peaks shows the number of defects of the material under consideration, I_D/I_G was 0.91. The degree of graphitization (G_f) was 25.76%.

3.4. Sorption of neodymium from nitrate media with a humic acid based sorbent

The efficiency of metal sorption depends on the characteristics of the structure and composition of the sorbent, the shape of the metal in the solution, the concentration of the metal, the acidity of the aqueous phase, the ratio of the phases of the sorbent and the solution, and many other factors.



	1	2	3	4
position	1227.889	1372.653	1568.545	1607.225
FWHM	206.0052	217.0959	94.28734	49.65718
area	10383.08	56686.82	27019.85	10776.93
intensity	32.08692	166.2304	182.4356	138.1635
	Gf	I(D)/I(G)	I(G)/I(D)	
	25.7659	0.911173	1.097486	

Fig. 3. RAMAN spectra of humic acid.

3.5. Effect of phase contact time

Neodymium sorption was carried out with varying phase contact times from 1 min to 2 h at room temperature. The dependence of the adsorption percentage of neodymium sorption on time was shown in Fig. 4. As follows from the above data, the equilibrium in the system was established in 30 min, while the degree of sorption reached 97.6%. With a further increase in the contact time of the phases, the sorption efficiency practically did not change.

3.6. Effect of the acidity of the aqueous phase

The acidity of the aqueous phase is an important parameter affecting the degree of sorption of metals since it affects the ionic forms of metals in solution, as well as the surface properties of the sorbent (acid-base properties, the charge of functional groups), which, in turn, affect the affinity of sorbents to metal ions.

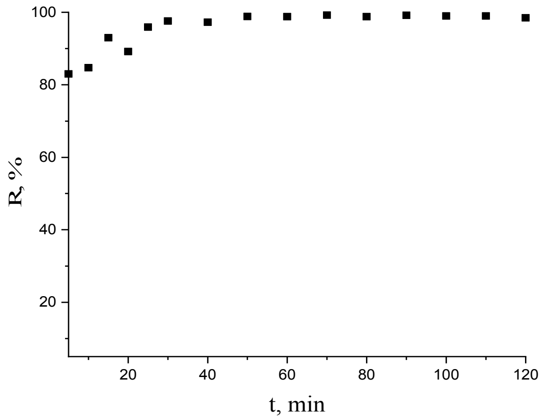


Fig. 4. Kinetic curve of neodymium sorption by humic acids: C(Nd) = 7·10^{-5} M; Solid : Liquid = 1:100.

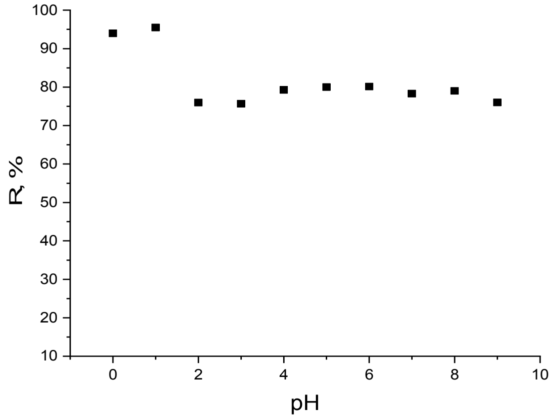


Fig. 5. The effect of pH on the sorption of neodymium by humic acids: C(Nd) = 7·10^{-5} M; Solid: Liquid = 1:100, τ = 30 min, t = 25 °C.

The effect of the acidity of the aqueous phase on the sorption extraction of neodymium was investigated. The pH values of the solutions varied in the range of 0.1–8.0. Increasing the pH above 9.0 was impractical since the sorbent humic acids form salts (humates). The experiments were carried out at room temperature and the ratio of the contacting phases was 1:100. The results obtained were shown in Fig. 5.

As follows from the above data, with an increase in the pH values of solutions, the adsorption percentage of neodymium decreases. Thus, at pH = 1.0, the sorption efficiency reached 95.5%, in the range of pH values 2.0–8.0, and the extraction of neodymium did not exceed 75–80%. The equilibrium pH values decreased in comparison with the initial ones. The pH from 2 to 9 was set to equilibrium.

3.7. Sorption of neodymium from real solutions

A humic acid based sorbent was tested to extract neodymium from a solution obtained by dissolving a spent neodymium magnet (24.7% Nd, 5.96% Pr and 2.40% Dy). Sorption was carried out under static conditions at pH = 1 and the ratio of the sorbent and solution phases of 1:100.

Figure 4 showed the morphology of the sorbent depending on the contact time of the phases. Figure 6 showed the surface of the sorbent was increased by 5000 times. When analyzing the morphology of the surface of the initial humic acids, it was found that heterogeneity of the structure represents the cleavage surface. After every 10 min of sorption, the surface of the sorbent gradually changes. This can explain why sorption was actively taking place over time.

For a more accurate determination of the sorbent structure after neodymium sorption, mapping was done. The distribution of metal and their percentage composition on the surface of the sorbent was shown in Fig. 7.

5 points (a, b, c, d) from different sides of the sorbent are considered. Then 10 points (e) on the surface of the sorbent were considered.

As follows from the above data, there was not neodymium and other rare earth metals on the surface of the sorbent since HA has a complex structure and surface heterogeneity as well as the possibility of simultaneous processes of sorption and desorption of competing metals. Therefore, the tested sorbent requires further careful studies of the sorption process in the entire sorbent volume, not only its surface.

3.8. Comparative composition of the sorbent before and after sorption

To determine the process before and after sorption, a comparative analysis of the sorbent was carried out using SEM analysis. Figure 8 shows micrographs of the sorbent in the initial sample and after sorption. In all cases, the micrographs are magnified 5000 times.

When analyzing the morphology of the surface of the initial humic acids (A), it was found that the sample's surface is represented by the heterogeneity of structure and has dense formations with strong agglomerates with particle sizes 1.15–10.47 microns. According to BET (the Brunauer – Emmett – Teller method), the specific surface area of humic acid was 0.42 m^2/g. Even though the

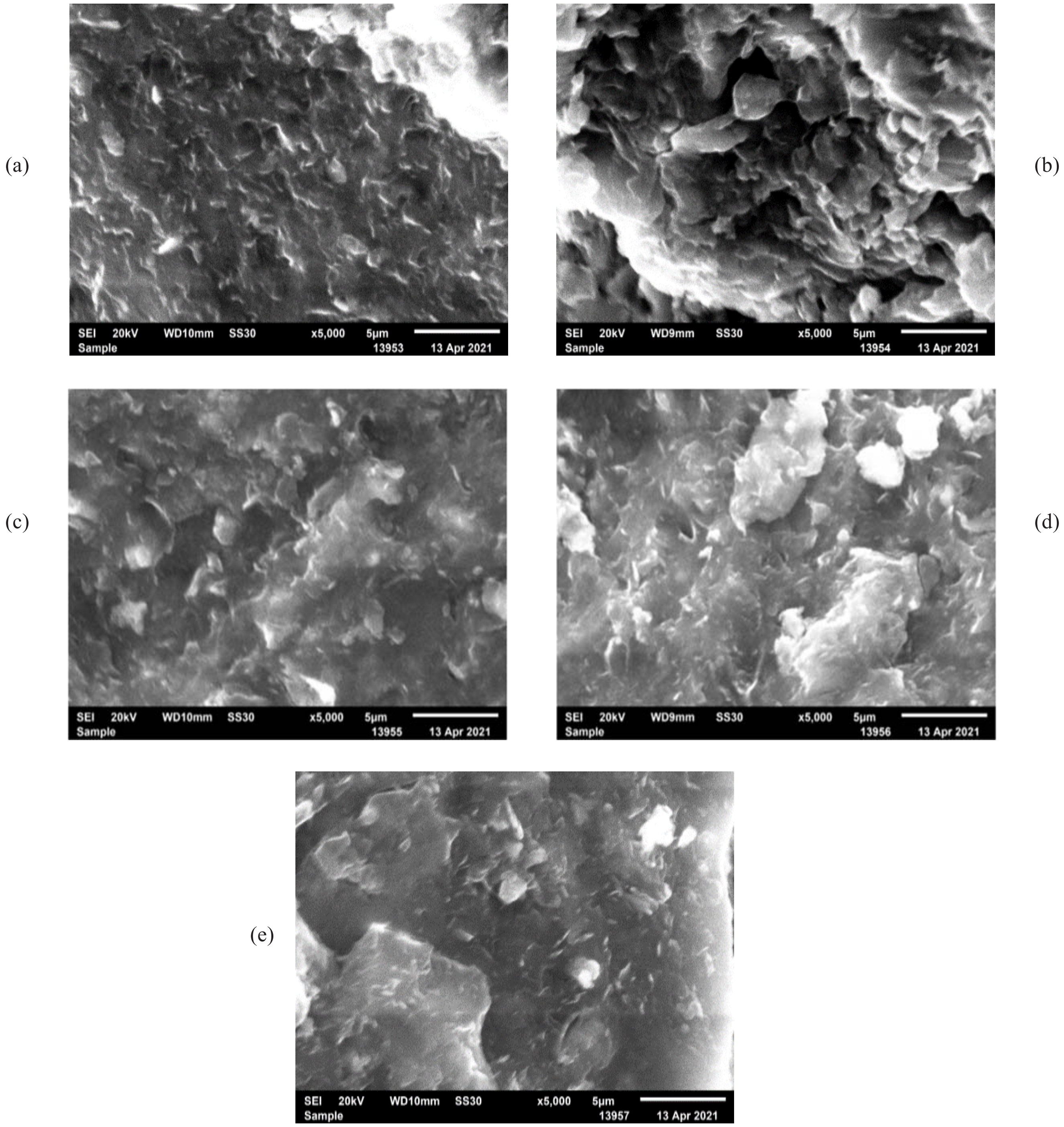
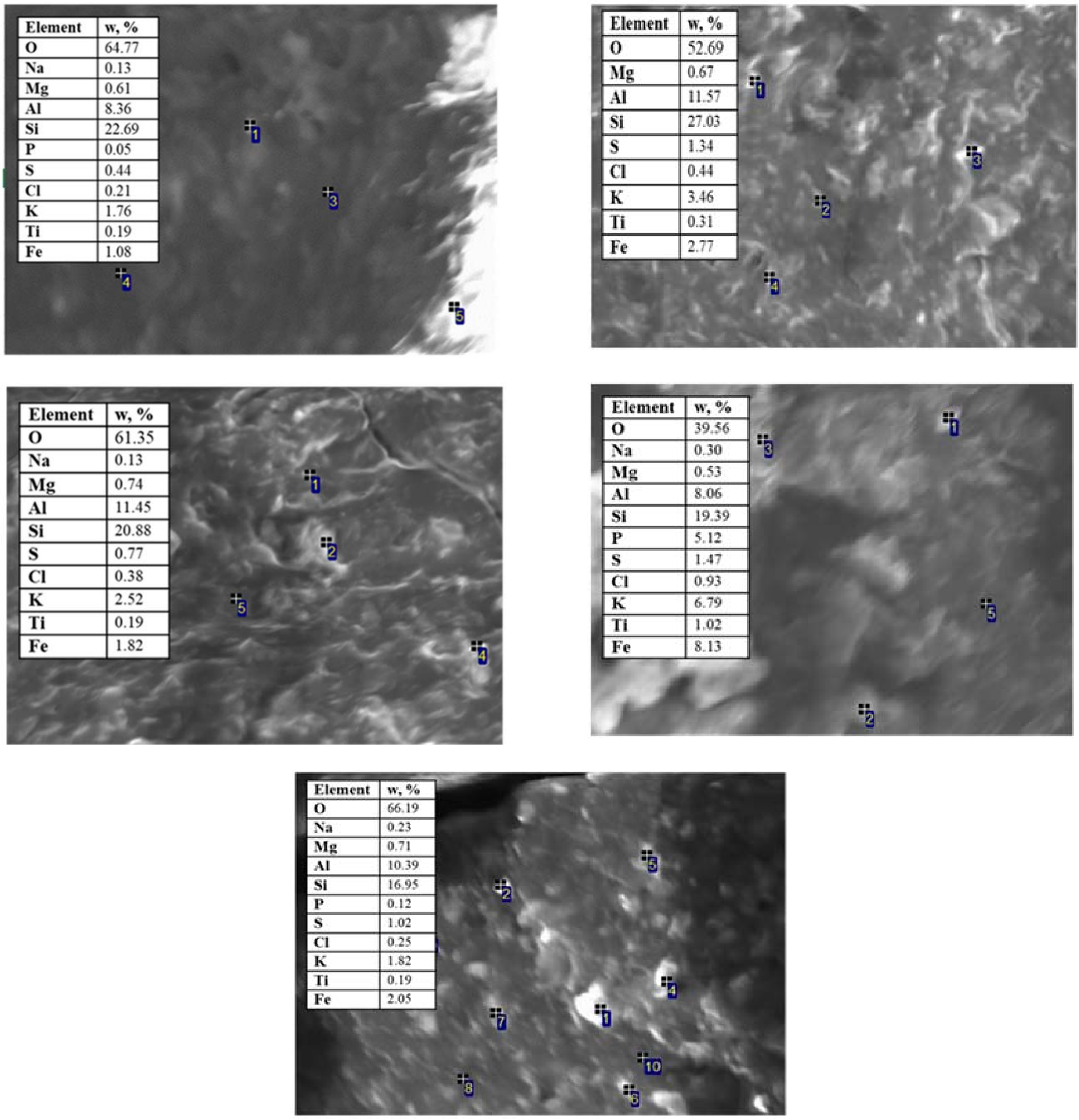


Fig. 6. Morphology of humic acids-based sorbent after neodymium sorption (according to SEM analysis). Phase contact time, min: (a) – 10, (b) – 20, (c) – 30, (d) – 50, (e) – 60.

specific surface area was not high, humic acid contains oxygen-containing functional groups (–COOH, phenolic and alcoholic -OH, as well as >C=O), which were involved in the formation of complex compounds with metal ions.

After sorption (B), the surface had become slightly homogeneous. Mapping of sorbent up to 10 points was done.

The magnetic solution contains various metals, such as aluminum, copper, nickel, iron, neodymium, praseodymium, dysprosium, etc. During sorption, these metals can interfere to absorb REE. The elemental composition of the HA-based sorbent in the initial sample and after sorption was shown in Fig. 8. The composition of the initial HA also contains aluminum, silicon, potassium, and iron. After sorption, the concentrations of these elements were decreased. Perhaps neodymium was not sorbed due to competing metals.



Element	w, %
O	64.77
Na	0.13
Mg	0.61
Al	8.36
Si	22.69
P	0.05
S	0.44
Cl	0.21
K	1.76
Ti	0.19
Fe	1.08

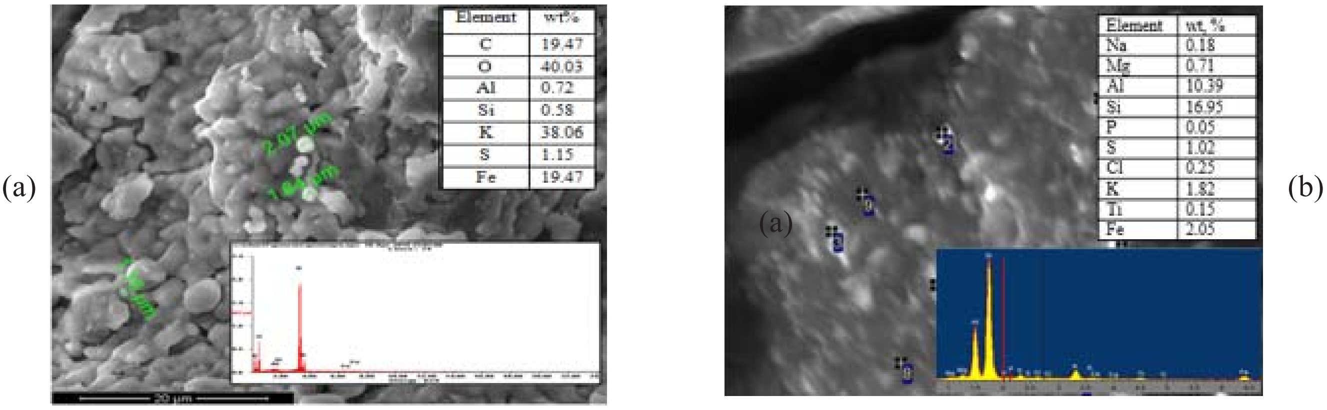
Element	w, %
O	52.69
Mg	0.67
Al	11.57
Si	27.03
S	1.34
Cl	0.44
K	3.46
Ti	0.31
Fe	2.77

Element	w, %
O	61.35
Na	0.13
Mg	0.74
Al	11.45
Si	20.88
S	0.77
Cl	0.38
K	2.52
Ti	0.19
Fe	1.82

Element	w, %
O	39.56
Na	0.30
Mg	0.53
Al	8.06
Si	19.39
P	5.12
S	1.47
Cl	0.93
K	6.79
Ti	1.02
Fe	8.13

Element	w, %
O	66.19
Na	0.23
Mg	0.71
Al	10.39
Si	16.95
P	0.12
S	1.02
Cl	0.25
K	1.82
Ti	0.19
Fe	2.05

Fig. 7. Mapping the surface of humic acid after neodymium sorption.



Element	wt%
C	19.47
O	40.03
Al	0.72
Si	0.58
K	38.06
S	1.15
Fe	19.47

Element	wt, %
Na	0.18
Mg	0.71
Al	10.39
Si	16.95
P	0.05
S	1.02
Cl	0.25
K	1.82
Ti	0.15
Fe	2.05

Fig. 8. Micrographs of humic acids in the initial sample (A) and after sorption (B).

4. Conclusion

In this work, the chemical composition and chemical-physical parameters of sorbent based on humic acids isolated from oxidized coal from the Maikuben deposit (Kazakhstan) were studied. For this purpose, IR spectrometric analysis, SEM analysis, Raman spectroscopy and thermogravimetric analysis were used. The sorption properties of the HA sorbent for neodymium had been studied. According to the morphology of the sorbent based on humic acids, the surface of the sorbent was heterogeneous and the specific surface area was not high.

The sorption of neodymium from real solution was performed at optimal values of metal sorption. An SEM analysis of the sorbent after neodymium sorption was performed, and the surface of the sorbent was mapped. It was shown that neodymium was not detected on the surface of the sorbent after sorption due to the complex composition of the real solution.

A study of the sorption of the standard solution of neodymium from nitrate solutions by a humic acid-based sorbent showed that at a phase contact time of 30 min and a pH value of 1.0, the efficiency of neodymium sorption reached 95.5%.

Acknowledgment

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