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Analysis of Slow-Released Fertilisers as a Source of Microplastics

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Abstract: One of the main strategies for improving the efficiency of agricultural production is the use of fertilisers with slow or controlled release of nutrients, in which the granules of mineral fertilisers are covered with polymeric shells. The composition of the polymer coatings of mineral fertiliser granules with slow or controlled release of two widespread manufacturers and their ability to adsorb some heavy metal ions on their surface were examined in this study. It was found that the base polymers used to encapsulate the fertilisers studied are the co-polymer polyethylene–polyacrylic acid in the Brand A, and polyacrylamide, polyacrylic acid, and its esters in the Brand B fertiliser coating. The maximum adsorption rate of heavy metal ions on the surface of the polymer coatings with the rest of the mineral filler of Brand A and Brand B fertilisers was 54.64 and 28.90 mg/g for Cd(II) ions, 30.77 and 14.03 mg/g for Pb(II) ions, respectively. Therefore, the solution to the problem of increasing the efficiency of agricultural production through the use of fertilisers with slow or controlled release of nutrients leads to environmental pollution by microplastics remaining in the soil after fertiliser application, which are also capable of adsorbing from the soil various toxic pollutants.

Keywords: microplastics; slow- or controlled-release fertilisers; polymeric coating; Cd(II) ions; Pb(II) ions; sustainable agriculture; nutrient management; climate change

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1. Introduction

The growing global population requires the intensification of agricultural production, one of the main sources of food. Cultivated plants require nitrogen, phosphorus, and potassium to maintain the physiological needs of their cells. Insufficient nutrient content in the soil has a negative effect on the growth of agricultural plants and leads to reduced yields. In order to increase crop yields, the doses of mineral fertilisers must also be increased. To meet the food demand of a growing population, the consumption of mineral and organic fertilisers containing nitrogen is projected to increase by 46% from 2010 levels by 2050 [1]. Each plant requires a certain amount of nutrients at different phases of its growth. However, plants assimilate no more than 40% of nutrients entering the soil with mineral fertilisers, while the remaining 60% of nutrients in the soil may pollute the environment as a result of leaching, volatilisation, and nitrification processes contributing to global warming, pollution of water streams as a result of excessive nutrient and mineral inputs causing algal growth, reduction in dissolved oxygen concentration, loss of biodiversity, and changes in the biogeochemical properties of the soil [2,3]. As a result, low nutrient

uptake by agricultural plants contributes to environmental pollution, and reduces the economic efficiency of agricultural production by increasing the consumption of mineral fertilisers [4–6]. Furthermore, the use of mineral fertilisers in significant quantities, in particular, urea, can lead to significant greenhouse gas emissions [7], and is restricted by current international agreements. Furthermore, most countries allow a certain amount of plastics in fertilisers; for example, Germany allows plastic content of up to 0.1 weight% (wt%). Particles smaller than 2 mm are not even counted [8]. It is therefore essential to reduce excessive use of mineral fertilisers without compromising crop productivity, which is in line with the multiple goals of sustainable agriculture.

Today, apart from targeted spot application of mineral fertilisers, one of the main strategies to improve the efficiency of agricultural production is the use of fertilisers with a slow or controlled release of nutrients (SRF or CRF, correspondingly). SRF and CRF production technologies allow for the inclusion of different mineral fertilisers in a granulate filler, thus obtaining complex fertilisers containing all the necessary nutrients for plants. The use of SRF/CRF enables the synchronisation of the nutrients in the soil with the needs of crops in different growth phases, which helps to reduce the dispersion of nutrients into the environment, as well as increasing crop yields [9,10]. However, in some cases, after the application of large quantities of damaged pellets or pellets with poor quality SRF and CRF coatings, there may be an abrupt transfer of nutrients into the soil medium, which in excessive amounts may have a toxic effect on plants.

One of the ways to create fertilisers with slow or controlled release of the nutrients in the mineral fertiliser granules is by coating them with different compounds, such as inorganic (sulphur, bentonite, gypsum, and other minerals), organic (natural and synthetic polymers), and others (graphene, nanomaterials), which regulate the rate of nutrients entering the soil.

The basis of the first coatings for SRF and CRF production was sulphur. Due to the technological peculiarities of production, these coatings contained a large amount of damage, which resulted in an immediate release of nutrients upon contact with water. Mineral coatings (bentonite, gypsum, poorly soluble inorganic compounds with the general formula $MeNH_4PO_4{*}H_2O$, where Me is a divalent metal—Mg, Fe, Zn, Mn, and others) unlike sulphur are poorly soluble in water, do not change soil pH, can improve physical and chemical properties, promoting plant growth [11]. The prolonged effect is achieved through gradual dissolution and depends on particle size, moisture, soil acidity, and temperature. Unlike inorganic coatings, synthetic organic polymeric materials (polyethylene, acrylic polymers, polyurethane, and others) are insensitive to environmental influences. The rate of nutrient release is determined by the thickness of the coating, the presence and size of pores in the coating, and soil temperature, which have a significant effect on their diffusion [12]. The use of single polymer coatings has the disadvantage of the initial abrupt release of nutrients. Thus, the design of some SRF/CRFs is based on the use of a combined coating to better control nutrient release, as well as the use of multiple layers of different materials to improve fertiliser properties. For example, an outer polymer layer with an insoluble inorganic mineral backing promotes better adhesion of the polymer film to the fertiliser particle as well as a smoother nutrient release [13]. However, the use of synthetic, hard-to-degrade polymers as coatings leads to the accumulation of plastic particles in the soil. Thus, the application of such SRF/CRFs becomes a source of soil contamination by microplastics (MPs) defined as polymer particles with a diameter < 0.5 mm [14,15]. In this regard, much attention is paid to the development of biodegradable coatings based on natural polymeric materials (starch, cellulose, agricultural waste, lignin, and others). Since, in their pure form, natural polymeric materials do not have sufficient mechanical strength, they are used in combination with other polymeric materials. A modern trend

in SRF and CRF production is the use of nanotechnology to create a physical barrier by coating fertiliser granules with a specific membrane or hydrophobic polymer having pores filled with nanoparticles [16–18].

However, for the production of SRF/CRF on an industrial scale, in most cases, mineral granules are covered with polymer shells made of the cheapest inert hydrophobic materials available (i.e., polyethylene, acrylic polymers, polyurethane, and their copolymers), materials that are not susceptible to biodegradation in the natural environment, which leads to environmental MP pollution [13,19–21]. Previous studies have shown that it would take at least 300 years for 60 μm thick polyethylene film to completely biodegrade [22]. Although polymers have already revolutionised all the industrial sectors and have produced relevant effects on the quality of life, their continuous accumulation in the environment constitutes a hazard that must be urgently addressed. From approximately 450 million tonnes of plastics produced worldwide annually, 12.5 tonnes are used in the agriculture sector, 76% of all the plastics produced become waste, 79% of which is accumulated in landfill and the natural environment [23,24]. The accumulation of plastics in the environment is the main source of secondary microplastics through gradual degradation and fragmentation [14,21,24].

Despite the fact that MP studies in soil are actively ongoing, there is yet no definitive answer to the question of the real danger of MPs in soil on human health. However, there are already noteworthy results about both the ingress of MP particles from agricultural soils into human food [25], and the negative impact of their presence on the physical, chemical, and biological properties of soils and crops [21,26,27]. Moreover, soil is currently considered to be the main environmental medium in which MP particles accumulate: the annual MP pollution of soils is estimated to be between 4 and 23 times higher than that of the oceans [28]. The possibility of adsorption of pollutants on microplastic particles present or introduced by human activity into the soil also requires extensive study. Some of the relevant ecotoxicants to be monitored are heavy metal ions, which are capable of prolonged presence in soil [29]. There are many ways of anthropogenic input of heavy metals like, for example, the deposition of dust and aerosol particles, corrosion of metal structures including galvanised roofs and fences, and also fertilisers or other agrochemical compounds [30]. Inorganic minerals used as SRF/CRF coatings may contain some heavy metals like Cd, Pb, Cr, Cr, Cu, Cu, Ni, Zn, and others [30].

Therefore, the purpose of this study is to investigate the composition of polymer coatings in SRF/CRFs, as well as to estimate the possible adsorption on their surface of heavy metal ions as typical examples of toxic pollutants present in the soil [31]. Cd(II) and Pb(II) ions were chosen to study the adsorption of heavy metal ions on the surface of polymer microparticles because they are among the priority soil pollutants due to their rapid rate of accumulation in soils as a result of anthropogenic human activities (i.e., mining, metallurgical, and chemical industries, use of fertilisers and pesticides in agriculture, etc.) and high toxicity to the environment, plants, animals and human health [30,32,33].

2. Materials and Methods

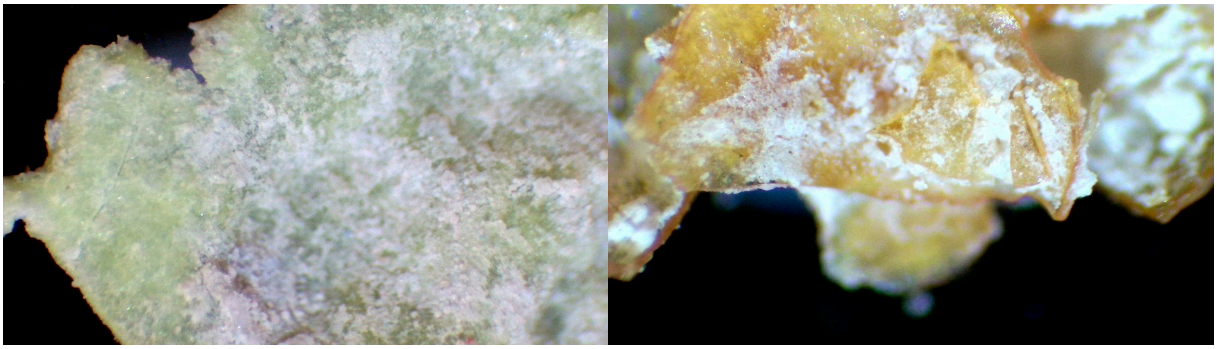
The widely used SRFs of Brand A and Brand B were selected for the study, the main characteristics of which are presented in Table 1. Brand A 6M and Brand A 12M fertilisers are homogeneous granules of nutrients uniformly coated with a flexible polymer that controls water penetration and therefore the dissolution of nutrients within the coating. The prolonged effect of the fertiliser is achieved by varying the thickness of the polymer coating, which determines the rate of water penetration into the granule and the diffusion of dissolved nutrients into the soil. Brand A 6M and Brand A 12M fertilisers are recommended for use in substrate mixtures, horticulture, nurseries, and fertilisation of planting pits. Brand B 2–3M, Brand B 5–6M, and Brand B 8–9M are complex mineral fertilisers based

on compounds of nitrogen, phosphorus, and potassium with prolonged action, which is achieved by a multi-layer porous polymer coating. When applied to the soil, water penetrates through the pores into the granule, causing it to swell, and through the enlarged pores, diffusion of dissolved nutrients into the soil takes place. Brand B 2–3M, Brand B 5–6M, and Brand B 8–9M are recommended for use in pots, containers, or beds for ornamental plants, flowers, and agricultural crops.

To determine the composition of the polymer coatings used and to further study the adsorption of heavy metals on them, the polymer coatings of selected SRF were separated from the fertiliser granules, washed once with 100 mL distilled water to remove a well-soluble filler component and dried (MP of Type 1) (Figure 1). To check how the fertiliser residues affect the adsorption of heavy metals, a more thorough removal of mineral filler from the surface of the SRF polymer coatings was carried out by repeating ten times their washing with 100 mL of distilled water heated to 60 °C (MP of Type 2). It is expected that it is possible to remove most of the insoluble components by this method. The completeness of the washing was monitored visually using a microscope. (Figure 2). Distilled water was used to wash the fertiliser to adopt a standard method allowing comparison of results in future studies.

Table 1. Base characteristics of SRF under study according to manufacturer specifications.

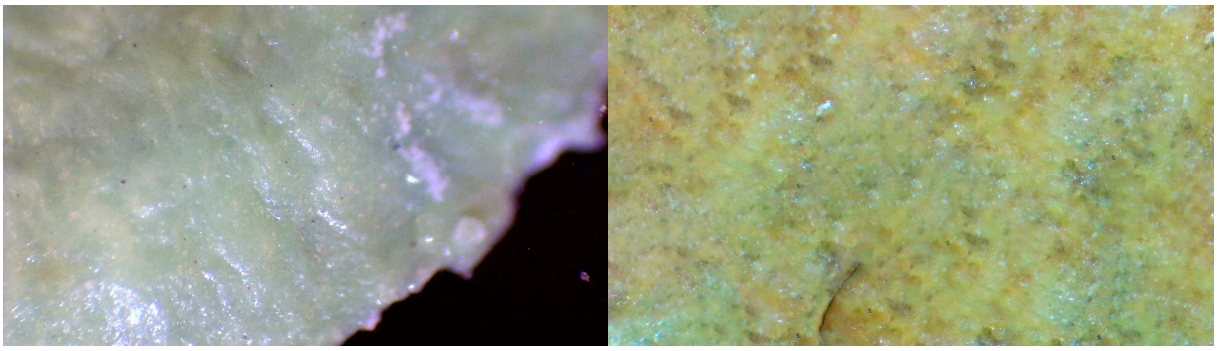
Product Name	Time of Prolonged Effect, Months	Granule Size, mm	Macronutrient Content						
			N_{tot} %	N_{NO3-} %	N_{NH4+} %	P_2O_5 %	K_2O %	MgO %	S %
Brand A 6M	5–6	2.5–3.5	15.0	7.0	8.0	8.0	12.0	2.0	5.0
Brand A 12M	10–12	2.5–3.5	15.0	7.0	8.0	8.0	12.0	2.0	5.0
Brand B 2–3M	2–3	1.5–2.0	12.0	5.3	6.7	7.0	18.0	-	-
Brand B 5–6M	5–6	1.5–2.0	19.0	6.2	8.2	9.0	10.0	2.0	-
Brand B 8–9M	8–9	1.5–2.0	11.0	4.3	6.3	11.0	18.0	-	-



(**a**) (**b**)

Figure 1. Typical pictures of Type 1 polymer coatings of Brand A and Brand B SRF at 10× magnification: Brand A 6M (**a**) and Brand B 5–6M (**b**).

The composition of the polymer coatings was determined using infrared spectroscopy. The spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) at a resolution of 2 cm^{-1}, the number of scans was 30, using a Pike single broken total internal reflection micropiece with a working element made of ZnSe. Commonly adopted IR Atlases [34,35] were used to determine the polymer composition.



(**a**) (**b**)

Figure 2. Typical pictures of Type 2 polymer coatings of Brand A and Brand B SRF at 10× magnification: Brand A 6M (**a**) and Brand B 5–6M (**b**).

The composition of the mineral filler remaining on the surface of the polymer coating was determined using X-ray diffraction. Diffractograms were registered on DX-27mini X-ray diffractometer (HAOYUAN INSTRUMENT Co., Dandong, China) using the following parameters: initial angle 20°, final angle 50°, step 0.03°, seconds per step 0.2, CuK radiation, voltage 40 kV, current 15 mA, 2° windowed one-dimensional detector. To reduce peak broadening and amorphousness, the mineral filler samples were manually ground to a particle size of less than 100 µm using an agate pestle and mortar. MDI JADE 9.0 diffractometer software was used to identify inorganic compounds by comparison with reference diffractograms of individual compounds contained in the international diffraction standards database PDF-4 [36–38].

Initial solutions of Cd(II) and Pb(II) ions for adsorption studies were prepared from $Cd(NO_3)_2$ and $Pb(NO_3)_2$ salts by dissolution in distilled water. A serial dilution method was used. Adsorption of Cd(II) and Pb(II) ions, was studied under static conditions from 100 mL solutions with Cd(II) and Pb(II) ion concentrations of 1, 10, 25, 50, and 100 mg/L [39,40]. To avoid precipitation of Cd(II) and Pb(II) ions from the solutions, pH was maintained at 5 by adding 0.05 M HNO_3 solution. In all solutions, 10 mmol/L $NaNO_3$ was added as an inert electrolyte to keep the ionic strength of the solutions constant. Solutions were shaken on an incubator shaker (25 °C, 150 rpm) with 0.1 g of polymer coatings; after 24 h, the adsorption equilibrium was established. The concentration of Cd(II) and Pb(II) ions in model solutions was determined by atomic absorption spectrometry on a Lumex MGA spectrometer (Lumex, Saint Petersburg, Russia) with electrothermal atomisation of the sample and high-frequency Zeeman correction of non-selective absorption. Electrode-free discharge lamps with higher intensity compared to traditionally used lamps with hollow cathodes were used as the radiation source, which allowed a reduction in the detection limits of Cd(II) and Pb(II) ions. The maximum temperature of sample atomisation is 3000 °C. The high-purity argon flow rate is 2 L/min, and the spectral range is 190–900 nm. The cooling system is closed and based on water.

The equations of the Langmuir (1) and Freundlich (2) adsorption theories were used to treat the isotherms of adsorption of Cd(II) and Pb(II) ions by the surface of polymer coatings:

$$q_e = \frac{q_{max} * K_L * C_e}{1 + K_L * C_e} \quad \frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} * K_L} * \frac{1}{C_e} \tag{1}$$

$$q_e = K_F * C_e^{\frac{1}{n}} \quad \ln q_e = \ln K_F + \frac{1}{n} * \ln C_e \tag{2}$$

where q_e is the ion adsorption equilibrium value, C_e is the equilibrium ion concentration in the model solution, q_{max} is the ion adsorption limit value, K_L and K_F are the Langmuir and

Freundlich adsorption equilibrium constants, and correspondingly, 1/n is the adsorption index. The linear dependence of the adsorption isotherms confirms the legitimacy of the application of these equations [41–43]. The linear dependence of adsorption isotherms in the linear coordinates of the equations of adsorption theories is a prerequisite for proving the validity of these equations.

3. Results

The infrared spectra of the polymer coatings of Brand A and Brand B SRF are presented in Figures 3 and 4.

Infrared spectra of the Brand A polymer coatings show the presence of absorption bands related to vibrations of methylene groups of polyethylene in the region of 2930–2850 cm^{-1}, 1464 cm^{-1}, 719 cm^{-1}, and absorption bands related to vibrations of the carboxyl group of polyacrylic acid (3400 cm^{-1}—vibration of the OH-group and 1700 cm^{-1}—vibration of the C=O group). Hence, it can be concluded that the base polymer in the coating is a polyethylene–polyacrylic acid copolymer.

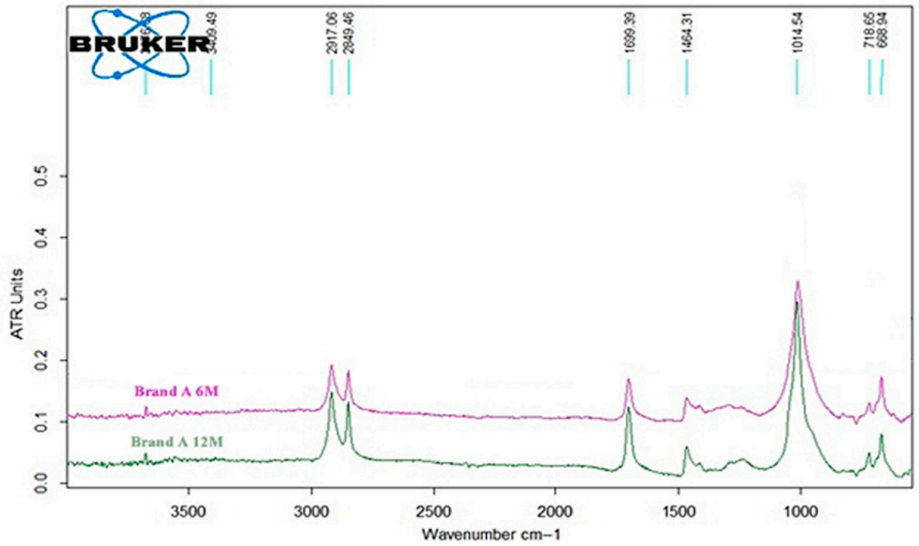


Figure 3. Infrared spectra of the polymer coatings of Brand A SRF.

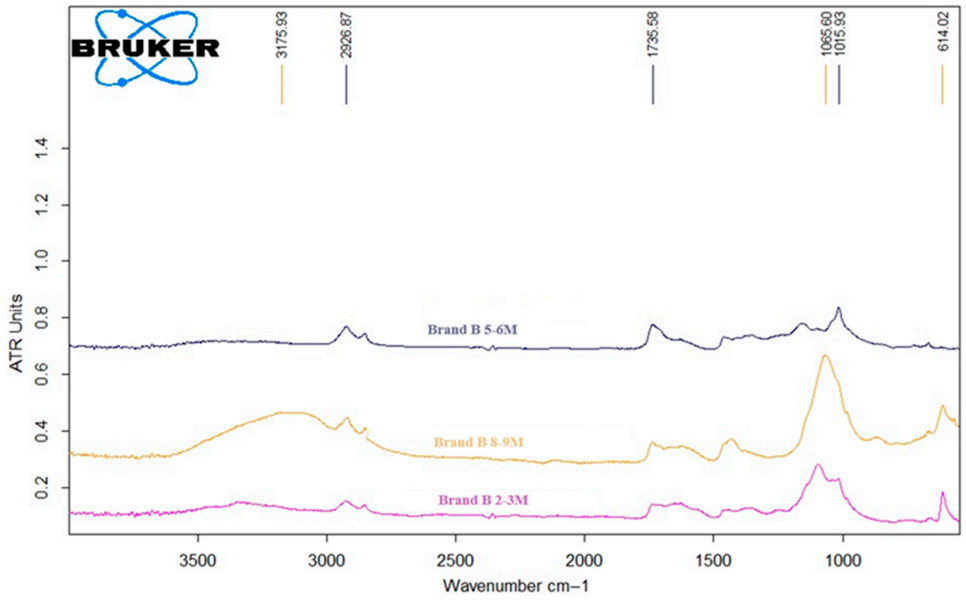


Figure 4. Infrared spectra of the polymer coatings of Brand B SRF.

Polyacrylamide, polyacrylic acid, and its esters (acrylates) are present in the polymer coatings of Brand B SRF, which is confirmed by the presence of absorption bands on infrared spectra associated with symmetrical valence vibrations of the N-H amide group (3176 cm^{-1}), valence vibrations of methylene groups (2927 cm^{-1}), valence vibrations of the C=O carboxyl group (1736 cm^{-1}), and valence vibrations of the C-O-C group (1066 cm^{-1}).

Diffractograms of the mineral filler remaining on the surface of the polymer coatings studied are rather similar for each product. Typical diffractograms are shown in Figures 5 and 6.

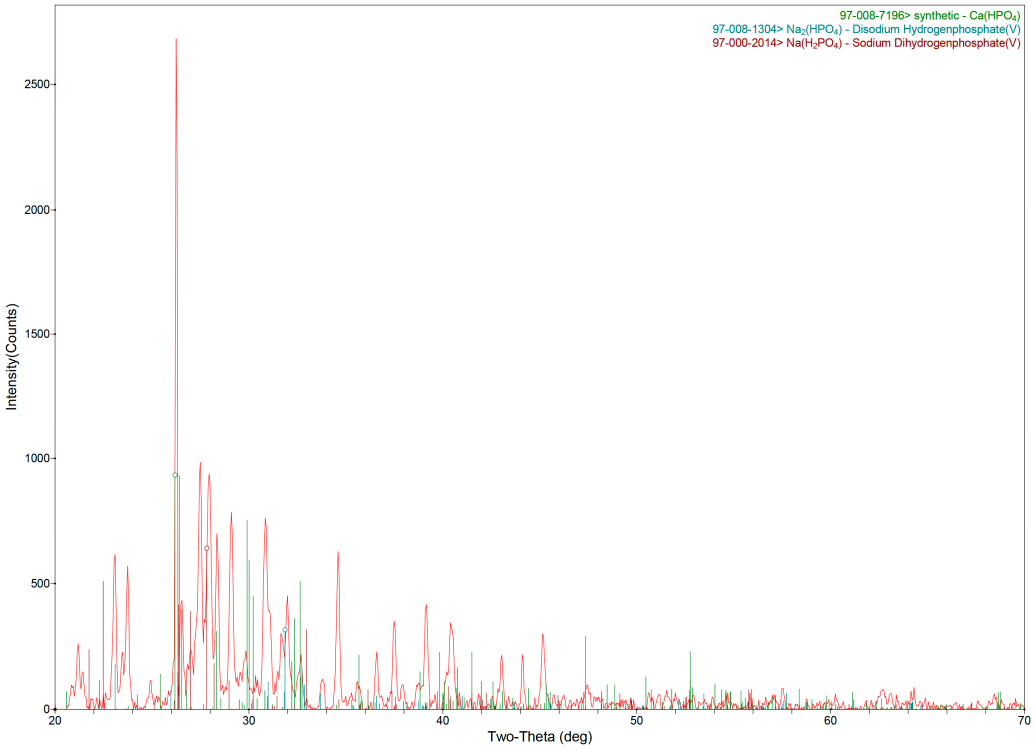


Figure 5. Diffractograms of mineral filler remaining on the surface of studied Type 1 polymer coatings of Brand A 6M SRF (red line).

The analysis of these diffractograms revealed the presence of sodium dihydrophosphates (diffraction peaks at 2θ = 21.80°, 22.52°, 26.40°, 26.93°, 27.87°, 40.32°), disodium hydrophosphates (diffraction peaks at 2θ = 24.46°, 24.89°, 28.14°, 29.36°, 31.34°, 34.00°, 36.84°, 43.04°), and calcium hydrophosphates (diffraction peaks at 2θ = 22.00°, 23.34°, 26.01°, 31.03°, 30.83°, 33.74°, 36.62°, 47.30°) on the surface of the polymer coatings of the Brand A fertilisers, and the presence of sodium dihydrophosphate (diffraction peaks at 2θ = 21.80°, 22.52°, 26.40°, 26.93°, 27.87°, 40.32°), potassium nitrate (diffraction peaks at 2θ = 23.62°, 23.86°, 29.24°, 32.22°, 32.49°, 33.68°), and ammonium nitrate (diffraction peaks at 2θ = 22.93°, 26.40°, 27.45°, 30.62°, 34.45°, 35.63°, 38.85°, 39.96°, 40.97°, 47.33°) on the surface of the polymer coatings of the Brand B fertilisers. The presence of these substances can influence the adsorption of pollutants present in the soil. In fact, previous reports have shown that composites consisting of polymers coated with inorganic substances can exhibit improved adsorption properties [44,45].

The adsorption isotherms of Cd(II) and Pb(II) ions by the surface of the polymer coatings of Brand A 6M and Brand B 5–6M SRF are presented in Figures 7 and 8.

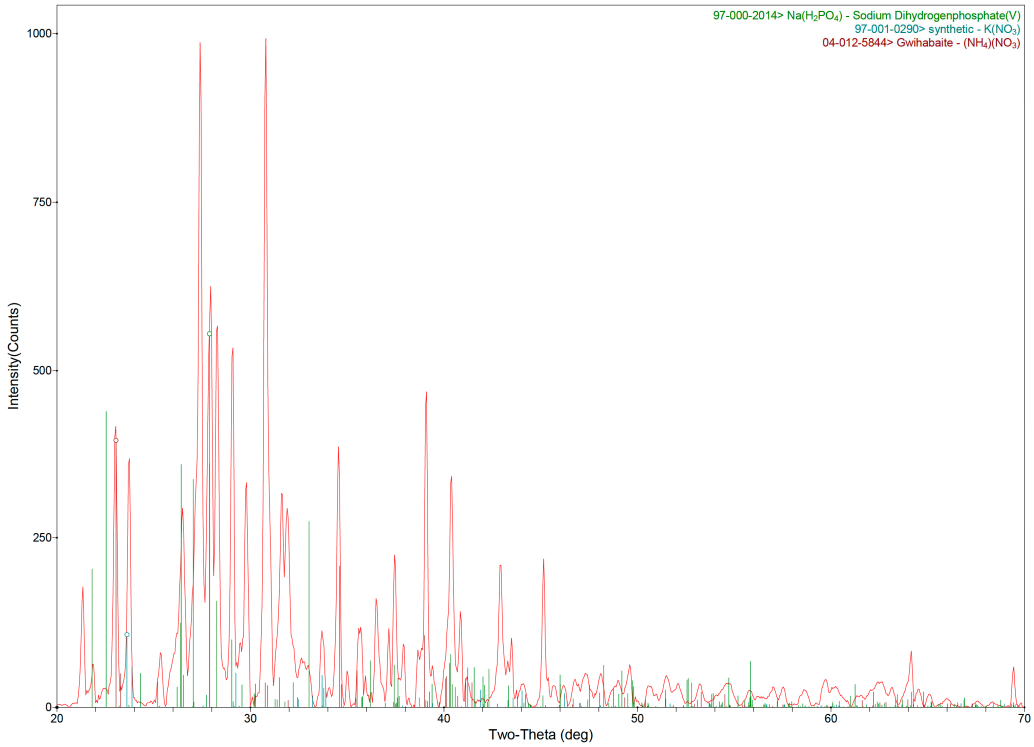


Figure 6. Diffractograms of mineral filler remaining on the surface of studied Type 1 polymer coatings of Brand B 5–6M SRF (red line).

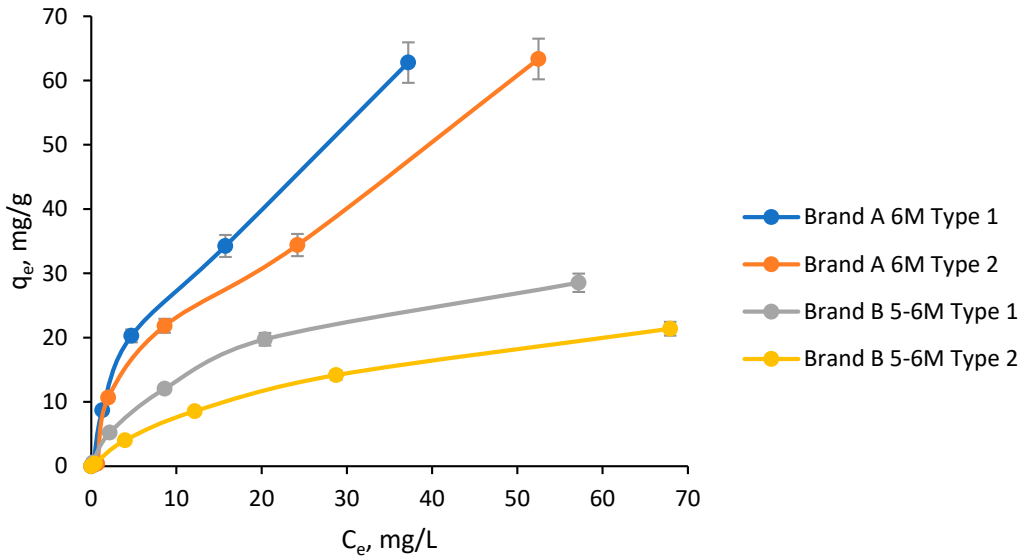


Figure 7. Adsorption isotherms of Cd(II) ions by the surface of the polymer coatings of Brand A 6M and Brand B 5–6M SRF.

The adsorption isotherms of Cd(II) and Pb(II) ions by the surface of Type 1 polymer coatings of the mineral fertiliser granules of Brand A 6M and Brand B 5–6M SRF in linear coordinates of the Langmuir (a) and Freundlich (b) adsorption theory equations are shown in Figures 9 and 10.

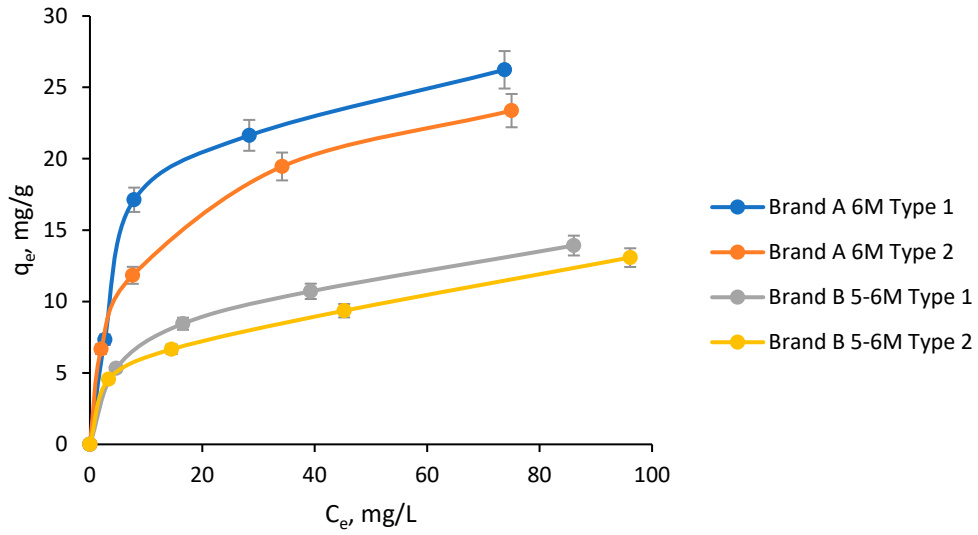


Figure 8. Adsorption isotherms of Pb(II) ions by the surface of the polymer coatings of Brand A 6M and Brand B 5–6M SRF.

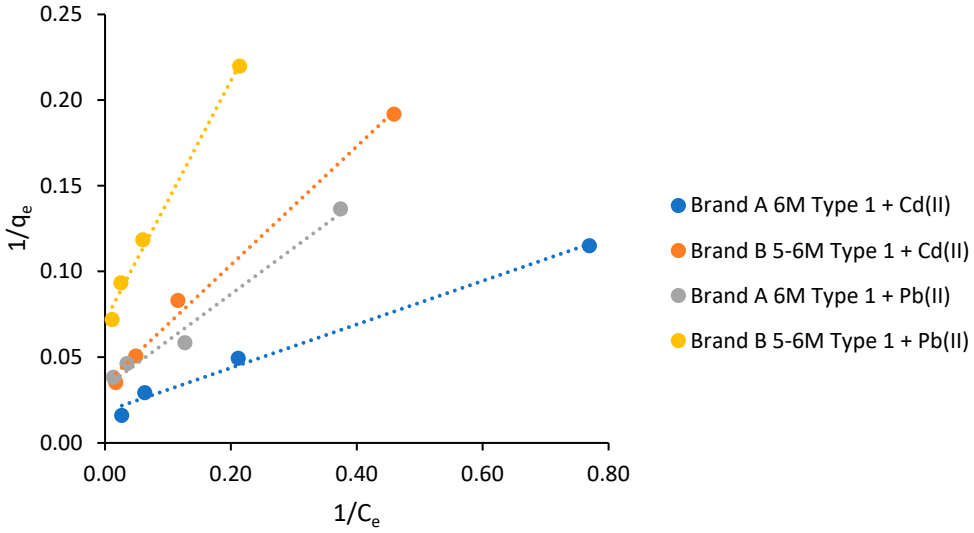


Figure 9. Adsorption isotherms of Cd(II) and Pb(II) ions by the surface of Type 1 polymer coatings of mineral fertiliser granules of Brand A 6M SRF in linear coordinates of the Langmuir adsorption theory equations.

The analysis of the data obtained shows that both adsorption theories perfectly describe the adsorption of Cd(II) and Pb(II) ions by the surface of the polymer coatings of the SRF examined. The values calculated by regression analysis for the constants in the equations of the Langmuir and Freundlich adsorption theories are presented in Tables 2 and 3.

The analysis of the data reported in Tables 2 and 3 shows that the limiting values of the adsorption of Cd(II) ions by the surface of Brand A and Brand B SRF polymer coatings (Type 1) are 54.64 mg/g and 28.90 mg/g, respectively, and of Pb(II) ions by the surface of the Brand A 6M and Brand B 5–6M SRF polymer coatings are 30.77 mg/g and 14.03 mg/g, respectively. The limiting values of Cd(II) ions adsorption by the surface of SRF polymer coatings (Type 2) of Brands A and B are lower (47.85 mg/g and 22.02 mg/g, respectively) compared to the worse-washed samples (Type 1). A similar picture is observed for the adsorption of Pb(II) ions on the surface of SRF polymer coatings Brand A 6M and Brand B 5–6M (type 2), which is 25.22 mg/g and 10.55 mg/g, respectively.

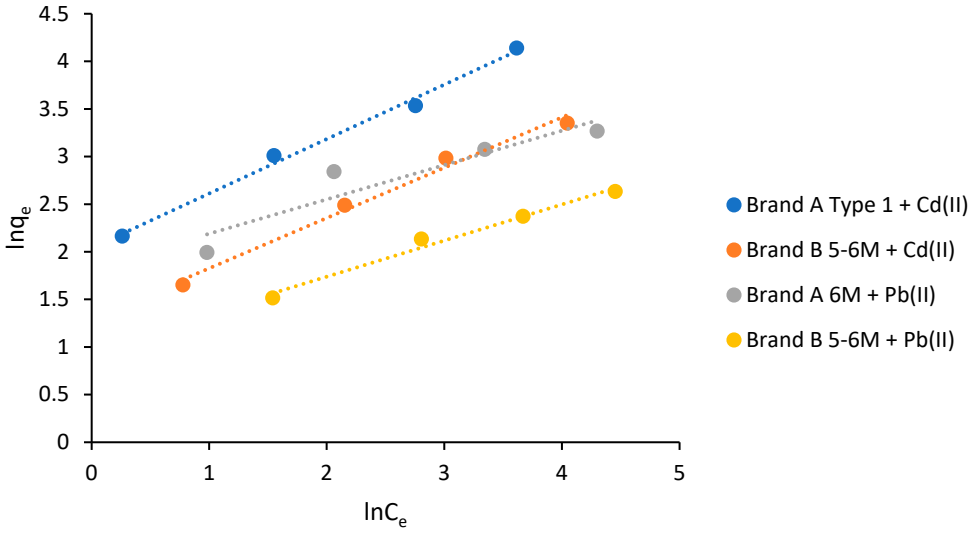


Figure 10. Adsorption isotherms of Cd(II) and Pb(II) ions by the surface of Type 1 polymer coatings of mineral fertiliser granules of Brand B 5–6M SRF in linear coordinates of the Freundlich (b) adsorption theory equations.

Table 2. Constants in the equations of the Langmuir and Freundlich adsorption theories describing the adsorption of Cd(II) ions by the surface of Type 1 and Type 2 polymers coatings of Brand A and Brand B SRF.

Type of SRF/CRF	Langmuir Equation		Freundlich Equation	
	q_{max}, mg/g	K_L, L/mg	K_F, mg/g*(L/mg)$^{1/n}$	1/n
Brand A 6M (Type 1)	54.64	0.14	7.71	0.57
Brand A 6M (Type 2)	47.85	0.15	7.14	0.53
Brand B 5–6M (Type 1)	28.90	0.10	3.67	0.53
Brand B 5–6M (Type 2)	22.02	0.11	2.54	0.50

Table 3. Constants in the equations of the Langmuir and Freundlich adsorption theories describing the adsorption of Pb(II) ions by the surface of Type 1 and Type 2 polymers coatings of Brand A 6M and Brand B 5–6M SRF.

Type of SRF/CRF	Langmuir Equation		Freundlich Equation	
	q_{max}, mg/g	K_L, L/mg	K_F, mg/g*(L/mg)$^{1/n}$	1/n
Brand A 6M (Type 1)	30.77	0.12	6.23	0.36
Brand A 6M (Type 2)	25.22	0.13	5.75	0.34
Brand B 5–6M (Type 1)	14.03	0.10	2.98	0.34
Brand B 5–6M (Type 2)	10.55	0.12	2.81	0.31

4. Discussion

In this study, we found that the polymer coatings of two slow-released fertilisers analysed are based on a polyethylene–polyacrylic acid copolymer (Brand A SRF granules) and polyacrylamide, polyacrylic acid, and its esters (Brand B SRF).

Polyethylene is an inert hydrophobic material consisting of long carbon chains, which makes it rather stable for biodegradation in natural conditions. High hydrophobicity and a small specific smooth surface prevent the formation of biofilms by polymer-degrading microorganisms. In addition, the catalytic properties of enzymes secreted by microorganisms are incompatible with the inert, hydrophobic surface of polyethylene. The resistance to

biodegradation of polyethylene decreases as a result of photodegradation and/or chemical degradation, as well as when it is modified with starch and pro-oxidant additives. All polyethylene films and coatings may contain a stabiliser that prevents oxidation. Attempts to add pro-oxidants (i.e., stearates of transition metals such as iron, manganese, titanium, and cobalt) in polymer coatings promote radical reactions and cleavage of the polymer chain, making it more accessible for biodegradation under certain conditions by some Gram-negative and Gram-positive bacterial species, belonging to the genera Pseudomonas, Ralstonia, Stenotrophomonas, Klebsiella, Acinetobactor, Rhodococcus, Staphylococcus, Streptococcus, Streptomyces, Bacillus, etc. [46,47]. Polyacrylic acid, polyacrylates, polyacrylamide, and polyacrylonitrile are the most widely used substances for the manufacture of SRF polymer coatings based on acrylic polymers in the coating of Brand B SRF. When assessing the biodegradability of acrylic polymers, it is necessary to take into account the polymer structure (hydrocarbon chain length, presence of side functional groups, presence of quaternary carbon atoms, and spatial molecular organisation) and the ability of microorganisms to form biofilms on the surface of acrylic polymers under natural conditions. Some species of microorganisms are capable of biodegrading certain types of acrylic polymers. The biodegradation process of acrylic polymers proceeds in two stages. At the first stage, side groups—amide, nitrile, or alkyl—are detached from the hydrocarbon chain under the action of hydrolytic enzymes and linked by ester bonds. To describe the second stage of hydrocarbon chain biodegradation, several pathways have been proposed: an aerobic pathway of biodegradation based on propionic acid metabolism carried out by cell-free extracts of Propionibacterium shermanii and an anaerobic pathway of hydrocarbon chain biodegradation under the action of amidases and other enzymes. Although some microorganisms are able to degrade acrylate monomers, biodegradation of acrylic polymers is inefficient, especially at high concentrations [14,19–22,48].

The data obtained in our research confirm earlier results [48–50], which showed that polymer coatings based on synthetic non-biodegradable polymers are often used for SRF/CRF industrial production. Moreover, these polymer coatings will be subjected to gradual degradation and fragmentation generating microplastics that may adsorb different hazardous substances [39,40,50].

The analysis of XRD diffractograms has shown the presence on the fertiliser polymer shells surface of compounds highly insoluble in water that are part of SRF mineral fillers: sodium dihydrophosphate, sodium hydrophosphate, and calcium hydrophosphate on the surface of polymer shells of fertiliser grade A, and sodium dihydrophosphate, potassium nitrate, and ammonium nitrate on the surface of polymer shells of fertiliser grade B. With these compounds, manufacturers ensure the macronutrient composition of fertilisers and regulate the rate of nutrient release (calcium hydrophosphate). The presence of inorganic compounds (e.g., calcium and sodium hydro/dihydrophosphates) on the surface of nonpolar polymer shells can lead to immobilisation of metal ions and other contaminants from the soil solution [51]. Thus, when using SRF, mineral fertiliser particles may remain on the inner surface of the polymer coating shell, as confirmed by XRD analysis of the mineral filler remaining on the surface of the Brand A and Brand B SRF polymer coating shells after washing with distilled water. These mineral particles remaining on the surface of the polymer coatings can act as additional active centres for the adsorption of pollutants.

The results of Cd(II) and Pb(II) ions adsorption by the surface of the polymer coating shells of Brand A 6M and Brand B 5–6M SRF are similar to the conclusions obtained previously [52,53], confirming that the Langmuir and Freundlich adsorption theories are able to describe the adsorption of these ions on polymers, and demonstrating that the Langmuir adsorption theory fits better the experimental results than the Freundlich one (Tables 4 and 5). The differences observed in the adsorption limits (q_{max}) can be explained by

differences in the polymers in Brand A and Brand B SRF versus polyethylene in [52,54,55], with different surface properties and particle sizes considered.

Table 4. Adsorption parameters of Cd(II) ions by polymer coatings.

Adsorption Theory	Parameters	Brand A (Type 1)	Brand A (Type 2)	Brand B (Type 1)	Brand B (Type 2)
Langmuir	q_{max}, mg/g	54.64	47.85	28.90	22.02
	K_L, L/mg	0.14	0.15	0.10	0.11
	R^2	0.9907	0.9931	0.9931	0.9956
Freundlich	K_F, mg/g*(L/mg)$^{1/n}$	7.71	7.14	3.67	2.54
	1/n	0.57	0.53	0.53	0.50
	R^2	0.9899	0.9868	0.9865	0.9884

The low K_L value for the adsorption of Cd(II) and Pb(II) ions by the surface of the polymer coatings of Brand A 6M and Brand B 5–6M SRF enables us to conclude that the affinity of adsorbent to adsorbent is rather low. The value of $1/n < 1$ leads to the conclusion that the interaction of adsorbent ions with each other is weaker than the interaction of the adsorbent with the adsorbate.

Table 5. Adsorption parameters of Pb(II) ions by polymer coatings.

Adsorption Theory	Parameters	Brand A (Type 1)	Brand A (Type 2)	Brand B (Type 1)	Brand B (Type 2)
Langmuir	q_{max}, mg/g	30.77	25.22	14.03	10.55
	K_L, L/mg	0.12	0.13	0.10	0.12
	R^2	0.9836	0.9895	0.9922	0.9943
Freundlich	K_F, mg/g*(L/mg)$^{1/n}$	6.23	5.75	2.98	2.81
	1/n	0.36	0.34	0.34	0.31
	R^2	0.8705	0.9783	0.9828	0.8872

The results of the study indicate that polymer coatings of slow-released fertilisers can generate microplastics that can adsorb and accumulate Cd(II) and Pb(II) ions in soil, which can have a negative impact on plants and soil biota. This agrees with earlier studies on the MP effect on the adsorption and desorption of Cd(II) ions in agricultural soils [56,57]. When MPs occur in agricultural fields, the ability of the soil to retain Cd(II) ions decreases, and the mobility of Cd(II) ions in the soil increases. As a result, such microplastics become more toxic to plants and soil biota, with an increase in the probability of the accumulation of Cd(II) ions by agricultural crops and their release into groundwater [57]. The accumulation of heavy metals is enhanced by the presence of inorganic residues in the microplastics produced by the fertiliser coatings [44,45].

There is no doubt that the use of plastics in agriculture has produced relevant benefits by increasing crop yield and quality as well as the efficiency of soil use. Moreover, plastics have also a relevant role in the safety of the food chain. Therefore, plastics will continue their contribution to feed the world population continuously increasing. On the other hand, we should continue our efforts to understand and control plastic pollution, and, in particular, the effects of microplastics in the environment.

5. Conclusions

According to the results obtained, we can conclude that the widely used Brand A and Brand B SRF/CRFs contain non-biodegradable polymers in the coating shell, such

as the co-polymers polyethylene–polyacrylic acid, polyacrylamide, polyacrylic acid, and its esters (acrylates). It should be noted that even if the production and further use of such fertilisers are reduced, their widespread previous use leads to the appearance of microplastics in the soil. These polymers not only remain in the soil for a long time due to their non-biodegradability, but also serve as significant adsorbents of various pollutants, for example, heavy metals. Moreover, fertiliser residues on polymer coatings increase the adsorption of heavy metal ions. As a result, the solution to the problem of improving the efficiency of agricultural production through the use of fertilisers with a slow or controlled release of nutrients leads to environmental pollution by microplastics remaining in the soil after fertiliser application.

This should be kept in mind when creating new technologies for the development and use of fertilisers with a slow or controlled release of nutrients and researching the environmental and human health hazards of microplastics, taking in mind that the final decision about microplastics danger is still open. We plan to continue and extend our studies to other products using polymers for the controlled release of substances in soils, their effects on microplastics pollution, and on the adsorption of other metallic and organic pollutants. Moreover, the long-term behaviour of microplastics in the soil, including degradation, will be also addressed in our future work.

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References

1. Bodirsky, B.L.; Popp, A.; Lotze-Campen, H.; Dietrich, J.P.; Rolinski, S.; Weindl, I.; Schmitz, C.; Müller, C.; Bonsch, M.; Humpenöder, F.; et al. Reactive nitrogen requirements to feed the world in 2050 and potential to mitigate nitrogen pollution. *Nat. Commun.* **2014**, *5*, 3858. [CrossRef]
2. Negi, P.; Thakur, R.; Manral, K.; Tomar, K.; Rawat, B.S.; Ramola, B.; Ahmad, W. Coated Controlled-Release Fertilizers: Potential Solution for Sustainable Agriculture. *Nat. Environ. Pollut. Technol.* **2022**, *21*, 1739–1745. [CrossRef]
3. Xu, P.; Li, G.; Zheng, Y.; Fung, J.C.H.; Chen, A.; Zeng, Z.; Shen, H.; Hu, M.; Mao, J.; Zheng, Y.; et al. Fertilizer management for global ammonia emission reduction. *Nature* **2024**, *626*, 792–798. [CrossRef]
4. Lawrencia, D.; Wong, S.K.; Low, D.Y.S.; Goh, B.H.; Goh, J.K.; Ruktanonchai, U.R.; Soottitantawat, A.; Lee, L.H.; Tang, S.Y. Controlled release fertilizers: A review on coating materials and mechanism of release. *Plants* **2021**, *10*, 238. [CrossRef]
5. Vejan, P.; Khadiran, T.; Abdullah, R.; Ahmad, N. Controlled release fertilizer: A review on developments, applications and potential in agriculture. *J. Control. Release* **2021**, *339*, 321–334. [CrossRef]
6. Zahir, S.; Ahmad, W.; Hira, K.; Ullah, B.; Khan, A.; Khan, F.A.; Naz, R.M.M. Role of Nitrogen Fertilizer in Crop Productivity and Environmental Pollution. *Int. J. Agric. Forest.* **2014**, *4*, 201–206.
7. Wesołowska, M.; Rymarczyk, J.; Góra, R.; Baranowski, P.; Sławiński, C.; Klimczyk, M.; Supryn, G.; Schimmelpfennig, L. New slow-release fertilizers—Economic, legal and practical aspects: A Review. *Int. Agrophys.* **2021**, *35*, 11–24. [CrossRef] [PubMed]
8. Weithmann, N.; Möller, J.N.; Löder, M.G.J.; Piehl, S.; Laforsch, C.; Freitag, R. Organic fertilizer as a vehicle for the entry of microplastic into the environment. *Sci. Adv.* **2018**, *4*, eaap8060. [CrossRef]
9. Nooeaid, P.; Chuysinuan, P.; Pitakdantham, W.; Aryuwananon, D.; Techasakul, S.; Dechtrirat, D. Eco-Friendly Polyvinyl Alcohol/Polylactic Acid Core/Shell Structured Fibers as Controlled-Release Fertilizers for Sustainable Agriculture. *J. Polym. Environ.* **2021**, *29*, 552–564. [CrossRef]

10. Jariwala, H.; Santos, R.M.D.; Lauzon, J.D.; Dutta, A.; Chiang, Y.W. Controlled release fertilizers (CRFs) for climate-smart agriculture practices: A comprehensive review on release mechanism, materials, methods of preparation, and effect on environmental parameters. *Environ. Sci. Pollut. Res.* **2022**, *29*, 53967–53995. [CrossRef] [PubMed]
11. Rajan, M.; Shahena, S.; Chandran, V.; Mathew, L. Controlled release of fertilizers -concept, reality, and mechanism. In *Controlled Release Fertilizers for Sustainable Agriculture*; Academic Press: Cambridge, MA, USA, 2021; pp. 41–56.
12. Adams, C.; Frantz, J.; Bugbee, B. Macro- and micronutrient-release characteristics of three polymer-coated fertilizers: Theory and measurements. *J. Plant Nutr. Soil Sci.* **2013**, *176*, 76–88. [CrossRef]
13. Shaviv, A. Advances in controlled-release fertilizers. *Adv. Agron.* **2001**, *71*, 1–49.
14. Shah, A.A.; Hasan, F.; Hameed, A.; Ahmed, S. Biological degradation of plastics: A comprehensive review. *Biotechnol. Adv.* **2008**, *26*, 246–265. [CrossRef] [PubMed]
15. Alshehrei, F. Biodegradation of Synthetic and Natural Plastic by Microorganisms. *J. Appl. Environ. Microbiol.* **2017**, *5*, 8–19.
16. Hazra, G. A Review on Controlled Release Advanced Glassy Fertilizer. *Global J. Sci. Front. Res.* **2014**, *14*, 25–36.
17. Purnomo, C.W.; Saputra, H. Manufacturing of slow and controlled release fertilizer. In *Controlled Release Fertilizers for Sustainable Agriculture*; Lewu, F.B., Volova, T., Thomas, S., Rakhimol, R.K., Eds.; Academic Press: Cambridge, MA, USA, 2021; pp. 95–110.
18. Beig, B.; Niazi, M.B.K.; Jahan, Z.; Hussain, A.; Zia, M.H.; Mehran, M.T. Coating materials for slow release of nitrogen from urea fertilizer: A review. *J. Plant Nutr.* **2020**, *43*, 1510–1533. [CrossRef]
19. Dong, L.; Du, C.; Ma, F.; Shen, Y.; Ke, W.; Jianmin, Z. Interaction between polyacrylate coatings used in controlled-release fertilizers and soils in wheat-rice rotation fields. *Agric. Ecosyst. Environ.* **2019**, *286*, 106650.
20. Gaytán, I.; Burelo, M.; Loza-Tavera, H. Current status on the biodegradability of acrylic polymers: Microorganisms, enzymes and metabolic pathways involved. *Appl. Microbiol. Biotechnol.* **2021**, *105*, 991–1006. [CrossRef] [PubMed]
21. Lian, J.; Liu, W.; Meng, L.; Wu, J.; Zeb, A.; Cheng, L.; Lian, Y.; Sun, H. Effects of microplastics derived from polymer-coated fertilizer on maize growth, rhizosphere, and soil properties. *J. Clean. Prod.* **2021**, *318*, 128571. [CrossRef]
22. Steinmetz, Z.; Wollmann, C.; Schaefer, M.; Buchmann, C.; David, J.; Tröger, J.; Muñoz, K.; Frör, O.; Schaumann, G.E. Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation? *Sci. Total Environ.* **2016**, *550*, 690–705. [CrossRef] [PubMed]
23. Hofmann, T.; Ghoshal, S.; Tufenkji, N.; Adamowski, J.F.; Bayen, S.; Chen, Q.; Demokritou, P.; Flury, M.; Hüffer, T.; Ivleva, N.P.; et al. Plastics can be used more sustainably in agriculture. *Commun. Earth Environ.* **2023**, *4*, 332. [CrossRef]
24. Geyer, R.; Jambeck, J.R.; Law, K.L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017**, *3*, e1700782. [CrossRef]
25. Van-der Veen, I.; Van Mourik, L.M.; Van-Velzen, M.J.M.; Groenewoud, Q.R.; Leslie, H.A. Plastic Particles in Livestock Feed, Milk, Meat and Blood. *Environ. Health* **2022**. Available online: https://www.plasticsoupfoundation.org (accessed on 1 December 2024).
26. Boots, B.; Russell, C.W.; Green, D.S. Effects of Microplastics in Soil Ecosystems: Above and Below Ground. *Environ. Sci. Technol.* **2019**, *53*, 11496–11506. [CrossRef] [PubMed]
27. Mongil-Manso, J.; Jiménez-Ballesta, R.; Trujillo-González, J.M.; San José Wery, A.; Díez Méndez, A. A Comprehensive Review of Plastics in Agricultural Soils: A Case Study of Castilla y León (Spain) Farmlands. *Land* **2023**, *12*, 1888. [CrossRef]
28. Horton, A.A.; Walton, A.; Spurgeon, D.J.; Lahive, E.; Svendsen, C. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. *Sci. Total Environ.* **2017**, *586*, 127–141. [CrossRef] [PubMed]
29. Naqash, N.; Prakash, S.; Kapoor, D.; Singh, R. Interaction of freshwater microplastics with biota and heavy metals: A review. *Environ. Chem. Lett.* **2020**, *18*, 1813–1824. [CrossRef]
30. Brian, J. *Alloway, Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*; Springer: Dordrecht, The Netherlands; Berlin/Heidelberg, Germany; New York, NY, USA; London, UK, 2013.
31. Sazykin, I.; Khmelevtsova, L.; Azholgina, T.; Sazykina, M. Heavy Metals Influence on the Bacterial Community of Soils: A Review. *Agriculture* **2023**, *13*, 653. [CrossRef]
32. Li, Y.; Liu, J.; Wang, Y.; Tang, X.; Xu, J.; Liu, X. Contribution of components in natural soil to Cd and Pb competitive adsorption: Semi-quantitative to quantitative analysis. *J. Hazard. Mater.* **2023**, *441*, 129883. [CrossRef]
33. Dang, V.M.; Van, H.T.; Vinh, N.D.; Duong, T.M.H.; Nguyen, T.B.H.; Nguyen, T.T.; Tran, T.N.H.; Hoang, T.H.; Tran, T.P.; Nguyen, L.H.; et al. Enhancement of exchangeable Cd and Pb immobilization in contaminated soil using Mg/Al LDH-zeolite as an effective adsorbent. *RSC Adv.* **2021**, *11*, 17007–17019. [CrossRef]
34. Hummel, D.O.; Scholl, F. *Atlas of Polymer and Plastic Analysis. Vol. I. Polymers Structure and Spectra*; Verlag Chemie: Weinheim, Germany, 1978; Volume 416.
35. Hansen, D.L. *Sprouse Collection of Infrared Spectra, Book 1: Polymers*; Sprouse Scientific Systems: Paoli, PA, USA, 1987.
36. Kabekkodu, S.N.; Faber, J.; Fawcett, T. New Powder Diffraction File (PDF-4) in relational database format: Advantages and data-mining capabilities. *Acta Crystallogr. Sect. B Struct. Sci.* **2002**, *58*, 333–337. [CrossRef] [PubMed]

37. Rodríguez-Pacheco, R.; García, G.; Caparrós-Ríos, A.V.; Robles-Arenas, V.; García-García, C.; Millán, R.; Pérez-Sanz, A.; Acolea-Rubio, L.A. Mineralogy, Geochemistry and Environmental Hazards of Different Types of Mining Waste from a Former Mediterranean Metal Mining Area. *Land* **2023**, *12*, 499. [CrossRef]
38. Alcolea-Rubio, L.A.; Caparrós-Ríos, A.V.; Robles-Arenas, V.; García-García, C.; García, G.; Millán, R.; Pérez-Sanz, A.; Rodríguez-Pacheco, R. Environmental Implications of Saline Efflorescence Associated with Metallic Mining Waste in a Mediterranean Region. *Land* **2023**, *12*, 4. [CrossRef]
39. Wang, L.; Guo, C.; Qian, Q.; Lang, D.; Wu, R.; Abliz, S.; Wang, W.; Wang, J. Adsorption behavior of UV aged microplastics on the heavy metals Pb(II) and Cu(II) in aqueous solutions. *Chemosphere* **2023**, *313*, 137439. [CrossRef] [PubMed]
40. Zou, J.; Liu, X.; Zhang, D.; Yuan, X. Adsorption of three bivalent metals by four chemical distinct microplastics. *Chemosphere* **2020**, *248*, 126064. [CrossRef] [PubMed]
41. Isakov, V.A. Research on the Adsorption of Heavy Metal Ions from Model Solutions by Humic Acids Isolated from Sapropel. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *852*, 012039. [CrossRef]
42. Isakov, V.A.; Zykova, I.V. Study of the adsorption of heavy metal ions from binary and multi-component solutions by ceramic chips. *IOP Conf. Series Earth Environ. Sci.* **2020**, *613*, 012168.
43. Ayawei, N.; Ebelegi, A.N.; Wankasi, D. Modelling and Interpretation of Adsorption Isotherms. *J. Chem.* **2017**, *2017*, 3039817. [CrossRef]
44. Karthik, V.; Dhivya Dharshini, G.; Senthil Kumar, P.; Kiruthika, S.; Rangasamy, G.; Periyasamy, S.; Senthil Rathi, B. Ferrite-supported nanocomposite polymers for emerging organic and inorganic pollutants removal from wastewater: A review. *Ind. Eng. Chem. Res.* **2023**, *62*, 13711–13733. [CrossRef]
45. Munir, N.; Javaid, A.; Abideen, Z.; Duarte, B.; Jarar, H.; El-Keblawy, A.; Sheteiwy, M.S. The potential of zeolite nanocomposites in removing microplastics, ammonia, and trace metals from wastewater and their role in phytoremediation. *Environ. Sci. Pollut. Res.* **2024**, *31*, 1695–1718. [CrossRef]
46. Ghatge, S.; Yang, Y.; Ahn, J.-H.; Hur, H.-G. Biodegradation of polyethylene: A brief review. *Appl. Biol. Chem.* **2020**, *63*, 27. [CrossRef]
47. Bombelli, P.; Howe, C.J.; Bertocchini, F. Polyethylene bio-degradation by caterpillars of the wax moth Galleria mellonella. *Curr. Biol.* **2017**, *27*, 292–293. [CrossRef] [PubMed]
48. Adegbola, T.A.; Agboola, O.; Fayomi, O.S.I. Review of polyacrylonitrile blends and application in manufacturing technology: Recycling and environmental impact. *Res. Eng.* **2020**, *7*, 100144. [CrossRef]
49. Tian, H.; Liu, Z.; Zhang, M.; Guo, Y.; Zheng, L.; Li, Y.C. Biobased polyurethane, epoxy resin, and polyolefin wax composite coating for controlled-release fertilizer. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5380–5392. [CrossRef]
50. Li, T.; Lu, S.; Yan, J.; Bai, X.; Gao, C.; Liu, M. An environment-friendly fertilizer prepared by layer-by-layer self-assembly for pH-responsive nutrient release. *ACS Appl. Mater. Interfaces* **2019**, *11*, 10941–10950. [CrossRef] [PubMed]
51. Sugiyama, S.; Ichii, T.; Fujisawa, M.; Kawashiro, K.; Tomida, T.; Shigemoto, N.; Hayashi, H. Heavy metal immobilization in aqueous solution using calcium phosphate and calcium hydrogen phosphates. *J. Colloid Interface Sci.* **2003**, *259*, 408–410. [CrossRef]
52. Wang, F.; Yang, W.; Cheng, P.; Zhang, S.; Jiao, W.; Sun, Y. Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere* **2019**, *235*, 1073–1080. [CrossRef] [PubMed]
53. Wang, T.; Yu, C.; Chu, Q.; Wang, F.; Lan, T.; Wang, J. Adsorption behavior and mechanism of five pesticides on microplastics from agricultural polyethylene films. *Chemosphere* **2020**, *244*, 125491. [CrossRef]
54. Holmes, L.A.; Turner, A.; Thopson, R.C. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* **2012**, *160*, 42–48. [CrossRef] [PubMed]
55. Nguyen, T.-B.; Ho, T.-B.-C.; Huang, C.P.; Chen, C.-W.; Chen, W.-H.; Chen, W.-H.; Hsieh, S.; Hsieh, S.-L.; Dong, C.-D. Adsorption of lead(II) onto PE microplastics as a function of particle size: Influencing factors and adsorption mechanism. *Chemosphere* **2022**, *304*, 135276. [CrossRef] [PubMed]
56. Zhang, S.; Han, B.; Sun, Y.; Wang, F. Microplastics influence the adsorption and desorption characteristics of Cd in an agricultural soil. *J. Hazard. Mater.* **2020**, *388*, 121775. [CrossRef]
57. Wang, M.; Jiang, X.; Wei, Z.; Wang, L.; Song, J.; Cen, P. Enhanced cadmium adsorption dynamics in water and soil by polystyrene microplastics and biochar. *Nanomaterials* **2024**, *14*, 1067. [CrossRef]