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Respiration of carbon rock spoil treated by municipal wastewater

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A b s t r a c t. The aim of the study was to determine under laboratory conditions the respiration rate of carbon rock spoil, after different time of storage, amended with municipal wastewater after mechanical and biological treatment in relation to pH, redox potential and temperature. The experiment was carried out on the coal mine rocks exposed to weathering for five and ten years under atmospheric conditions. Respiration rates show growing tendency with increase of temperature. Respiration rate of the 5-year material was higher than that of the 10-year material. The respiration values after addition of wastewater were 1.30 and 2.72 times greater than after addition of distilled water for the 5- and 10-year, respectively. Flux of carbon dioxide showed positive linear correlation with pH and negative linear correlation with Eh values.

K e y w o r d s: respiration, carbon spoil rock, flooding, pH, Eh

INTRODUCTION

Biological weathering of carbon wastes liberates from the rocks and minerals, elements and compounds, that constitute nutrients for plant. According to Włodarczyk and Strzyszcz (2007), the degree of biological weathering of carbon wastes dependents on the kind of carbon rocks, microbial activity, and on the nutrient availability of the rocks. These quantities are usually too low to create optimum conditions for plant growth which are needed for example to afforestation of heap. To enrich the waste rock in nutrients a municipal wastewater can be used. The results of adding of the biologically active sludge or wastewater to soil are connected with oxygen demand. The oxygen deficiency induces increasing activity of soil anaerobic microorganisms, which are responsible for a series of reduction processes. These processes are particularly intense when stagnant water limits gas exchange with atmospheric air, what contributes to the increase of anaerobic processes intensity as a consequence of respiration of soil microorganisms and plant roots, connected with physical processes of gas exchange between soil and atmosphere. The strongest effect on this activity have soil physicochemical factors such as: temperature, carbon dioxide concentration, moisture content, density and pH (Gliński *et al*., 2000; Komosa *et al*., 2004; Zawiślak, 2000). Soil respiration is one of the main fluxes in the global carbon cycle, second in magnitude after gross primary production (Schlesinger and Andrews, 2000).

Carbon dioxide is the most important anthropogenic greenhouse gas considered to be responsible for 60% of the expected 21st century increase of the greenhouse effect. The concentration of atmospheric CO_2 has increased from a preindustrial value of about 280 to 379 mg kg^{-1} in 2005 (IPCC, 2007). The rate of annual increase of carbon dioxide concentration was greatest during the last 10 years. The sources of increased level of atmospheric CO_2 are emissions of CO_2 from fossil fuel use and from the effects of land use change on plant and soil carbon (IPCC, 2007; Kirkham, 2011; Kutilek and Nielsen, 2010). Literature gives rather little information about respiration of carbon waste rock. This question is a very important because, the heaps are located on very large area and represent a huge potential source of CO_2 emissions.

The aim of the study was to determine under laboratory conditions respiration of carbon rock spoil at different weathering time after addition of wastewater in relation to changes of pH, Eh and temperature.

MATERIALS

The experiment was carried out on the natural carbon wastes originated from Bogdanka coal mine situated in the Lublin Coal Basin, East of Poland.

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Two types of rock waste were taken for the investigations: material exposed to weathering (storing in a pile) for five (B5) and for ten (B10) years. Main minerals in composition of mine wastes from Lublin Coal Basin are claystones (up to 70%) and siltstones (up to 20%). The remaining 10% consists of other minerals and from 5 to 10% of coal. The clay minerals of the waste rocks under study were dominated by kaolinite and illite. The waste rocks accumulated on the dump for 5 years contained magnesium sulphate (VI) (hexahedrite) and calcium sulphate (gypsum). In the material accumulated for 10 years were found gypsum and anhydrite (Stefaniak *et al*., 2004).

After being transported to the laboratory, the waste rocks were crumbled, sieved through 4 and 1 mm mesh (fraction 4-1 mm) and stored at room temperature. In the thus-prepared samples the pH values in waste water and distilled water suspensions (1:2.5) after 30 min with a portable pIONneer 10 Ion Analyser were determined (Thunjai *et al*., 2001).

The waste rock portions of 10 g in brown glass bottles (59.8 cm^3) were flooded with 20 ml of distilled water or municipal wastewater (after II step purification). The rock spoil suspension samples were mixed and left for 3 h. After this time, pH and Eh were measured and the vessels were closed with rubber stoppers and aluminium caps. Incubation was conducted in darkness for 40 days at temperatures 5, 10, 15 and 30°C. All the treatments had three experimental replicates.

Redox potential (Eh) and pH were measured after 1, 3, 7, 16, 31 and 40 days of the incubation, directly after opening the vessels with the rock suspensions. The Eh was measured with platinum wire (0.5 x 5 mm) electrodes in relation to the calomel electrode used as a reference electrode (Gliński and Stępniewski, 1985) using a pIONneer 10. The pH measurement was performed by a combined electrode with Radiometer pH Meter.

Composition of gas samples from the headspace was tested after 1, 3, 5, 7, 10, 13, 16, 19, 22, 25, 28, 31, 43, 37 and 40 day of the incubation by gas chromatography technique Varian 3800. Concentrations of O_2 and CO_2 were determined using a capillary column and a thermal conductivity detector (TCD). The column temperature was set at 80°C and the injector and detector at 40 and 60°C, respectively. The gas sample volume for separate analysis was 50 µl.

Results of all measurements represent averages of three replications. Standard deviation bars were included on the graphs to show the variation of the data. Analysis of variance by the least significant difference test (95% LSD-test) was performed to determine a significant difference ($p<0.05$) between the means of respiration value, type of rock waste and temperature with the Statgraphics Plus 5.1 software. Relationships between rock waste CO_2 fluxes and pH as well as redox potential, was examined with linear regression.

RESULTS AND DISCUSSION

In the investigated carbon rocks, after 5 and 10 years of weathering (B5 and B10), the content of the silica did not differ significantly (45.08 and 45.53%, respectively) (Stefaniak *et al*., 2004). The both materials was characterized by similar pH values (2.24 and 2.39 for B5 and B10, respectively). Acidic pH of storage materials was the result of pyrites oxidation to sulphate, the content of which was on the level 0.2 and 0.32 % S_{SO_4} , for B5 and B10, respectively. The reaction of carbon wastes was much more acid than of the fresh one (directly after bringing out), which was on the level of about 6.3.

Generally the mean respiration rate of rocks B5 (17.61 and 22.92 mg C-CO_2 kg^{-1} d^{-1}) was 4 to 2 times greater than that of the B10 rock (3.92 and 10.68 mg C-CO_2 kg^{-1} d^{-1} after addition of water and wastewater, respectively. These differences were statistically significant ($p=0.05$). The largest difference occurred during incubation at 30°C.

The respiration rate of the tested carbon wastes was always greater for the samples with addition of wastewater than for samples flooded with distilled water and these differences were statistically significant in the case of material B10 (Fig. 1). Generally the respiration rate of rock spoil after flooding with wastewater was 1.3 and 2.7 times greater than that for pure water for B5 and B10, respectively, what indicats on stimulatory effect of waste water connected with the

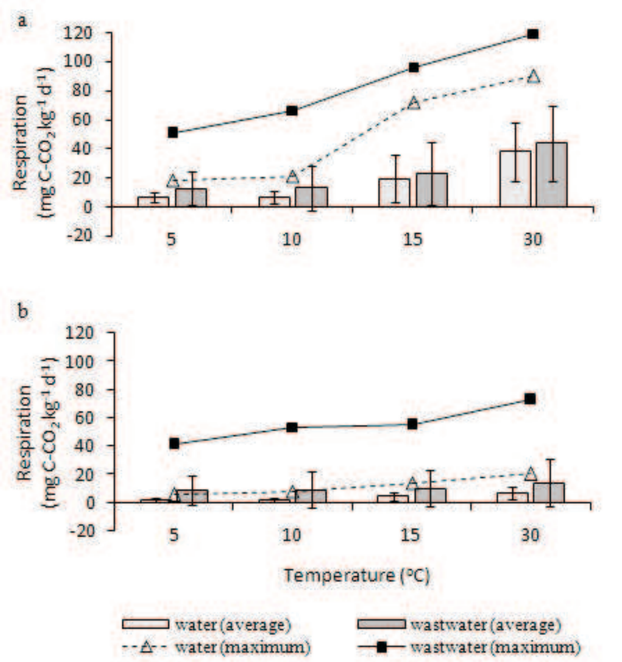


Fig. 1. Respiration of: a – carbon waste rock (B5), b – carbon waste rock (B10), after flooding with distilled water and wastewater, as a function of temperature (standard deviation is given as bars).

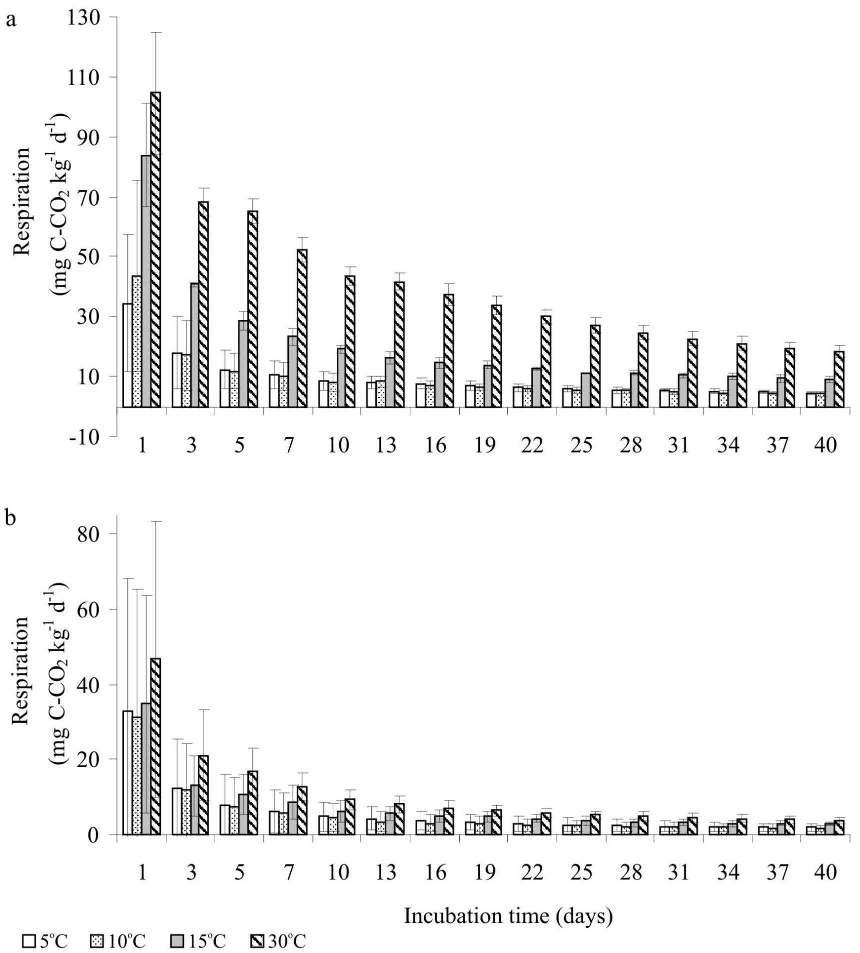


Fig. 2. Changes of respiration (average for flooding with distilled water and wastewater): a – carbon waste rock B5, b – carbon waste rock B10, during incubation time (standard deviation is given as error bars).

increase in organic C and nutrient availability and plays a crucial role in the response of the soil microorganisms to environmental factors (Brzezińska *et al*., 2006; Liu *et al*., 2006; Stępniewska *et al*., 2003).

The highest respiration rate was observed on the first days of incubation (Fig. 2). In the studies of Bennicelli *et al.* (2009) and Włodarczyk (2000) maximum CO_2 emission from soil material was also observed during the first days of experiment. During incubation a decrease of respiration rate with time was observed. The most easily decomposable fraction of soil organic matter probably has been exhausted due to microbial decomposition which caused a decrease in respiration rate (Fang and Moncrieff, 2001).

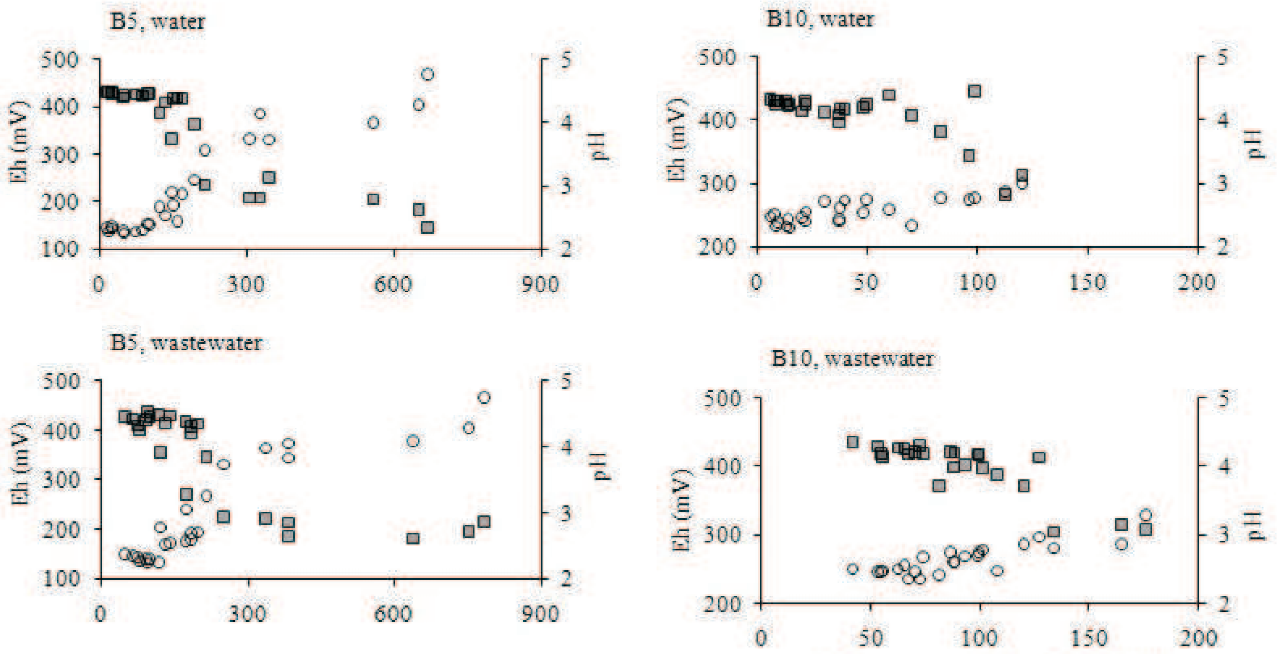
Respiration rates of rock wastes grow with increasing of temperature (Fig. 1) and this differences were significant for both the rock materials, except B10 after wastewater flooding (Table 1). Respiration rate was linearly correlated with temperature (R^2 = 0.956 for both rocks). Many studies have shown that the soil respiration rate increases linearly or exponentially with increasing of temperature (Fang and Moncrieff, 2001; Liu *et al*., 2006; La Scala *et al*., 2009). Temperature and moisture content interact to control enzyme activity and substrate pool size and hence microbial respiration (Pendall *et al*., 2004). The maximum respiration rate (119.13 mg $C\text{-}CO_2$ kg^{-1} d^{-1}) was observed in rock wastes B5 on the first day of the experiment after flooding with wastewater during incubation at the temperature of 30°C, when Eh was relatively high (429 mV) and pH at the level of 2.24. In the same conditions, on the 40th day of incubation, the same rock emitted 43.56 mg $C\text{-}CO_2$ kg^{-1} d^{-1} at Eh = 213 mV and pH = 4.73. Minimum value of respiration (1.25 mg $C\text{-}CO_2$ kg^{-1} d^{-1}) was found at the end of the experiment in the combination of waste rock B10 with distilled water at 5°C, when Eh and pH were at a level of 424 mV and 2.67, respectively.

Relation between CO_2 concentration and the headspace air and Eh in the soil suspension is shown in Fig. 3. The presented results have shown, that carbon dioxide concentration (mg $C\text{-}CO_2$ kg^{-1}) was negatively linearly correlated with Eh. The initial redox potential of the incubated materials ranged from + 418 mV (B10, wastewater, incubation at 15°C) to +454 mV (B5, water, incubation at 15°C) what indicates on

T a b l e 1. Statistical significance of differences in respiration of rock waste B5 and B10 after flooding with distilled water and wastewater at different temperatures of incubation (calculations were made on the basis of 95% LSD method)

Temperature (C°)	Differences in respiration			
	B5		B10	
	Water	Wastewater	Water	Wastewater
5/10	0.0874	-0.5654	0.1963	0.6855
5/15	-12.4808*	-10.1142	-2.4693*	-0.2567
5/30	-30.9514*	-31.0724*	-5.0334*	-4.192
10/15	-12.5683*	-9.5486	-2.6657*	-0.0942
10/30	-31.0389*	-30.5069*	-5.2298*	-4.8775
15/30	-18.4705*	-20.9582*	-2.5640*	-3.9352

*Denotes a statistically significant difference.



Carbon dioxide concentration (mg C-CO_2 kg^{-1}); ■ Eh, ○ pH.

Fig. 3. Dependence of carbon dioxide concentration in the head space air on redox potential (R^2 = 0.877; 0.830; 0.586 and 0.714 for B5 water, B5 wastewater, B10 water and B10 wastewater, respectively) and pH (R^2 = 0.818; 0.675; 0.528 and 0.709 for B5 water, B5 wastewater, B10 water and B10 wastewater, respectively) in rock waste suspension.

the presence of molecular oxygen, as a dominant electron acceptor in formation of the Eh value. During incubation we observed decreasing of Eh values to the lowest level of 143 and 306 mV (B5 incubation with distilled water at 30°C and B10 incubation with wastewater at 30°C, respectively). According to Yu *et al*. (2001), a well-oxidized soil is characterized by redox potential range from +400 to +700 mV. Flooded soils may reach redox potential values lower than +400 mV due to the absence of O_2 and the activity of facultative and obligate anaerobic bacteria. Stępniewska *et al.*

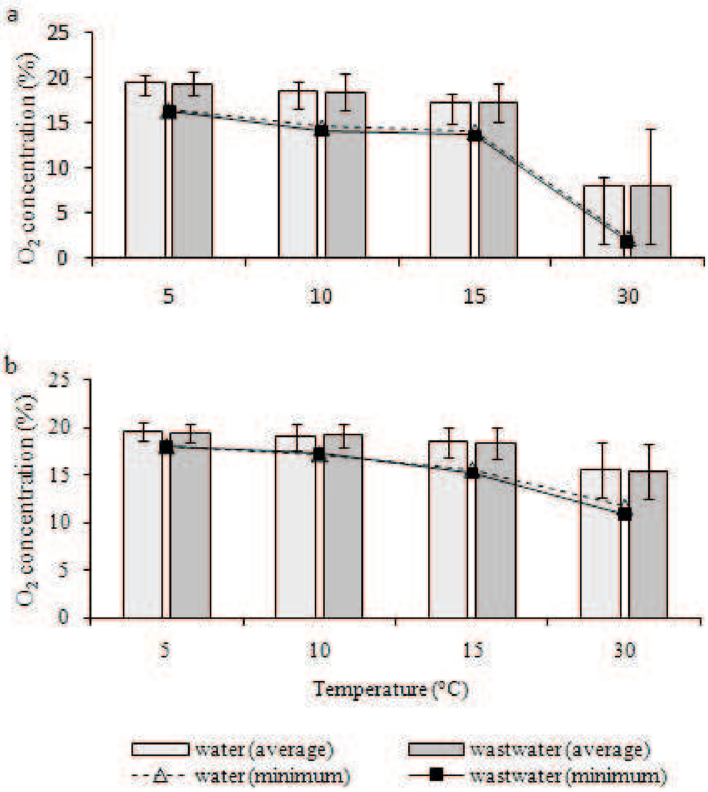


Fig. 4. Oxygen concentration in: a – carbon waste rock (B5), b – carbon waste rock (B10), after addition water or wastewater, as a function of temperature (standard deviation is given as bars).

(2003) observed soil redox potential decrease from about +400 mV down to about 100 mV during first two days of incubation of flooded loess soil at 20°C. During the incubation of B10 at temperatures 5, 10 and 15°C the changes of Eh values were smaller and a stepwise decrease of redox potential was observed with equal rate during the whole period of incubation. In other variants of the experiment the Eh decrease was more intensive at the beginning of the experiment. In the studies conducted by Gliński and Stępniewski (1985) and Włodarczyk (2000), the highest decrease of the Eh value was also noted during the first stage of flooding.

Dependence of pH in soil suspension on carbon dioxide emission is presented in Fig. 3. The carbon dioxide concentration showed a positive correlation with pH. On the first day of incubation, the mean pH value was 2.3 and 2.4 for the materials B5 and B10, respectively. During the incubation time we observed an increase of pH value in the rock spoil suspensions, in average by 1.3 and 0.4 unit for rocks B5 and B10, respectively. That means that pH of acidic soils increases what was observed in the tested rock wastes, but no differences in pH values were noted in the samples treated with water or wastewater. Under anoxic conditions the same tendency of pH value changes and approaching to the neutral level was described by Gliński and Stępniewski (1985), and in the experiment conducted by Kashem and Singh (2001), an increase of pH was at a level of about 2, 1 and 0.6 units in the case of tannery, municipal sewage and alum shale soils, respectively, after 65 days of submergence. The increase in soil pH after flooding of soil is a result of uptake of hydrogen ions by oxygen during reduction processes (Gliński and Stępniewski, 1985; Jezierska-Tys and Frąc, 2009).

Changes in oxygen concentration, in the headspace of incubation vessels, as a function of temperature are presented in Fig. 4. In the all analysed samples, oxygen concentration was gradually decreasing with increasing of temperature. The maximal decrease of O_2 concentration to 2.15% and 1.79% v/v (respectively for water and wastewater) was observed in the rock spoil B5 at 30°C. Concentrations of O_2 in the headspace were negatively correlated with the carbon dioxide emission and pH values but showed a positive correlation with Eh, what was also confirmed by the experiments conducted by Castaldi (2000).

CONCLUSIONS

1. Emission of carbon dioxide from the rock material stored on the heap for 5 years was 4 and 2 times greater than that for the material stored for 10 years after the addition water and wastewater, respectively.

2. Carbon dioxide flux was maximum in the first days of incubation and showed a positive linear correlation with pH, and a negative linear correlation with Eh value and oxygen concentration.

3. Respiration rate of the rock waste was linearly correlated with temperature ($R^2 = 0.956$).

4. Respiration rate of the waste rock after flooding with wastewater was 1.3 and 2.7 times greater than that with distilled water for 5- and 10-year materials, respectively.

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