

Determining the possibility of using selected composts to remove aqueous solutions from zinc ions in concentrations of up to 1000 mg·L⁻¹

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Abstract. The high sorption capacity of compost indicates that it can be a cheap alternative to the currently used sorbents, also in the case of heavy metals. The sorption of zinc from aqueous solutions with the use of the selected compost types not meeting standards was carried out in accordance with the batch method in the constant contact conditions of a liquid (100 mL) and a solid (5,0 g) when the concentrations of Zn²⁺ were 100, 250, 500, 750 and 1000 mg·L⁻¹. The efficiency of the process decreased with an increasing Zn²⁺ concentration and was strongly dependent on the quality of the compost and the composition of the initial compost mixture. For the highest concentration of zinc, the best efficiency (nearly 70%) was obtained in case of the commercial compost, while the lowest one (only 25%) in the case of the compost made only from green waste and prepared in a garden compost bin. The experimental results were described using the Freundlich isotherms and the obtained equation parameters show the adsorption process. It was found that compost can serve as an efficient sorbent with regard to zinc ions.

1 Introduction

The growing demand for cheap and efficient sorbents capable of removing various types of pollutants from water and sewage spurs multidirectional studies which aim at finding new materials with adsorptive properties [1-3]. Researchers frequently resort to unconventional materials [4, 5], as they prove to be much more economical than the widely used but rather costly activated carbon. Compost is a very promising product in this group: it is easy to make and cheap to produce, it is obtained from waste material produced in large numbers by people. All this makes necessary for the verification of compost use as sorbent with regard to diversified types of pollutants [6, 7].

Regardless of the composting method and the quality and purity of substrates it is not uncommon to obtain compost which for various reasons should not or cannot be used to fertilize the soil [8]. If it does not meet the respective requirements it becomes a useless waste material, and very often it is disposed of on landfill sites [9]. However, even such material has useful physical and chemical properties which could be made use of, i.e. it could serve as a sorbent of heavy metals. It was just such waste composts (not meeting standards) that were used in the experiment.

The level of heavy metal concentration, which is constantly growing, is considered the most serious problem of environment contamination. What poses special threat to human health is the permanent character

of this type of contamination as well as the fact that heavy metals are easily incorporated in the food chain [10]. As a consequence of the growth of numerous industrial branches, such as mining, electroplating, fertilizing, paper, pesticide ones, as well as tanneries and battery production ones, the sewage, contaminated by heavy metals, is directly or indirectly discharged into the environment. The heavy metals it contains are not biodegradable and are prone to accumulate in living organisms. They are proved to be tumorigenic or toxic.

Heavy metals can be removed from aqueous solutions by means of a number of methods and mechanisms, i.e. chemical precipitation, ion exchange, adsorption, membrane processes, coagulation and flocculation as well as flotation or electrochemical methods [11]. Sorption has turned out to be both an extremely efficient and economical process in comparison to the other techniques.

The sorbents used in the research are of different types: there are traditional ones such as activated carbon, clay minerals, zeolites, fly ash, metal oxides or even carbon nanotubes and biosorbents [12-15].

One may also find a few cases when the high level of compost efficiency in removal of heavy metals from water and sewage has been noticed in the specialist literature [16], including copper (Cu), lead (Pb) and zinc (Zn) in the following sequence Pb>Cu>Zn [17, 18].

The objective of the study was to test four types of compost with regard to their zinc sorption capacity in aqueous solutions by means of the batch method. On the

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basis of what was reported in the specialist literature, the best method employed to describe experimental results was the Freundlich isotherm [16, 19].

2 Materials and methods

2.1 Characteristics of the sorbents

In the study, 4 types of compost were verified with different compositions of the batch mixture and different techniques of the production process.

The first type of compost (K1) was prepared in a backyard composter and was made exclusively from garden waste, 70 % of which was grass. It was aerated by turning it over two or three times during the summer time.

In the initial composition of the second type of compost (K2) which was produced in compost heaps, apart from the garden waste (about 50% of the compost weight) and the household waste (about 30% of the compost weight) there was waste peat obtained from a private ornamental shrub nursery.

The third type of compost (K3) made in a backyard composter contained in its initial composition garden waste (about 60%), mainly grass, as well as household green waste. In the composter the substrates were put in layers, there was no turning it over/aerating, but instead water was recurrently added into it.

The last type of compost (K4) was a commercial garden compost by the firm 'KIK' produced in the controlled process of composting grass, leaves and branches.

2.2 Testing of the composts

The composts were tightly closed right after the collection from their place of production and transported to the laboratory where their natural moisture was measured (according to PN-EN 14346:2011). Next, the material was prepared for further analysis in accordance with the respective methodologies and instructions. The selected composts were marked to enable the estimation and comparison of their quality. The following parameters were measured and marked:

- organic substance content according to PN-EN 15169:2011,
- pH value in distilled water according to PN-Z-15011-3:2001,
- total organic carbon by means of the TOC analyzer Multi N/C 2100, the final result, in $\text{mg}\cdot\text{g}^{-1}$, as the arithmetic mean of three repetitions,
- nitrogen measured according to the Kjeldahl method based on PN-Z-15011-3:2001, after mineralization in the SpeedDigester K - 439 device, the arithmetic mean of two analyses,
- zinc content measured by the emission spectroscopy method with inductively coupled plasma (ICP),
- total specific surface calculated by the sorption method of methylene blue according to PN-88/B-04481:1988.

The sorption capacity was determined according to formula 1:

$$MBC = \frac{100m}{2m_s}(V_i + V_{i-1}) \quad (1)$$

where:

MBC – sorption capacity with regard to methylene blue per 100 g dry mass of composts [$\text{g}\cdot 100\text{ g}^{-1}$],

m - the mass of methylene blue contained in 1 mL of the solution, per trihydrate substance [g],

m_s - the mass of compost used to mark per the dry mass at the temperature of 105 °C [g],

V_i - the solution volume at which the sorption capacity was exceeded [mL],

V_{i-1} - the solution volume corresponding to the next to last methylene blue portion before the sorption capacity was exceeded [mL].

The specific surface (S_t) was calculated according to the formula 2:

$$S_t = k_1 \times MBC \quad (2)$$

where:

S_t – specific surface [$\text{m}^2\cdot 100\text{ g}^{-1}$],

k_1 - the coefficient the value of which is to be assumed to equal 20,94 [$\text{m}^2\cdot\text{g}^{-1}$],

MBC - sorption capacity with regard to methylene blue per 100 g dry mass of composts [$\text{g}\cdot 100\text{ g}^{-1}$].

2.3 Conditions of sorption

This part of testing covered composts which were dried to the solid mass at the temperature of about 60°C, crushed and sieved through a sieve whose mesh diameter was 0,1 mm. The sorption of zinc from aqueous solutions using the selected composts was conducted by the batch method in the constant contact conditions of liquid (100 mL) and a solid (5,0 g). The base solution with the concentration of 10 g Zn^{2+} was obtained by dissolving the mass of ZnCl_2 (Chempur, p.a.) in distilled water determined on the basis of the stoichiometric reaction. The working (initial) concentrations of Zn^{2+} amounted successively to 100, 250, 500, 750 and 1000 $\text{mg}\cdot\text{L}^{-1}$ and were made by dilution of the base solution. The compost mixtures with the working solutions (with the ratio 1:20) were shaken for 24 h and then filtered. The residual content of Zn^{2+} ions in the mineralized liquid was measured with the use of the atomic emission spectroscopy with the inductively coupled plasma (ICP).

Adsorption of zinc in the composts (q), was calculated according to the formula 3:

$$q = \frac{(C_0 - C_k) \times V}{m} \quad (3)$$

where:

q – adsorption [$\text{mg}\cdot\text{g}^{-1}$],

C_0 - the initial concentration of metal in the solution [$\text{mg}\cdot\text{L}^{-1}$],

C_k - the equilibrium concentration of metal in the solution [$\text{mg}\cdot\text{L}^{-1}$],

M - the compost mass [g],

V – the volume of solution [L].

The sorption efficiency (S) was determined according to the formula 4:

$$S = \frac{(c_0 - c_k)}{c_0} \times 100 \quad (4)$$

where:

S – sorption efficiency [%],

C₀ - the initial zinc concentration in the solution [mg·L⁻¹],

C_k - the equilibrium zinc concentration in the solution [mg·L⁻¹].

So as to estimate the sorption capacity of the tested composts the zinc sorption isotherms were determined. To describe the isotherms the following Freundlich equation [20] was used (5):

$$q = k_F \cdot c_k^{1/n} \quad (5)$$

where:

q - the sorption capacity [mg·g⁻¹],

C_k - the equilibrium zinc concentration in the solution [mg·L⁻¹],

K_F, 1/n - the Freundlich equation coefficient [-].

The values of k_F and 1/n were determined by means of a graphic method, presenting the experimental results on a logarithmic scale chart where the equation shows the linear relationship between the variables q and C_k (6).

3 Results and discussion

3.1 Characteristics of the composts

In the study there were tested 3 different types of compost produced in the uncontrolled backyard or household conditions (K1 ÷ K3) and one commercial compost (K4). That is why it was important to compare their quality and determine their usefulness in fertilization and the sorption process. Based on reports in the specialist literature [21] there were measured and marked significant compost parameters, which are presented in Table 1.

The moisture of composts that are mature and ready for fertilization should fall within the range of 25 - 50 % [21]. Composts K1 and K2 meet this requirement, while the commercial compost K4 exceeds slightly the limit value. The highest value of moisture, almost 70%, was found in compost K3, which was periodically watered – too high water content during the composting process may disturb the composting process, cause anaerobic conditions, and thus reduce compost properties.

Table 1. Results of physical and chemical analyses of the selected composts.

Tested composts	K1	K2	K3	K4
Moisture [%]	25.8	43.2	68.6	50.9
pH [-]	6.5	6.3	5.7	8.0
Organic substance content [% d.m.]	10.5	38.2	44.3	26.0
Total organic carbon [% d.m.]	6.35	15.45	26.22	15.29
Nitrogen [% d.m.]	0.379	0.606	2.268	1.101
C:N [-]	16.8	25.5	11.6	13.9

The pH values of mature composts which are favorable for fertilization amount from 5,5 to even 8 [21]. All the selected composts fall within the given range. The pH value = 8,0, being the most favorable one from the point of view of agriculture, was measured in the commercial compost K4; the less favorable pH values (soil acidification) were observed in case of the other composts.

Organic fertilizers in the solid form should contain at least 30 % of organic substance per the dry mass [22] – composts K1 and K4 do not meet this criterion. In both cases the very low organic substance content may result from the poor composition of the batch mixture (only garden waste). What is worth mentioning is the fact that the commercial compost K4 does not comply with the Polish regulations [8].

The minimal Kjeldahl nitrogen in organic fertilizers should equal 0,3 % [22] and all the tested composts fulfill this condition. However, the relatively low nitrogen content in composts K1 and K2 may mean that the composting process went incorrectly (NH₃ was released). It is not favorable when it comes to fertilization [23].

During the composting process the total organic carbon content diminishes because of the gradual transformation of organic carbon to carbon dioxide and its release to the atmosphere. As a result, the total organic carbon to nitrogen ratio decreases as well. The C:N ratio in the mature compost should amount to <20:1 [24] and indicates the degree of reaction of the batch mixture components as well as a possible usage of this product. The highest C:N ratio (more than 25) was estimated in case of compost K2, and this is a desirable value but only for the waste mixtures just being prepared for the composting process. It is worth noticing that compost K2 was the only one which was produced by means of compost heap method and its additional substrate was peat (visible precipitations in the finished compost).

In the composts selected for the test, only the basic parameters typical to the composts were measured which are mature and ready for fertilization. However, none of them fulfilled all the conditions. In such cases, when the properties of the obtained composts are not appropriate enough for fertilization, it is worth considering another exploitation of such materials.

The use of composts as sorbents of numerous substances described in the specialist literature [7] can be confirmed by their sorption capacity. As composts are quite frequently used as sorbents of dyes from aqueous solutions [2, 6], the method of methylene blue was chosen to determine the sorption capacity of the selected composts [25]. The results are listed in Table 2.

The highest MBC sorption capacity value amounting to 0,8 g·100 g⁻¹ (specific surface S_t = 17,24 m²·g⁻¹) was observed in the case of compost K2 containing waste peat which has a high sorption capacity. Composts K3 and K4 showed similar and slightly lower values. The lowest sorption capacity, the MBC result = 0,68 g·100 g⁻¹ (specific surface S_t = 14,24 m²·g⁻¹) was observed in case of compost K1 which was made mostly from garden waste, mainly grass. The specific surface values obtained

for the selected composts in comparison to specific surface of activated carbons reaching $2000 \text{ m}^2 \cdot \text{g}^{-1}$ seem to be low, however, they are comparable to zeolite materials [26]. Thus, the obtained results do not diverge from the values reported in the specialist literature [2].

Table 2. MBC sorption capacity of the selected composts.

Composts	MBC – mean [g/100g]	Standard deviation
K1	0.68	0.121
K2	0.82	0
K3	0.75	0.127
K4	0.73	0.081

As the aim of the experimental study was to determine the zinc sorption capacity of the selected composts, it was necessary to measure the initial content of zinc in those composts (Table 3).

All the tested composts showed low zinc concentration (Table 3). Although compost K1 had the highest content of this metal, it was quadruple in comparison to the values measured in case of the other composts, it still could not influence the results of the planned experiment. An average zinc content in composts produced from various wastes amounts to about 0,01 % [21], whereas the regulations on the permissible values of heavy metals in composts do not specify the maximum content of this element in composts [22].

Table 3. Zinc content in the selected composts.

Composts	Content Zn^{2+} [% d.m.]
K1	0.04
K2	0.01
K3	0.01
K4	0.01

3.2 Zn^{2+} sorption capacity of compost

Sorption capacities of composts in case of Zn^{2+} ions were estimated by the batch method. Initial concentrations of zinc (C_0) in aqueous solutions were equal 100, 250, 500, 750 and 1000 $\text{mg} \cdot \text{L}^{-1}$ respectively. The tests were carried out with the composts having their typical natural pH value (Table 1). Sorption efficiency results for the selected composts are shown in Figure 1.

As the initial concentration of zinc ions in the solution increased, the sorption efficiency of all the sorbents diminished (Figure 1). The highest sorption efficiency was observed in case of compost K4: its sorption capacity was more than 90 % when the zinc concentration did not exceed 500 $\text{mg} \cdot \text{L}^{-1}$; next this value decreased slightly and when the zinc concentration reached its maximum, the sorption capacity was still high – 67,5 %. It is worth mentioning that the pH value of this compost was 8,0, which may have a significant impact on the zinc distribution in the solution and

consequently lead to the higher zinc removal efficiency from aqueous solutions [27].

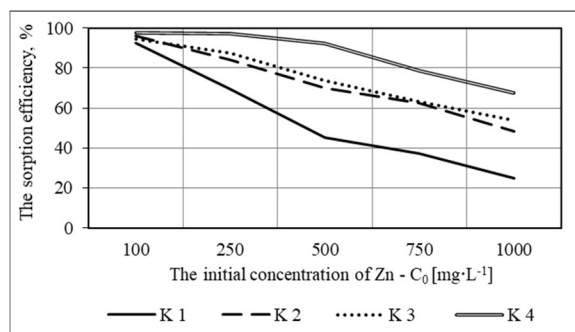


Fig. 1. Zinc sorption efficiency for the selected composts.

Composts K2 and K3 were observed to have a similar batch sorption efficiency with a narrow margin in case of compost K3. Their pH values were 6,3 and 5,7 respectively – the solubility of zinc increased as the pH value dropped [28]. Although compost K2 had the highest sorption capacity value with regard to the methylene blue (Table 2) it did not translate to the better zinc sorption. It could be caused by the pH value or insufficient decomposition degree of the substrates (the ratio of C/N > 25:1).

The lowest sorption efficiency for all zinc concentrations was observed in the case of compost K1. It may result from a very low content of organic substance in this compost (Table 1).

Additionally, in order to compare the tested composts Figure 2 presents sorption isotherms of zinc showing dependence of equilibrium concentration C_k on the sorption capacity q .

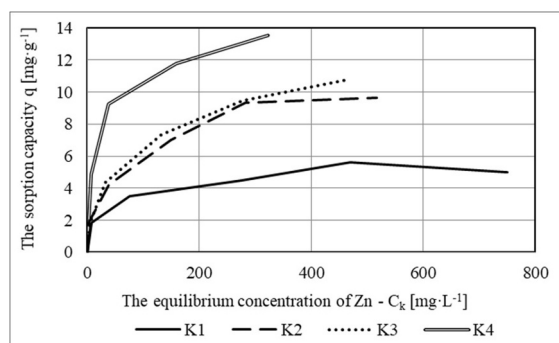


Fig. 2. Sorption isotherms of zinc for composts K1 ÷ K4.

The graph of the sorption isotherms (Figure 2) shows that the higher values were observed in case of compost K4, while the distinctly lower values were obtained in case of compost K1. As long as the concentration did not exceed 250 $\text{mg} \cdot \text{L}^{-1}$, the sorption capacities of the tested composts were of similar value. When the initial zinc concentration range was 500 ÷ 1000 $\text{mg} \cdot \text{L}^{-1}$, there was observed a significant difference between the sorption capacities of composts K1 and K4 – it amounted to 63.1%. The maximum sorption capacity during the tests carried out on compost K4 was 13.55 $\text{mg} \cdot \text{g}^{-1}$. Lower, but equally satisfactory, results were obtained while testing composts K2 and K3. Although compost K1 turned out

to have the poorest sorbent capacity, it could still be used for relatively lower concentrations. The zinc content in surface waters and municipal sewage is much lower [10] than in aqueous solutions used for the purpose of tests.

From the reports in the specialist literature [2, 20] one may learn that the Freundlich isotherm was the only method employed to describe the zinc sorption of the selected composts. This is an empirical model widely used to describe heterogeneous systems. The Freundlich isotherms in a logarithmic system together with the equations of trend lines for all the tested composts were presented graphically in Figures 3 ÷ 6; additionally, the values of the constant isotherms were shown together in Table 4.

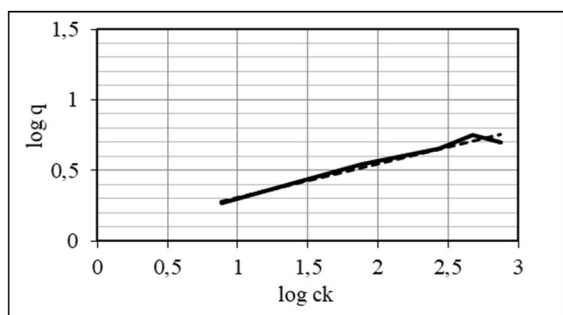


Fig. 3. The linearized Freundlich sorption isotherms of zinc for compost K1.

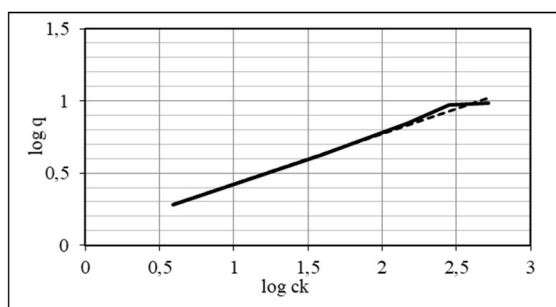


Fig. 4. The linearized Freundlich sorption isotherms of zinc for compost K2.

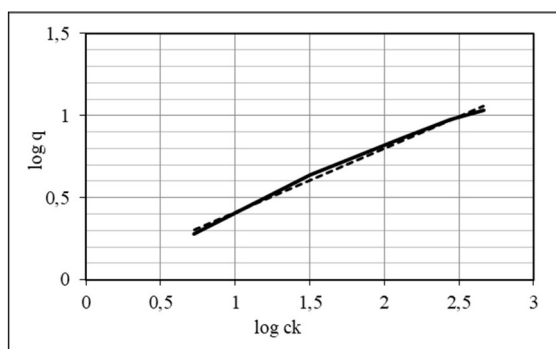


Fig. 5. The linearized Freundlich sorption isotherms of zinc for compost K3.

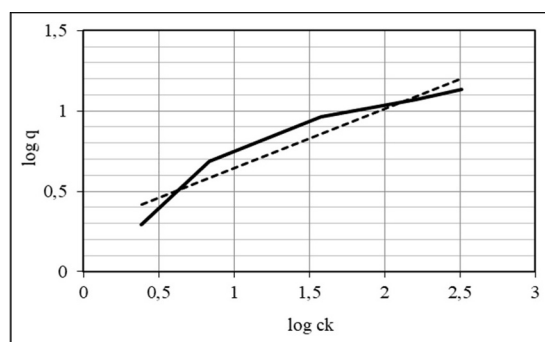


Fig. 6. The linearized Freundlich sorption isotherms of zinc for compost K4.

Table 4. The Freundlich isotherms constants for the sorption of zinc onto selected composts.

Marking	k_F [$\text{mg} \cdot \text{g}^{-1}$]	$1/n$ [-]	R^2 [-]
K1	1.195	0.235	0.962
K2	1,206	0.347	0.991
K3	1.046	0.390	0.992
K4	1.887	0.369	0.908

The calculated values of the square correlation coefficient R^2 for the four composts listed in Table 4 proved that the measurements were accurate and the Freundlich isotherm was rightly applied. The highest estimated value of coefficient k_F was observed in case of the commercial compost K4, while the lowest one in case of compost K1. Curiously enough, both composts were produced exclusively from garden waste; the difference is found in the applied technique of the compost's production.

For the Freundlich equation the constant k_F , indicating the zinc content adsorbed by compost (Table 4), grows respectively: $K3 < K1 < K2 < K4$; the difference between the worst (K3) and the best (K4) sorbents is quite significant and amounts to 45 %. It is not consistent with the results presented in Figure 2, but in this way (the constants of the Freundlich isotherms) the goodness-of-fit is determined.

4 Conclusions

Regardless of the initial mixture composition and the applied composting technique none of the tested composts fulfilled the basic criteria to serve as organic fertilizers. Each of them must be treated as waste material. In case of waste composts K1, K2 and K3, made in the uncontrolled backyard conditions, it was rightly assumed that their quality would not comply to the requirements. The commercial compost K4 should also be used otherwise since the content of organic substance in it is too low to make it a good quality fertilizer.

Determining the sorption capacity by means of the methylene blue (cationic dye) indicated that the most

favorable sorption properties were observed in compost K2 containing waste peat; it did not translate to the batch sorption of zinc. Thus, it is worth considering employing another method to determine the sorption capacity in further research.

The best sorption efficiency, as far as the whole range of the analyzed Zn concentrations is concerned, was observed in case of compost K4 – its efficiency for the highest concentration (1000 mg·L⁻¹ Zn²⁺) was equal to almost 50 % – this result is comparable to typical sorbents. It was concluded that the least efficient zinc sorbent among the tested composts was compost K1; however, using it in case of concentrations of up to 250 mg·L⁻¹ also produced positive effects.

The tested waste composts may be used for zinc sorption from aqueous solutions within the Zn concentration range 100 ÷ 1000 mg·L⁻¹ or even higher. The sorption results, in particular the ones obtained in case of waste composts K2, K3 and K4, were very promising and showed that the initial zinc concentration range may even be increased.

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