

Brown coal waste in South Kazakhstan: Assessment of physicochemical and biological characteristics

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Abstract

This study aimed to determine the physico-chemical and biological characteristics of brown coal waste in southern Kazakhstan and to understand the processes occurring within the waste column and surrounding storage areas, particularly as industrial waste storage increasingly encroaches on metropolitan limits due to rapid urbanization. The research employed scanning electron microscopy (SEM) with combined elemental analysis to identify chemical components. Diffractometric analysis was conducted to determine the mineralogical composition of the crystalline part of waste samples. SEM analysis revealed the presence of elements including Na, Mg, Al, Si, S, K, Ca, Ti, and Fe. Diffractometric analysis identified numerous mineral compounds including quartz (SiO₂), gypsum (CaSO₄×2H₂O), kaolinite (Al₂Si₂O₅(OH)₄), cronstedtite (Fe₃((Si_{0.74}Fe_{0.26})₂O₅)(OH)₄), margarite (CaAl₂(Si₂Al₂)O₁₀(OH)₂), muscovite (H₂KAl₃(SiO₄)₃), calcite (CaCO₃), laumontite (CaAl₂Si₄O₁₂(H₂O)₂), and lead aluminum sulfate hydroxide (Pb_{0.5}Al₃(SO₄)₂(OH)₆), with varying ratios across samples. The phytocenoses were dominated by ruderal species of local flora, particularly Dodartia orientalis L., Polygonum aviculare L., Elytrigia repens (L.) Nevski, and Centaurea pseudosquarrosa Mikheev ex Gabrieljan et Mikheev. The study established that natural biological transformation of carbon-containing waste components occurs at storage sites, with microorganisms from genera Rhodococcus, Bacillus, Pseudomonas, Penicillium, Trichoderma, and Dietzia playing significant roles in these processes. Natural biological transformation of carbon-containing waste components occurs in brown coal waste storage sites in southern Kazakhstan. These findings can inform the development of bioremediation approaches specifically tailored to brown coal waste sites in Kazakhstan and similar regions.

Keywords: Anthropogenic phytocenoses, Biotransformation of waste, Brown coal waste, Elemental composition of brown coals, Mineralogical composition of coals, Waste characteristics, Waste microflora, waste storage.

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1. Introduction

A huge amount of waste is being produced together with the expansion of manufacturing and the planet's expanding population. Agricultural, industrial, and domestic trash totaling more than a billion tonnes each year enter the environment, which undoubtedly has a negative impact on it Bećirović et al. [1]. According to a conservative estimate made by the World Bank [2], the volume of municipal solid waste alone in urban areas of Asia will increase from 760,000 tons per day in 1999 to 1.8 million tons per day in 2025 [3]. This exceeds the assimilation capacity of natural systems for waste disposal, resulting in degradation and replacement of natural systems [4]. The majority of the natural resources utilized are released back into the environment as waste, most of which is hazardous. Due to waste generation and insufficient industrial waste collection, transportation, treatment, and destruction, the globe is currently experiencing severe environmental issues. The amount of waste produced by industrial facilities is too much for most countries' modern systems to handle, which has negative effects on the environment and public health [5, 6]. New and expanded urban agglomerations provide a new natural and technological environment where social elements appear and play a significant role in determining how well they function [7]. The generated natural-technical systems considerably alter the material-energy flows in natural environment is that modern production uses a large quantity of chemicals that are in economic circulation but whose resource cycles are not closed, leading to significant losses of the substance in the form of emissions, discharges, and waste.

Currently, many methods of waste disposal are used (incineration, burial in the subsoil, placement in landfills, or equipped landfills) [8]. The most commonly used types of landfills are (a) solid waste landfills, (b) industrial waste landfills, and (c) hazardous waste landfills. There are many developing nations where there are unlawful and unregulated landfills more commonly known as open landfills. Studying any environmental issues that have emerged is crucial because garbage disposal is still widely practiced today [9].

In an attempt to prevent the aforementioned forms of environmental pollution, most countries have developed ways to prevent or minimize any resulting impacts through proper disposal of waste. The complex use of various types of waste is often proposed for waste disposal, such as joint recycling of household waste in a cement kiln [10] or transformation into new marketable products such as fertilizers [11]. A landfill, on the other hand, is seen as a perfectly constructed structure that is buried beneath the ground or built on top of it. The essential separation of waste from the environment occurs with the aid of a landfill. According to Chakravarty and Kumar [12], plant communities can be used to stop erosion processes. Solid waste that has been chemically or biologically contaminated poses a threat to the soil, atmospheric air, underground and surface water bodies, and vegetation, and it can either directly or indirectly affect population health, as in the case of the release of arsenic into the atmosphere, [13]. In order to discover the correlations between important parameters and to comprehend many processes of chemical transformations occurring inside waste storage facilities, it is therefore possible to examine the physico-chemical and biological features of solid and liquid waste materials [3]. In this regard, evaluating the condition of industrial waste to ascertain its influence on the environment is a very serious environmental issue. The purpose of this study was to assess the physical, chemical, and biological properties of brown coal waste in the southern part of Kazakhstan in order to comprehend the processes taking place in the thickness and the vicinity of the storage location.

2. Sample Sites and Methods

The waste brown coal stockpiled on the border of Lenger, a city in the Turkestan region, 40 kilometers from Shymkent, was the subject of the study (Figure 1). The waste was conditionally divided into two groups: A – anthracite-like solid dense waste, dark or black in color; B – slag-like waste, gray in color and porous.

Sampling was carried out in accordance with GHOST 33770-2016 from sites near the storage site of brown coal waste (Figure 2, Table 1).

X-ray analyses were carried out on the Shimadzu IRPrestige-21 infrared Fourier spectrometer with the prefix of the disturbed total internal reflection (NPVO), Miracle of Pike Technologies.

Diffractometric analysis of the crystal part of the samples was carried out on the D8 Advance (Bruker) apparatus, α -Cu, tube voltage 40 kV, current 40 mA. Processing of the obtained diffractogram data and calculation of interplanar distances were carried out using EVA software. The decoding of samples and the search for phases were conducted using the Search/Match program with the PDF-2 Powder Diffractometric Database.

The chemical composition of the ore was determined using IR spectroscopy on the SPECORD 75 IR spectrophotometer and inductively coupled plasma spectrometer with Varian-820 MS mass spectrometric detection (Australia), and the elemental composition was analyzed by atomic absorption analysis on the Analyst 800 spectrometer (Perkin-Elmer) and on the Varian-Pro high-performance liquid chromatograph (Holland).

Microorganisms were isolated on media: cellulolytic bacteria – on Getchinson medium, g/l: NaNO₃ - 2.5; FeCl₃ - 0.01; K₂HPO₄ – 1.0; MgSO₄×7H₂O - 0.3; NaCl - 0.1; CaCl₂ - 0.1; pH of the medium was adjusted to 7.2 by adding 20% Na₂CO₃ solution, distilled water, agar; Heterotrophic bacteria on medium MPA, g/l: peptone — 10.0; NaCl — 5.0; meat broth —

1000.0, agar - 1.0-20.0; pH 7.3 \pm 0.2; Micromycetes on medium Chapek, g/l: sucrose - 30.0; NaNO₃ - 3.0; K₂HPO₄ - 1.0; MgSO₄ - 0.5; KCl - 0.5; FeSO₄×7H₂O - 0.0 1; yeast extract - 2.0; peptone - 5.0; agar - 15.0; distilled water to 1,0 l.

Identification of bacteria to the species level was carried out with determinants (Bergey's Manual..., 2001). Microscopy of microbiological preparations was conducted using microscopes "Mikmed -5" (Russia) and "Tayda" (Japan) at magnifications of x40, x600, and x1000, as well as an electron scanning microscope (Jeol) at magnifications of up to x3300 times.



Figure 1.

Brown coal waste storage sites near the city of Lenger in the south of Kazakhstan.

Note: a. map of the city of Lenger (42°12'12" N, 69°53'06" E, Google Map); B. top view of waste A (42°11'23" N, 69°52'06"E, Google Earth); C. top view of waste B (42°12'11" N, 69°52'06"E, Google Earth); D & E. side view of wastes



Figure 2. Soil sampling sites near waste A.

Table 1.

Sample	Sampling places	Coordinates	(WGS 84)	Sampling	pН	T^0 . C
		n.l.	e.l.	depth, m	(KCl)	, -
A1	On the border with the terricon	42 ⁰ 11'23"	69 ⁰ 52'07"	0.0-0.5	4.15	24
A3	Raw waste from the waste heap	42 ⁰ 11'22"	69 ⁰ 52'05"	0.1-0.5	2.92	21
A7	A small hill inside the landfill	42 ⁰ 11'24"	69 ⁰ 52'04"	0.1-0.3	5.24	22
A8	A small pile inside the landfill	42 ⁰ 11'22"	69 ⁰ 52'05"	0.1-0.3	5.97	22
A9	Small piles around the perimeter of the landfill	42 [°] 11'22"	69 ⁰ 52'04"	0.1-0.5	5.22	23

Brief description	of waste	sampling	sites A

Taxonomic analysis of plant species was carried out using an illustrated plant determinant in 6 volumes "Flora of Kazakhstan, 1969". The assessment of the abundance of vegetation in the studied areas was carried out according to the Drude scale in the modification, where the abundance of the species was determined by the following criteria: Soc – entirely, Sor1 – quite abundantly, Sor2 – abundantly, Sor3 – very abundantly, Sp – rarely, Sol – singly, Un – in one copy.

The video recording of the material was carried out using a Samsung digital camera and a CCC 649LV electron scanning microscope video card manufactured by JEOL (Japan), with an Inca energy dispersive microanalysis system with an energy of 350 eV by Oxford Instruments (Great Britain), associated with an LGC-based structural analysis system for polycrystalline objects.

Statistical processing of the results was conducted by calculating the arithmetic mean and standard deviation. All definitions were performed in 3- and 5-fold repetitions.

3. Results and Discussion

The sampling sites can be distinguished visually as follows: In sample S-A, there is a clear separation between the area that is vegetated and the waste, with 55.0% of the projective plant cover. Sample 2's soil is covered in plants, is a little loose in spots, and there are dark layers of carbon-containing garbage visible beneath the turf. Plants create a layer of grass; their roots cannot reach deeper layers, which account for 20% of the projected plant cover. Sample 3: Anthracite-like wastes that are dense, dark in color, and devoid of flora. The waste also contains marked bits of petrified wood. Sample S-C is a tiny hill that is almost entirely covered in plants. It has a loose substrate that is dark brown in color, reminiscent of soil, and has an earthy odor., with 80% of the projective plant cover. Sample S-D is a small, occasionally vegetated pile found inside a landfill. The pile's substrate is loose, and it contains mechanical contaminants like sand and stones that account for 45.0 percent of

the projective plant cover. Sample No. 9 is taken from small piles that are only faintly vegetated. The heap's substrate is heterogeneous, containing both mechanical impurities and dark waste in loose with 10 percent of the projective plant cover. Sample 0 served as the control and was taken from a location 30 m from the dump along a road where 95.0 percent of the projective plant cover was present. Both the species mix of the community and the projective coverage of the soil surface by vegetation dramatically decreased as we got closer to the waste storage location (Table 2).

Table	2.
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Species	Estimation of abundance by Drude					
	S-A	S-B	S-C	S-D	S-E	Control
Centaurea pseudosquarrosa	cop3	-	-	-	-	Sol
Centaurea iberica Trev.	-	-	-	-	cop1	-
Cichorium intybus Linn.	Sol	-	-	-	-	-
Cousinia cyrdariensis Kult.	-	-	Sol	-	-	-
Achillea millefolium L.	-	-	-	-	-	Sol
Thlaspi arvense L.	-	-	-	-	cop1	-
Arctium tomentosum Mill.	-	-	-	-	-	Sol
Onopórdum acánthium L.	-	-	-	-	-	Sp
Agropyron cristatum (L.)	cop3	-	-	-	-	-
Phleum pratense(L.)	sp	-	-	-	-	-
Erytrigiarepens (L.) Nevski /Agropyron repens(L.)	cop3	-	cop2	-	cop1	cop3
Cynodon dactylon (L.) Pers.	-	-	-	cop2	-	Soc
Polygonum aviculare L.	sp	-	cop2	-	cop1	Sol
Capparis spinosa L.	Sol	-	-	-	-	Sol
Dodartia orientalis L.	-	Un	-	-	-	-
Althaea officinales L.	-	-	-	-	-	Sol
Alhagi pseudalhagi (Bieb.) Desv.	-	-	cop2	cop2	-	Soc
Peganum harmala L.	-	-	-	-	-	Sol

Note: Soc -entirely, Sor1-quite abundantly, Sor2 -abundantly, Sor3-very abundantly, Sp - rarely, Sol - singly, Un-in one copy.

A change in the projective coating of the surface of brown coal waste by plants from 0 to 80.0% was found, while the most toxicotolerant species are represented by ruderal species: Dodartia orientalis L., Polygonum aviculare L., Elytrigia repens (L.) Nevski, Centaurea pseudosquarrosa Mikheev ex Gabrieljanet Mikheev (Figure 3), promising for environmental purposes.



Dodartia orientalis L.



Polygonum aviculare L



Erytrigia repens (L.) Nevski



Centaurea pseudosquarrosa Mikheev ex Gabrieljan et Mikheev

Figure 3. Toxicotolerant plant species of the local flora.

The results obtained in this study show the potential of bioremediation of brown coal wastes by plants in conjunction with microorganisms. A similar study has been carried out in South Africa that exploits the fungi-plant mutualism, called Fungcoal, as a viable and alternative strategy for rehabilitating coal discard dumps and opencast spoils. The C4 grasses *Cynodon dactylon, Eragrostis tef*, and *Pennisetum clandestinum* are all part of Fungcoal, and these can be found growing in the brown coal sampling sites. These plants have been found to create a symbiosis with *Aspergillus ECCN 84* and/or *Neosartorya fischeri ECCN 84*, which decompose coal, and the arbuscular mycorrhiza containing *Glomus clarum, Paraglomus occultum, Glomus mossea*, and *Gigasporagigantea* in South African research [14]. Fungcoal was developed as a solution to a wide range of problems, such as the promotion of mutualism between plants and microbes, the activation of important rhizosphere bacteria, and the biodegradation of carbon pollutants [15]. The authors hypothesized, on the basis of in-situ research, that a microbial consortia, so-called 'humifiers,' can increase soil fertility ex nihilo, and that combinations of certain biocatalysts function synergistically in maintaining soil dynamics.

The plots differ slightly in terms of how nitrogen, phosphorus, and potassium are distributed biogenically, with section 7 being the only location where the content of these elements is higher than that of other plots with comparable values. The degree of nitrogen supply is very low in samples S-A, S-B, S-D, and S-E, according to the level of alkaline hydrolyzable nitrogen (Figure 4), with the exception of section S-C, where a normal degree of nitrogen supply was found. Samples S-A and S-B, which are characterized as substrates with a relatively low degree of mobile phosphorus availability, contained 8.1 and 4.8 mg/kg of P_2O_5 , respectively, according to the concentration of mobile phosphorus. According to the average level of mobile phosphorus availability, samples S-D and S-E had P_2O_5 contents of 21.2 and 21.8 mg/kg, respectively. The mobile phosphorus concentration in sample S-C was 60.5 mg/kg, indicating a high level of phosphorus supply.

The samples S-B and S-A both had extremely low potassium contents, with 21.5 and 52.7 mg/kg of K₂O, respectively. Sample S-E, which has a low potassium content of 118 mg/kg, is next in the category of the degree of exchangeable potassium availability. The samples S-D and S-C, which both had high potassium contents of 600.0 mg/kg, were found to have higher potassium contents. It is reasonable to link the analyzed samples to substrates with an average humus level because the samples' humus contents differ slightly and range from 5.08 to 5.53% (Figure 4).

According to the findings of X-ray electron microscopy and energy dispersive microanalysis, the anthracite-like waste samples S-A and S-B contain components including Na, Mg, Al, Si, S, K, Ca, Ti, and Fe (Figure 5), with a Si content that ranges from 13.81 to 14.21 weight percent. All samples contain 0.20-0.33% of Ti. Samples S-A and S-B have carbon contents of 24.63 and 22.31 wt%, respectively.

The mineralogical makeup of the samples was identified using diffractometric examination of the crystal portion of the samples (Figure 6). It is known that quartz/Silicon Dioxide SiO₂, gypsum CaSO₄-H₂O, and kaolinite Al₂Si₂O₅(OH)₄ represent the mineralogical composition. Cronstedtite Fe₃(Si_{0.74}Fe_{0.26}O₅)(OH)₄, Margarite CaAl₂(Si₂Al₂)O₁₀(OH)₂, H₂KAl₃(SiO₄)₃ from muscovite, Laumontite CaAl₂Si₄O₁₂(H₂O)₂, Calcite CaCO₃, and Lead Aluminium Sulphate Hydroxide Pb_{0.5}Al₃(SO₄)₂(OH)₆ are shown in various ratios depending on the sample (Figure 7).



b)

Figure 4. Nitrogen (a) and humus(b) content in the studied areas, mg/kg.



Figure 5. SEM images and IR spectra of S-A and S-B samples.







Figure 6.

Results of diffractometric analysis of waste samples A.



Figure 7.

Mineralogical composition of substandard brown coal (inorganic part).

The analysis of the microflora of anthracite-like brown coal waste revealed that only the initial untransformed waste (sample S-B) has a significantly lower number of cellulolytic microorganisms than the other samples taken from different sites of brown coal waste storage (Table 3). In samples S-D and S-E, where the waste was naturally converted into humus-like substances and reached the level of the control version, the quantity of heterotrophic microorganisms and micromycetes is the highest.

The isolates are identified as R.R. *Rhodococcus, Bacillus, Pseudomonas, Penicillium; Trichoderma, Dietzia.* The analysis of the phytotoxicity of brown coal waste samples revealed that sample 3, which is an unmodified anthracite-like waste, had an acute toxic effect on both test plants: red beans and seed barley (Figure 8). Sample S-B was the most toxic, as it completely halted the growth of both of these plants. This is followed by sample S-A, which caused a retardation in both plant growth parameters tested (Figure 8). As the levels of nitrogen, phosphorus, and humus are nearly similar in all of the samples, as shown above, this inhibition of growth might be due to other factors such as high heavy metal or hydrocarbon contents. The inhibition of plant growth attributed to coal dust has been reported [16].

The level of waste transformation affects the toxicity of the waste, in addition to the distance between the honey site and the main pile. In contrast, samples S-D and S-E showed a smaller volume, a larger area of projective plant coverage, and a humus-like appearance despite being near the terricon.

Table 3.

Microflora of	brown	coal	wastes,	CFU/g.

Sample number	Microorganisms, CFU/g				
	Cellulolytic bacteria on the	Heterotrophs on the MPA	Micromycetes on the		
	Getchinson medium	medium	Chapek medium		
Control	$(3.6\pm0.3)\times10^4$	$(2.6\pm0.2)\times10^5$	$(5.6\pm0.5)\times10^4$		
S-A	$(2.5\pm0.2)\times10^4$	$(5.3\pm0.5)\times10^4$	$(3.3\pm0.3)\times10^3$		
S-B	$(4.3\pm0.4)\times10^3$	$(1.0\pm0.1)\times10^3$	$(4.3\pm0.4)\times10^3$		
S-D	$(4.5\pm0.4)\times10^4$	$(7.0\pm0.5)\times10^4$	$(7.3\pm0.5)\times10^{3}$		
S-C	$(9.2\pm0.8)\times10^4$	(1.6±0.1)×10 ⁵	$(2.1\pm0.2)\times10^4$		
S-E	$(7.7\pm0.5)\times10^4$	$(2.4\pm0.1)\times10^5$	$(1.2\pm0.1)\times10^4$		

Coal depolymerization and solubilization can be achieved through catalytic metabolism, especially with lignin-degrading enzymes, because the structure of low-rank coal is very similar to that of lignin. These enzymes play a critical role in humic acid depolymerization by breaking the covalent bonds within the coal macromolecule. These enzymes can be divided into oxidative (lignin peroxidase, manganese peroxidase, and laccase) and non-oxidative (esterases). Numerous microorganisms (*Penicillium* sp., *Trichoderma* sp., *Bacillus* sp., *Mycobacterium* sp., *Acinetobacter* sp., *Enterobacter* sp., *Rhodococcus* sp.) have been documented to secrete ligninolytic enzymes in culture media containing coal. Saprotrophic fungi and, in particular, ligninolytic microorganisms may act as biocatalysts for coal transformation [17, 18].





The influence of various brown coal wastes on the morphometric parameters of test plants: a. Red beans, b. Seed barley

4. Conclusion

Anthracite-like (A) and slag-like (B) waste, which resemble anthracite and slag, respectively, are two kinds of brown coal waste that are located on the edge of the city of Langer. It was discovered that the degree of toxicity of various sites influences both the reduction of projective vegetation on the soil's surface and the species composition of phytocenoses dominated by ruderal species like Dodartia orientalis L., Polygonum aviculare L., Elytrigia repens (L.) Nevski, and Centaurea pseudosquarrosa Mikheev ex Gabrieljanet Mikheev. The sites are slightly different based on their levels of humus, nitrogen, phosphorus, and other biogenic components. The results of X-ray electron microscopy with elemental analysis showed that waste samples S-A and S-B are represented by such components as Na, Mg, Al, Si, S, K, Ca, Ti, and Fe. Diffractometric analysis of the crystalline part of the samples revealed the mineralogical composition of the samples, quartz/SiliconOxideSiO₂, GypsumCaSO₄×2H₂O, represented by Kaolinite - $Al_2Si_2O_5(OH)_4$, Cronstedtite-Fe₃((Si_{0.74}Fe_{0.26})₂O₅)(OH)₄, Margarite-CaAl₂(Si₂Al₂)O₁₀(OH)₂, MuscoviteH₂KAl₃(SiO₄)₃, CalciteCaCO₃, LaumontiteCaAl₂Si₄O₁₂(H₂O)₂, LeadAluminumSulfateHydroxidePb_{0.5}Al₃(SO₄)₂(OH)₆, the ratios of which vary depending on the sample. A microbiological analysis of the waste column revealed that biological transformation of the carboncontaining waste component occurs naturally. The intensity of these processes depends on the confluence of factors that are ideal for the vital activity of the native microflora, including humidity, temperature, and gas-air regime, which promotes the formation of humus-like substances.

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