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BCR METHOD IN ASSESSING ALTERATIONS OF COPPER FORMS IN SLUDGE COMPOSTED ACCORDING TO DIFFERENT METHODS

The aim of the investigation was to assess the effect of the composting and vermicomposting of pure sludge, as well as sludge with 20% addition of brown coal, on the alterations of chemical form of copper contained in these organic materials. Sample collection for analysis took place six times within 12 months. In order to assess the alterations of copper forms, BCR method was used. The results obtained proved that the methods of composting and vermicomposting allowed us to differentiate between total copper content and the contribution of the fractions of this metal to its pool. In a raw sludge and in composts based on it, 51–73% of copper were bonded to a residual form (F4), while the rest – to its reducible fraction (F2). The proportion of the copper form being soluble in acid environment (F1) and the form bonded to the organic matter (F3) increased with time, while the reducible copper fraction (F2) and its residual form (F4) decreased with time. The most considerable increase in F1 and F3 proportion took place due to the composting and vermicomposting of sludge and brown coal mixture, while the lowest one involved pure sludge composting.

1. INTRODUCTION

Recently, the amount of sewage subjected to treatment has increased significantly, which, in turn, results in a continuous increase in sludge mass to be utilized. As has been estimated, in 2010, there will be produced 612800 Mg d.m. (dry mass) of sewage, while in 2018, its amount will approach 706600 Mg d.m. [14]. Negative balance of organic matter in our soils inclines us towards utilization of sludge in agriculture. According to the regulations in force [10], based on a total content of heavy metals it is possible to decide whether sludge can be used for agricultural purposes. However, the sludge effect on environment can be assessed only if a chemical form of copper in sludge will be determined. Raw sludges are greasy and have disadvantageous chemical composition. One

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of the methods leading to the improvement of these properties is sludge composting: sludge is mixed with organic materials, e.g. brown coal, or decomposed by Californian earthworms [4], [6]. This treatment results in the alteration of chemical forms of all metals present in sludge, including copper [1], [5], [12].

The purpose of this research was to assess of the effect of 4 methods of sludge composting and the time of its conducting on the alteration of copper forms occurring in this material.

2. MATERIAL AND METHODS

A secondary sludge collected from mechanical–biological municipal sewage treatment plant in Kluczbork was used for the tests. This sludge, either alone or mixed with brown coal, was subjected to both composting (composts I and III) and vermicomposting (composts II and IV). The latter were prepared according to the following pattern: 20 kg of brown coal (95% d.m.) were added to 80 kg of sludge (16.4% d.m.). Californian earthworms (*Eisenia fetida* Sav.) were introduced to composts II and IV. The process of composting was conducted in 100-dm^3 polyethylene containers, in natural conditions (sheltered place) for 12 months. The mass moisture was maintained at the level of 60–70% of water capacity. The samples for the tests (of ca. 1-kg mass) were collected on the 10th May 2004 (term I), the 10th July 2004 (term II), the 10th September 2004 (term III), the 10th November 2004 (term IV), the 10th March 2005 (term V), and on the 10th May 2005 (term VI). In the samples, the following parameters were determined: moisture – according to a dryer method, pH (KCl) – with potentiometer, C – organic carbon content according to the Tiurin method, N – organic nitrogen by Kjeldahl method, and a total copper content after mineralization with aqua regia by AAS method. The concentrations of various copper forms were determined by BCR method [6], which consists in the separation of subsequent fractions: the fraction soluble in acid environment (F1), a reducible fraction bonded to Fe and Mn (F2), an oxidable fraction – Cu bonded to organic matter (F3) and residual fraction (F4).

3. RESULTS

Municipal sludge subjected to examinations showed acid reaction, low content of organic carbon and high content of nitrogen (the table, figure 1). A detailed characteristics of the materials used was given in [7]. Brown coal added to sludge resulted in an increase in the content of organic carbon and a decrease in the content of nitrogen. Similar relations were also reported by SYMANOWICZ and KALEMBASA [13]. C : N ratio calculated for sludge was 4.4 and based on the criteria set by SMITH [12]. This value enabled sludge classification into the group of materials containing nitrogen compounds easily undergoing mineralization. This relation was confirmed by our investigations.

Table

Alterations in pH, C : N ratio and total copper content due to composting processes

Material	Term	pH KCl	C:N	Cu (mg·kg^{-1} d.m.)
Compost I Sludge	1 6	6.4 5.4	4.4 4.8	218.3 258.7
Compost II Vermicomposted sludge	1 6	5.7 5.2	6.3 11.3	223.0 239.0
Compost III Sludge + brown coal	1 6	6.2 5.0	9.1 10.7	117.8 127.5
Compost IV Vermicomposted sludge + brown coal	1 6	6.3 5.0	9.6 12.2	117.8 138.0

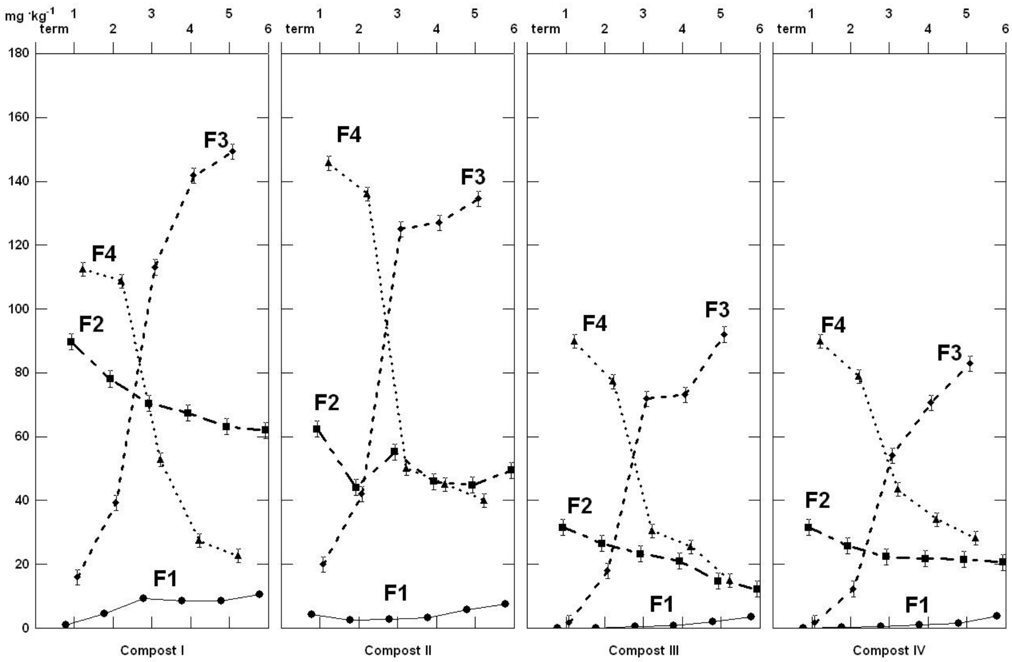

Fig. 1. Influence of compost type and time of composting on content of copper fractions (mg kg^{-1} d.m.): F1 – acid exchangeable fraction, F2 – reducible fraction, F3 – oxidizable fraction, F4 – residual fraction

Noticeable mineralization processes in composts within 12-month period caused a significant decrease in nitrogen content and, to a lesser degree, a decrease in organic carbon content (a decrease by 20–32%) (figure 1).

The differences in reduced concentrations of carbon and nitrogen caused an increase in the ratio of C : N (table). The vermicomposting of sludge II affected most significantly the value of this ratio, while the composting of sludge I proved to be least effective.

A total copper content in a raw sludge was 218 mg kg^{-1} d.m., which is much below its permissible concentration [10], [11]. Mineralization process, leading to the loss of organic matter, resulted in an increased copper content in all the materials composted, but this increase depended on the time and composting method applied (figure 1). After 12 months there was recorded the most significant increase in copper content (by 19%) as a result of pure sludge composting, while the smallest increase in copper content (by 7%) was achieved due to vermicomposting and composting the mixture of sludge and brown coal.

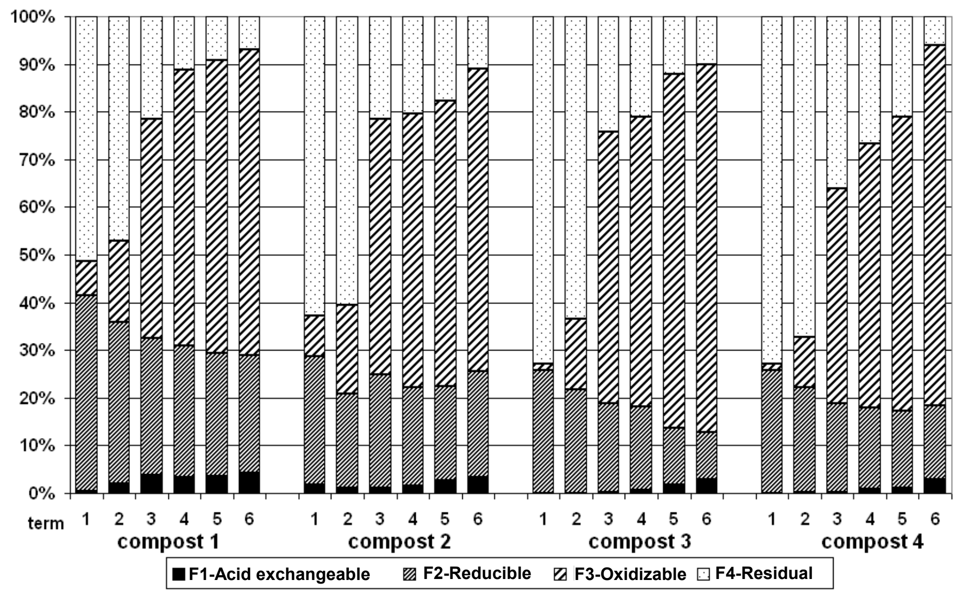

Fig. 2. Influence of composting time and compost type on proportion of copper fractions in total copper pool

Copper speciation (figure 2) showed that both in raw sludge and in composts prepared on its basis, from 51% to 73% of this metal pool were bonded to a residual form (F4), and a smaller amount – to a reducible fraction (F2). The proportion of an exchangeable form, soluble in acid environment (F1), was very low, ranging from 0.08% (composted and vermicomposted sludge + brown coal) to 1.84% (composted sludge). High per cent of copper bonded to a residual fraction was also reported by other authors [3], [9]. However, in the sludge investigated by GONDEK and KOPEĆ [2], 78–87% of total copper (determined according to the Tessier method) were bonded to organic matter. Copper belongs to chemical elements showing a strong affinity with the organic matter, and the type of the complexes formed depends on the type of chemical bonds. High-molecular organic fractions contribute to the immobilization of chemical compounds, while low-molecular fractions, i. e. organic acids, polysaccharides, amino acids, polyphenols and others, promote the formation of easily soluble compounds (SMITH [12]).

The processes occurring in the materials composted for 12 months did diversify the proportion of the copper forms analyzed. In all the composts examined, the proportion of copper soluble in acid environment (F1) and bonded to the organic matter (F3) increased, while the proportion of reducible (F2) and residual (F4) forms decreased (figure 2). The composting and vermicomposting of sludge and brown coal mixture contributed to the highest proportion of F1 and F2 fractions in a total copper pool, while composting of pure sludge resulted in the lowest proportion of those fractions in the pool mentioned. Using BRC method for the assessment of copper form alterations, GREENWAY and SONG [3] proved that after 162 days of composting, the dominant copper form in sludge was bonded to organic matter (F3), which was connected with forming complex ligand bonds as a result of humification. An increase in the proportion of F1 fraction with time, recorded in this investigation, resulted, among others, from the increase in the acidity of the mass composted (the table).

4. CONCLUSIONS

1. The alterations of copper within a 12-month period depended on the composting method applied. A total copper content increased most considerably when pure sludge was composted, while the lowest increase in a total copper per cent took place after the vermicomposting of the same material.

2. Sludge vermicomposting decreased the proportion of F1 and F2 fractions and increased the amount of residual fraction (F4) in comparison to those of composted sludge.

3. Brown coal added to sludge that was subjected to composting and vermicomposting proved to be advantageous for bonding copper to organic matter.

LITERATURE

[1] Uchwała Rady Ministrów nr 233 w sprawie *Krajowego planu gospodarki odpadami 2010*.

[2] *Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi w sprawie wykonania niektórych przepisów ustawy o nawozach i nawożeniu z dnia 19 października 2004 r.* DzU Nr 236, poz. 2369.

[3] HURY G., *Wpływ rodzaju dodatków organicznych do osadu ściekowego na skład chemiczny kompostu i wermikompostu*, Zesz. Probl. Post. Nauk Rol., 2004, 498, 81–86.

[4] KRZYWY E., IŻEWSKA A., *Gospodarka ściekami i osadami ściekowymi*, Agricultural Academy in Szczecin, 2004.

[5] BACON J., DAVIDSON Ch.M., *Is there a future for sequential chemical extraction?* Analyst, 2008, 133, 25–46.

[6] KALEMBASA S., WYSOKIŃSKI A., *Wpływ dodatku popiołów do osadów ściekowych oraz kompostowania otrzymanych mieszanin na zawartość miedzi i cynku w wydzielonych frakcjach*, Zesz. Probl. Post. Nauk Rol., 2004, 502, 825–830.
[7] SMITH S.R., *Agricultural recycling of sewage sludge and the environment*, CAB International, 1996.
[8] RAUERT G., LOPEZ-SANCHEZ J.F., SAHUQUILLO A., RUBIO R., DAVIDSON C., URE A., QUEVAUVILLER P., *Improvement of the BCR three step sequential extraction of new sediment and soil reference materials*, J. Environ. Monit., 1999, 1, 57–61.
[9] PATORCZYK-PYTLIK B., *Przydatność metody BCR do oceny mobilności cynku w osadzie ściekowym kompostowanym różnymi metodami.* Cz. I. *Wpływ metody kompostowania oraz czasu na zmiany formy chemicznej cynku w kompostowanej masie*, Zesz. Probl. Post. Nauk Rol., 2006, 512, 449–455.
[10] SYMANOWICZ B., KALEMBASA S., *Zmiany zawartości węgla i azotu w kwaśnych wyciągach podczas inkubacji mieszanin węgli brunatnych z osadami ściekowymi*, Rocz. Glebozn. LV, 2004, 2, 435–445.
[11] *Rozporządzenie Ministra Środowiska w sprawie komunalnych osadów ściekowych z dnia 1 sierpnia 2002 r.* DzU Nr 134, poz. 1140.
[12] GREENWAY G., SONG Q., *Heavy metal speciation in the composting process*, J. Environ. Monit., 2002, 4, 300–305.
[13] ROSIK-DULEWSKA CZ., *Impact of municipal wastewater treatment and processing technologies on the total content of trace metals and their fractions in sewage sludge*, Chemia i Inżynieria Ekologiczna, 2003, 10, No. 5, 427–436.
[14] GONDEK K., KOPEĆ M., *Heavy metal binding by organic substance in sewage sludge of various origin*, EJPAU, 2006, 9, 3, 1–13.

WYKORZYSTANIE METODY BCR DO OCENY PRZEMIAN FORM MIEDZI W OSADZIE ŚCIEKOWYM KOMPOSTOWANYM RÓŻNYMI METODAMI

Oceniano wpływ kompostowania oraz wermikompostowania samego osadu ściekowego oraz osadu z 20% dodatkiem węgla brunatnego na zmiany formy chemicznej miedzi obecnej w tych materiałach organicznych. W ciągu 12 miesięcy prowadzenia badań 6-krotnie pobierano próbki do analiz. Aby ocenić przemiany form miedzi, wykorzystano metodę BCR. Stwierdzono, że zastosowane metody kompostowania różnicowały zarówno całkowitą zawartość miedzi, jak i udział oznaczanych frakcji tego metalu w jego puli. W osadzie wyjściowym oraz w przygotowanych na jego bazie kompostach od 51 do 73% miedzi było związane w formie rezydualnej (F4), a w dalszej kolejności we frakcji podatnej na redukcję (F2). We wszystkich badanych kompostach z czasem wzrósł udział formy miedzi rozpuszczalnej w środowisku kwaśnym (F1) i związanej z materią organiczną (F3), zmniejszył się natomiast udział formy podatnej na redukcję (F2) oraz rezydualnej (F4). Najbardziej wzrósł udział F1 i F3 w wyniku kompostowania i wermikompostowania mieszaniny osadu i węgla brunatnego, a najmniej – podczas kompostowania samego osadu.