Environmental Chemistry Letters (2022) 20:2235–2242
https://doi.org/10.1007/s10311-022-01433-w

ORIGINAL PAPER

Exposure of microplastics to organic matter in waters enhances microplastic encapsulation into calcium carbonate

Nives Matijaković Mlinarić[1] · Atiđa Selmani[2] · Antun Lovro Brkić[3] · Branka Njegić Džakula[1] · Damir Kralj[1] · Jasminka Kontrec[1]

Received: 25 November 2021 / Accepted: 8 March 2022 / Published online: 14 April 2022

Abstract

Plastic pollution in water ecosystems is threatening the survival of wildlife. In particular, microplastics may be encapsulated into calcium carbonate, a crucial building block of hard tissue in many species such as molluscs, corals, phytoplankton, sponges, echinoderms, and crustaceans. Actually little is known on the effect of humic acids, a common component of dissolved organic matter, on the encapsulation of microplastic into calcium carbonate. Here, we precipitated calcium carbonate with humic acids and polystyrene microspheres. The precipitation process was followed by measuring pH during the reaction. Composition, structure, morphology, surface properties and microspheres encapsulation extent were analysed by infrared spectroscopy, X-ray powder diffraction, atomic force microscopy, scanning electron microscopy, total organic carbon analysis, thermogravimetric analysis, nuclear magnetic resonance spectroscopy, electrophoretic and dynamic light scattering. Results show, for the first time, that encapsulation of polystyrene microspheres into calcite crystals occurs only after the treatment of the microspheres with humic acids, leading to encapsulation of about 5% of the initial microspheres mass. On the contrary, untreated microspheres did not encapsulate in calcium carbonate. Our findings imply that exposure of microplastics to dissolved organic matter in water ecosystems could result in enhanced encapsulation into the exoskeleton and endoskeleton of aquatic organisms.

Keywords Microplastic · Polystyrene · Humic acid · Calcium carbonate precipitation · Biomineralisation

Introduction

Calcium carbonate is the most relevant mineral in exoskeletal and endoskeletal formations in species inhabited in different ecosystems, ranging from land to freshwaters, seas, and oceans. In water ecosystems, calcium carbonate is most known as a mineral forming shells in molluscs and skeleton in corals, but it can also be found in phytoplankton, Protista, sponges, echinoderms, and crustaceans. In these organisms, the mineralised tissues are most commonly built of calcite, the most stable modification of calcium carbonate or aragonite, while vaterite is rarely found (Mann 2001).

Organisms inhabiting water ecosystems are exposed to human influence and different forms of pollution, among which plastic pollution plays a significant role. A wide range of marine organisms incidentally takes up microplastics with food from sediment or the water column. Many marine organisms accumulate microplastics, mainly in the gut (Pirsaheb et al. 2020) and in stomachs and gills (Białowąs et al. 2022). The presence/accumulation of microplastic in marine organisms can cause coral tissue necrosis and microplastics overgrowth (Reichert et al. 2022), alteration of intestinal function and disordered metabolism (Feng et al. 2021) and retarded growth (Prata et al. 2021). Also, microplastic particles can be digested by smaller organisms like corals, sponges, and even foraminifera (Guzzetti et al. 2018).

✉ Nives Matijaković Mlinarić
nives.matijakovic@irb.hr

✉ Jasminka Kontrec
jasminka.kontrec@irb.hr

[1] Laboratory for Precipitation Processes, Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

[2] Institute of Pharmaceutical Sciences, Pharmaceutical Technology and Biopharmacy, University of Graz, Universitatsplatz 1, 8010 Graz, Austria

[3] Institute of Physics, Bijenička cesta 46, 10000 Zagreb, Croatia

Each year 8 million tons of plastic waste is disposed of into water ecosystems and causes the death of whales, birds, turtles and fish (Häder et al. 2020). The primary microplastic occurs from consumer products, and secondary microplastic occurs from plastic deterioration (John et al. 2021; Othman et al. 2021). This problem is becoming more pronounced, especially since, in the pandemic time, the increase in plastic production and plastic waste is noticeable, and it presents a considerable threat to environmental sustainability (Gorrasi et al. 2021). The problem of microplastic simultaneously involves economic, social and technological aspects. Solutions for a sustainable and circular economy require radical innovations, consumer education and political willingness.

Only a few studies reported the effect of plastic particles on the precipitation of calcium carbonate. It was found that poly(methyl methacrylate) nano- and microparticles induced calcite crystal nucleation from the solution (Mahadevan et al. 2021). Their results showed the presence of plastic particles on the surface of the crystals. Kim et al. showed that polystyrene particles functionalised with acrylic and fumaric acid get encapsulated in the calcite crystals during crystal growth (Kim et al. 2010). In contrast, nonfunctionalised polystyrene did not cause the same effect. Also, they showed that obtained crystals expressed decreased stiffness and hardness compared with the Icelandic spar calcite and the sea urchin spine.

In 2021, researchers found microplastic encapsulated into the calcite shell of foraminifera and also in the aragonite skeleton of corals (Birarda et al. 2021; Hierl et al. 2021; Reichert et al. 2022). Interestingly, older findings showed that microplastic was not encapsulated in the mineralised tissues of water organisms (Hankins et al. 2018; Chapron et al. 2018). This raises a question, what if the possible change of the microplastic characteristics in the last couple of years is the reason for encapsulation of microplastic into growing calcium carbonate mineralised tissues, leading us to speculate that with time the situation will only get worse.

In freshwaters, seas, and oceans, dissolved organic matter is ubiquitous, and among others, it consists of humic substances, which unavoidably interacts with microplastic (Chen et al. 2018a). Organic matter is adsorbed on the surface, which leads to increased transport to the sediment, where organisms producing calcium carbonate can be found (Kniggendorf et al. 2021). Different polymers are present in microplastic, and among others, one of the most predominant is polystyrene (John et al. 2021). It was shown that the environmental behaviour of polystyrene microplastic changes after adsorption of reactive fractions of dissolved organic matter (humic and fulvic acid) (Abdurahman et al. 2020). Numerous articles have been published previously regarding the interaction of humic acid and pure polystyrene materials, and it is optimal to use it as a model for plastic pollution (Cai et al. 2018; Lu et al. 2018; Singh et al. 2019).

This study investigates the difference between the encapsulation of fresh microplastic particles and those exposed to the dissolved organic matter, into calcium carbonate. Polystyrene microspheres served as model plastic particles to estimate the behaviour of microplastics in the environment and humic acid as the reactive fraction of dissolved organic matter. It was hypothesised that the microplastic encapsulation into calcium carbonate could enhance due to inevitable organic matter adsorption onto microplastic. We used batch laboratory precipitation experiments and calcium carbonate systems to verify this hypothesis. Any obtained change may indicate a significant alteration in biomineralisation processes and consequently changes in exoskeleton formation in numerous species.

Experimental

Analytical grade chemicals sodium carbonate (Na_2CO_3) (Sigma Aldrich), calcium chloride ($CaCl_2 \cdot 2H_2O$) (Acros Organics), polystyrene microspheres (size 1.6 ± 0.2 μm, Tianjin Baseline Chromtech Research Centre), humic acid (Sigma-Aldrich) and deionised water (conductivity < 0.055 μS cm^{-1}) were used. The calcium carbonate precipitation experiments were performed using initial reactant concentrations, $c(CaCl_2)=c(Na_2CO_3)=2.5$ mmol dm^{-3}. The following systems were investigated: reference (without polystyrene microspheres or humic acid) and with the addition of 1 mg dm^{-3} of humic acid or 20 mg dm^{-3} untreated/humic acid treated polystyrene microspheres. The composition of the precipitated samples has been determined by Fourier transform infrared spectroscopy on TENSOR II (Bruker) and X-ray powder diffraction analysis on EMPYREAN (Panalytical). The morphology of the samples was determined by JEOL JSM-7000F (Jeol Ltd.) without coating. The size and electrokinetic potential of samples were measured on Litesizer 500 (Anton Paar).

The humic acid treated polystyrene microspheres were prepared by rotating 8 mg of microspheres in 300 μL of humic acid solution (4000 mg dm^{-3}) for 10 min. Untreated and humic acid treated polystyrene microspheres have been analysed with ^{1}H and ^{13}C-DEPTq nuclear magnetic resonance spectra in deuterated chloroform on a Bruker Avance III HD 400 MHz spectrometer. The microsphere surface characteristics were determined by atomic force microscopy imaging in the AC mode using the NanoWizard 4 ULTRA AFM (Bruker). The analysis of the amount of encapsulated microspheres (as total dissolved organic carbon) was determined by TOC-Analyser (Elementar) and thermogravimetric analysis on the STA 449 F5 Jupiter (Netzsch). The amount of encapsulated microspheres was determined in the samples after treatment with chloroform. All experimental procedures and analyses are described in more detail in the Supplementary Information.

Results and discussion

To investigate the difference in microplastic encapsulation into calcium carbonate, due to the humic acid treatment, we performed calcium carbonate precipitation experiments with humic acid as the reactive fraction of dissolved organic matter and polystyrene microspheres as model microplastic particles. The characterisation of untreated and treated polystyrene microspheres, as well as precipitation and characterisation of calcium carbonate in the presence of untreated and treated polystyrene microspheres, was studied.

Characterisation of polystyrene microspheres

We performed atomic force microscopy imaging to study differences in surface morphology of untreated and treated microspheres. A large-scale image of the untreated polystyrene microsphere is shown in Fig. 1a. The microsphere's surface features are shown on a smaller scale (to remove the sphere's curvature) in Fig. 1b, c for untreated and treated microsphere surfaces, respectively. Analysis in Fig. 1d shows the higher root-mean-square surface roughness of the polystyrene microsphere treated with humic acid (1.40 ± 0.03 nm) than the untreated sample (0.9 ± 0.2 nm). These results clearly show that due to humic acid adsorption, the humic acid treated microspheres have a higher surface roughness and distinct high features not found on the untreated samples.

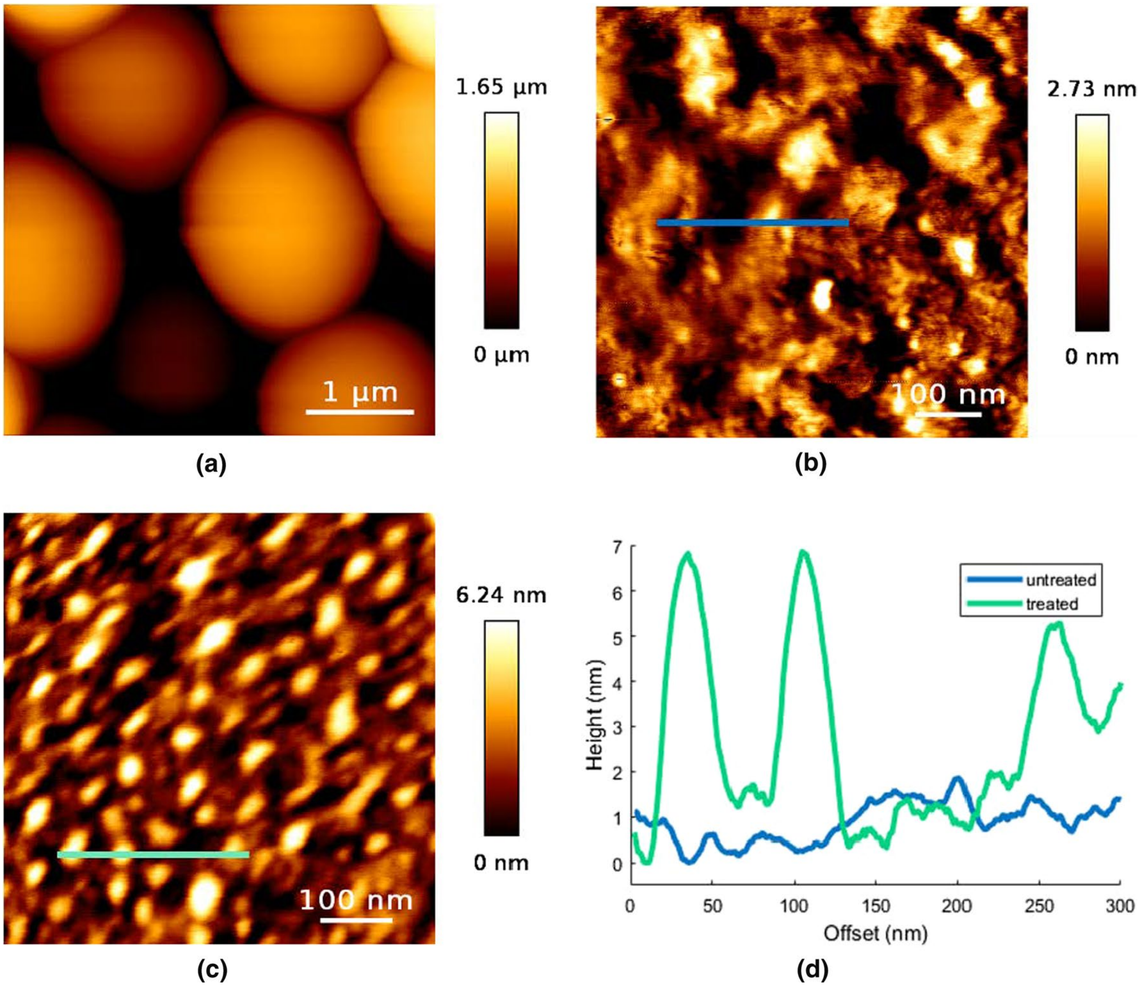

Fig. 1 Atomic force microscopy measurement of polystyrene microspheres. Large-scale topography of untreated microspheres (**a**). Topography image of surface features on a smaller scale: untreated (**b**) treated microsphere (**c**). Profiles of untreated and treated polystyrene surfaces (**d**) (indicated with blue and green lines in (**b**, **c**). Note the higher surface roughness of the humic acid treated microsphere compared to the untreated one. Adsorbed humic acid molecules in the treated microspheres cause the increase in polystyrene microspheres' surface roughness

Moreover, dynamic light scattering showed that the size of the untreated microspheres was 1.63 ± 0.17 µm and for humic acid treated it was 1.84 ± 0.03 µm. The literature shows that particle size increases due to humic acid coating on the polystyrene microspheres (Chen et al. 2018b). The microspheres were coated with humic acid molecules with a layer of an approximate thickness of 0.10 µm, which increased the overall particle size. Both atomic force microscopy and dynamic light scattering have shown that after the treatment with humic acid, the surface of polystyrene microspheres is altered, which can be expected to occur in natural water ecosystems. Calcium carbonate precipitation experiments with polystyrene microspheres were conducted to determine the impact of the microplastic with adsorbed organic matter on calcium carbonate crystals.

Precipitation and characterisation of calcium carbonate in the presence of polystyrene microspheres

To investigate the influence of organic matter on microplastic encapsulation into calcium carbonate, spontaneous precipitation of calcium carbonate in the presence of pure humic acid and untreated or humic acid treated microspheres was performed. Supersaturation, *S*, (definition in Supplementary Information) is the key parameter that controls precipitation. In all investigated systems, relatively high initial supersaturation ($S_c = 19$) resulted in instantaneous precipitation which can be seen as solution turbidity that appeared immediately after mixing the reactant solutions and a sudden drop of supersaturation (Fig. 2a). A change in the slope of progress curves indicates a change in crystal growth rate.

In comparison with the reference system, that is the system without pure humic acid and polystyrene microspheres (Fig. 2a, black line), lowering of the slope of the precipitation progress curve in the presence of humic acid (Fig. 2a, red line) indicates crystal growth inhibition. As was previously observed by Hoch et al., crystal growth inhibition occurred due to the adsorption of humic acid onto the surface of growing calcite crystals (Hoch et al. 2000). Therefore, the interaction of carboxyl groups contained in the humic acid and Ca^{2+} ions on the surface of the calcium carbonate crystals is expected, resulting in the inhibition of crystal growth. Contrary, Mahadevan et al. reported that micro- and nanoplastic particles induced precipitation of calcium carbonate (Mahadevan et al. 2021). Similarly, in our study, the slope of the progress curves for the precipitation in the presence of untreated (Fig. 2a, green line) or treated (Fig. 2a, blue line) polystyrene microspheres increased in comparison with the reference system indicating, in both cases, crystal growth rate enhancement.

The phase composition of samples in the reference system as well as in all other systems was determined by infrared

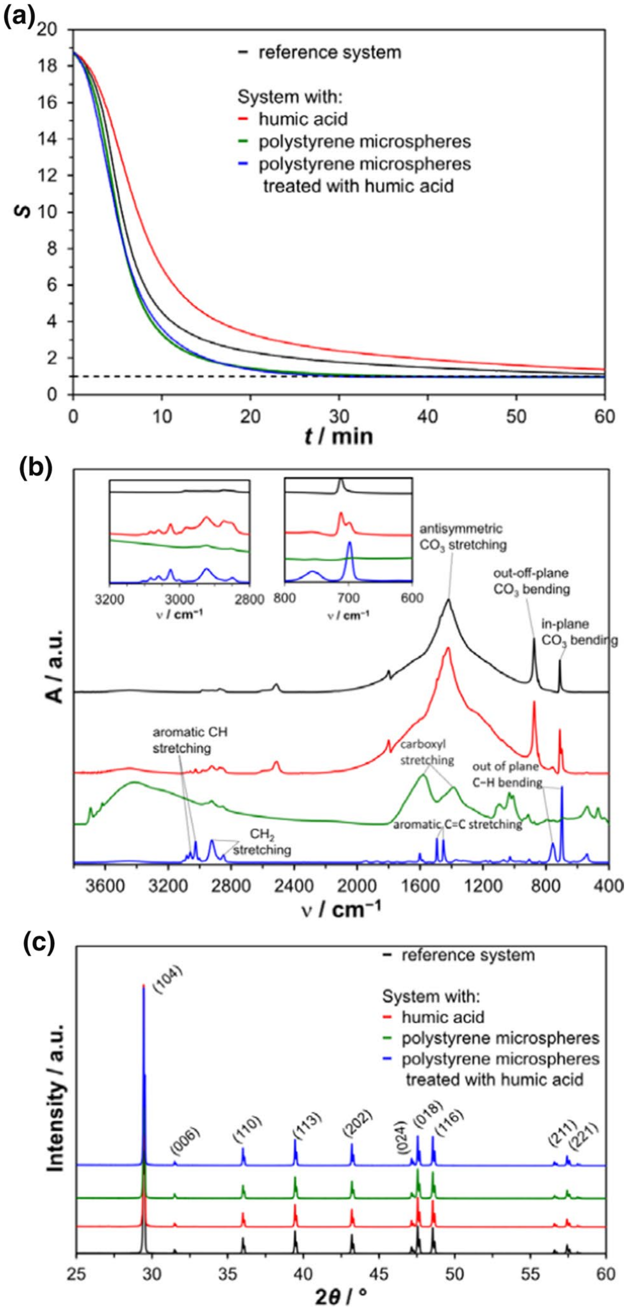

Fig. 2 (**a**) Change of solution supersaturation in time during calcium carbonate precipitation. The dashed line corresponds to the calculated value of solubility of stable calcite ($S = 1$). Change in progress curve slope indicates crystal growth rate enhancement in the presence of microspheres and inhibition in the presence of humic acid in comparison with reference systems (without humic acid or polystyrene microspheres). (**b**) Representative infrared spectra: untreated and humic acid treated microspheres (blue line), pure humic acid (green line), calcium carbonate precipitates obtained in the reference system or with humic acid (black line), calcium carbonate precipitates obtained with untreated or humic acid treated polystyrene microspheres (red line). Insets show a specific wavenumber range. Noted specific groups and bond vibrations show the most important functional groups occurring in the samples. Carbonate bond vibrations show only the presence of calcite. Comparing the pure humic acid bond vibrations and the calcite and polystyrene spectra no noticeable vibrations of adsorbed humic acid were observed due to undetectable humic acid amount. (**c**) X-ray diffractograms of calcium carbonate samples. Expressed peaks show reflections corresponding only to calcite without any other phase present

spectroscopy (Fig. 2b; Table S1) and peaks corresponding to carbonate group vibration of calcite were obtained at 1420.2 cm^{-1} (ν_3), 1073.1 cm^{-1} (ν_1), 872.9 cm^{-1} (ν_2) and 712.5 cm^{-1} (ν_4) (Andersen and Brečević 1991). In the precipitation systems with untreated and humic acid treated microspheres, peaks corresponding to pure polystyrene at 1601.8, 1493.1 and 1452.6 cm^{-1} indicated the presence of benzene rings and at 757.1 and 698.4 cm^{-1} indicated one substituent in the benzene ring (Raghu and Jeong 2008; Fang et al. 2010). The spectra of the pure humic acid showed characteristic functional stretching vibrations for OH^{-} at 3693.6 cm^{-1}, COO^{-} at 1580.3 and 1383.9 cm^{-1} and C–O–C in the 1010–1033 cm^{-1} region (Chin et al. 1994; Perminova et al. 2003). After adsorption on polystyrene microspheres, the amount of adsorbed molecules was lower than 5% which is the limit for spectral bands observation. We also performed nuclear magnetic resonance analysis of untreated and humic acid treated microspheres, and the results showed no significant difference between them. Overall, we found only calcite precipitated in all systems, and the humic acid adsorption was confirmed by surface change, as shown by atomic force microscopy.

All samples have been analysed using X-ray diffraction, and the results (Fig. 2c) are in accordance with infrared analysis and show calcite peaks at 2θ 29.4°, 35.9°, 39.4°, 43.1°, 47.5° and 48.5° corresponding to (104), (110), (113), (202), (018) and (116) reflections of calcite (JCPDS card No. 05-0586). No significant change in calcite unit cell parameters was observed, and this is in accordance with other studies about calcite composites with gold and iron oxide nanoparticles (Kulak et al. 2014; Kim et al. 2019). For a noticeable change in the crystal unit cell parameters incorporation of ions and molecules is necessary (Pokroy et al. 2006; Štajner et al. 2018). Overall, we found that microspheres do not incorporate into calcite lattice.

The study of the occlusion of polystyrene particles (carboxylated and functionalised with acrylic and fumaric acid) (Kim et al. 2010) and iron oxide nanoparticles (with adsorbed copolymers) (Kulak et al. 2014) in calcite showed that surface charge density plays a vital role in whether particle occlusion occurs within the crystals. Compared with the Icelandic spar calcite and the sea urchin spine, calcite and polystyrene particles composite structures displayed decreased indentation modulus (stiffness and hardness) (Kim et al. 2010). No occlusion within calcium carbonate was observed in the presence of nonfunctionalised polystyrene particles. Our results in the system with untreated microspheres where no encapsulation occurred confirmed this observation, indicating that interaction between the charged particles and the growing crystals is a prerequisite to their encapsulation. Overall, this confirms our hypothesis that microplastic encapsulation into calcium carbonate can be enhanced due to humic acid adsorption.

Encapsulation of polystyrene microspheres

Scanning electron microscopy images of calcium carbonate samples isolated from the reference system, and all other systems are shown in Fig. 3. The sample in the reference system consisted of typical rhombohedral calcite crystals

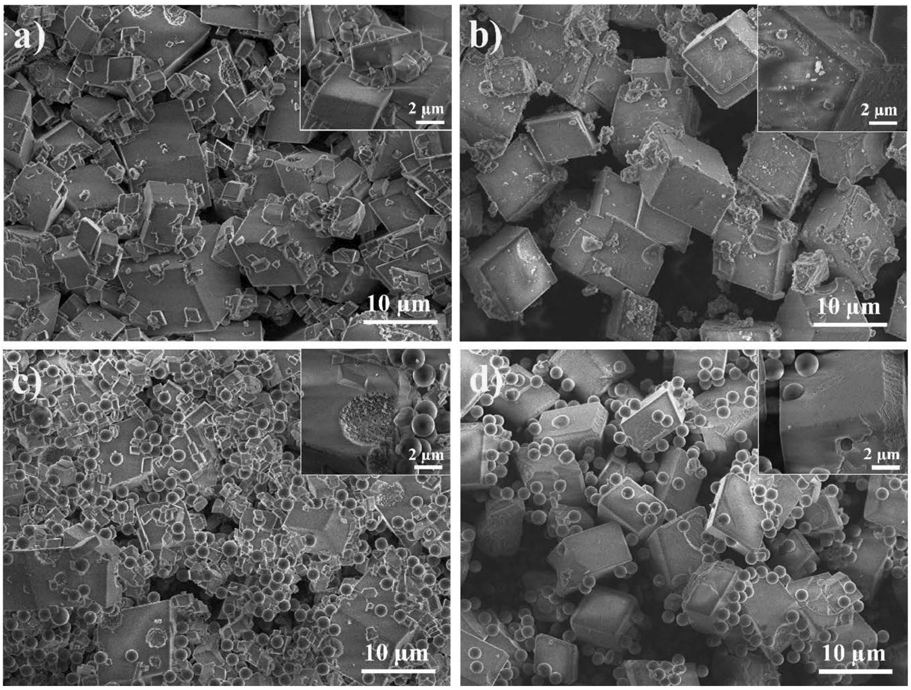

Fig. 3 Scanning electron microscopy images of calcium carbonate samples in the reference system (**a**) and the system with: humic acid (**b**), polystyrene microspheres (**c**), and treated polystyrene microspheres (**d**). Calcite crystals with rhombohedral morphology were observed in all the samples. The presence of humic acid caused the edge truncations in rhombohedral crystals. The microsphere encapsulation occurred in the sample with humic acid treated polystyrene microspheres as can be seen in the inset (**d**)

with expressed {104} faces (Fig. 3a). The addition of pure humic acid caused truncations on the edges of the rhombohedral calcite crystals alongside particles with irregular morphology (Fig. 3b). The morphology of rhombohedral calcite crystals precipitated in the presence of untreated microspheres was not dramatically affected, and the crystals had smooth and sharp edges without noticeable microsphere encapsulation (Fig. 3c).

Calcite crystals prepared with humic acid treated polystyrene microspheres showed the development of truncations on the edges of rhombohedral calcite (Fig. 3d). Compared to the sample with untreated microspheres, the treated microspheres were attracted to the growing {104} plane of rhombohedral calcite crystals. Since humic acid molecules are negatively charged (carboxylic groups) at used experimental conditions, they interact with calcium ions on the surface of calcite crystals. Similarly, it was shown that dissolved organic matter, microplastic and metal cations can aggregate and adsorb onto minerals, due to electrostatic attraction (Brewer et al. 2021; Sharma et al. 2021). The scanning electron microscopy characterisation showed that only treated microspheres get preferentially encapsulated in the growing calcium carbonate due to the humic acid adsorption on the surface of microspheres, as confirmed by the dynamic light scattering analysis and atomic force microscopy (Fig. 1).

During crystal growth, humic acid treated microspheres get adsorbed onto the growing planes of calcium carbonate. As the crystals grow, adsorbed microparticles get overgrown by newly formed layers of calcium carbonate. The number of microspheres was counted in samples in each scanning electron image using Dot Dot Goose (Ersts 2016). Total organic carbon and thermogravimetric analyses of samples obtained after washing with chloroform confirmed encapsulation into calcite crystals. In the growing calcite crystals, only humic acid treated microspheres were encapsulated in amounts 5.7 ± 2.1%, 5.68 ± 0.15% and 4.94 ± 0.9% of initial microspheres mass, as estimated from scanning electron microscopy, total organic carbon and thermogravimetric analysis, respectively.

We performed the experiments in controlled conditions (concentration, time). In contrast, the encapsulation of microplastic in natural materials is not limited, and the skeletal growth is continuous, which indicates that the amount of encapsulated microplastic could accumulate with time. Up to 2.82% of bioavailable microplastic accumulates in reef-building corals, which highlights the problem of plastic pollution (Reichert et al. 2022). Hierl et al. and Reichert et al. showed that during long-term exposure (5 months and 18 months respectively), microplastic particles did indeed get encapsulated in the coral skeletal structures. Moreover, in both studies, authors concluded that the consequences of inclusions on skeletal properties such as stability are yet unknown (Hierl et al. 2021; Reichert et al. 2022). Therefore, to determine the influence of encapsulated microspheres on the skeleton of aquatic species, more in-depth in vivo investigations are needed.

The obtained scanning electron microscopy results are in good correlation with the results of the electrokinetic potential measurements (Fig. 4). The electrokinetic potential of polystyrene microspheres was – 8.35 ± 1.09 mV, while it decreased to – 13.45 ± 1.08 mV after the microspheres' treatment with humic acid. Humic acid is rich in acidic functional groups (carboxyl and phenolic OH), which participate in the adsorption processes. As the pH increases, these groups get deprotonated. At pH greater than 4.7, humic acid is strongly negatively charged (Stevenson 1982), and its adsorption onto the polystyrene microspheres consequentially results in a higher negative charge of the polystyrene microspheres.

The electrokinetic potential of samples isolated from systems in which calcium carbonate precipitated alongside polystyrene microspheres increased compared to the electrokinetic potential of polystyrene microspheres only. In the system containing calcite crystals and untreated microspheres, the electrokinetic potential was – 5.04 ± 0.99 mV, and it further increased to – 3.44 ± 1.09 mV in the system with humic acid treated microspheres. For comparison at similar pH (pH ≈ 6), the electrokinetic potential for calcite is – 2.88 mV (Moulin and Roques 2003). Since the number of polystyrene microspheres and the solution composition was constant in each experiment, regarding calcium and carbonate ions and temperature, the most significant increase in electrokinetic potential can be attributed to more pronounced calcium carbonate encapsulation of humic acid treated

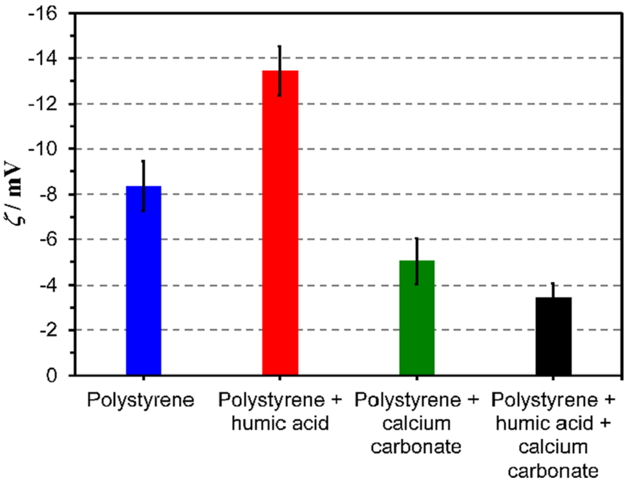

Fig. 4 Electrokinetic potential of samples in water. Polystyrene microspheres untreated and treated with humic acid and calcium carbonate with polystyrene microspheres untreated and treated with humic acid. Note the decrease in the electrokinetic potential of treated polystyrene caused by humic acid adsorption. In calcium carbonate samples, the increase in electrokinetic potential occurred due to calcium carbonate encapsulation of treated polystyrene microspheres

microspheres. Up to date, no research has investigated how the adsorbed humic acid (the reactive fraction of dissolved organic matter) influences the microplastic encapsulation into calcium carbonate. This research shows that humic acid changes the surface characteristics of the polystyrene microspheres and facilitates the encapsulation of polystyrene microspheres into growing calcite crystals. The results presented show the risk for biomineralisation processes, indicating that microplastic exposure to the dissolved organic matter could cause higher microplastic encapsulation into calcium carbonate in the next decades. This could result in the change of the skeletal structure as a result of high amounts of encapsulated microplastic particles. To develop conservation strategies and mitigate the effects of microplastic on biomineralised tissues, our future studies will focus on in vivo research in organisms producing calcium carbonate biominerals.

Conclusion

The research regarding the influence of dissolved organic matter on the microplastic encapsulation in calcium carbonate is necessary due to the recent findings showing microplastic encapsulation into the skeleton of different species. Our study shows that encapsulation of polystyrene microspheres in growing calcite crystals occurs when the microspheres are treated with humic acid leading to encapsulation of about 5% of the initial microspheres mass. On the contrary, we have shown that untreated microspheres do not encapsulate into calcium carbonate. During calcium carbonate crystal growth, humic acid treated polystyrene microspheres get adsorbed onto the growing planes of calcium carbonate. As the crystals grow, adsorbed microparticles get overgrown by newly formed layers of calcium carbonate and, at the same time, do not cause changes in crystal morphology.

The new findings raise concern regarding the influence of long-term exposure of microplastics to the dissolved organic matter in water ecosystems resulting in enhanced encapsulation into the exoskeleton and endoskeleton of species producing calcium carbonate. As this area is new, it is not yet shown in the literature how encapsulated microplastics, after exposure to dissolved organic matter, affect the skeleton of organisms and what will be the consequences of such inclusions on skeletal properties. To elucidate the influence of encapsulated microspheres on the exoskeleton and endoskeleton of species, in vivo experiments are planned as a continuation of this research.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10311-022-01433-w.

Acknowledgements A.L.B. appreciates the help from Ida Delač Marion and acknowledges the financial support from the European Regional Development Fund for the “Center of Excellence for Advanced Materials and Sensing Devices” (No. KK.01.1.1.01.0001). A.S. would like to thank Anton Paar Croatia d.o.o. Zagreb, Croatia, for providing the instrument Litesizer 500 for use and analysis. We thank Katarina Kajan for BioRender.com use for graphical abstract preparation, Giuseppe Falini for XRD discussions and Ana Čikoš for NMR discussions.

Authors' contributions All authors contributed to the study’s conception and design. Material preparation, data collection and analysis were performed by Nives Matijaković Mlinarić, Atiđa Selmani, Antun Lovro Brkić, Jasminka Kontrec and Branka Njegić Džakula. The funding was provided by Nives Matijaković Mlinarić and Damir Kralj. The first draft of the manuscript was written by Nives Matijaković Mlinarić, and all authors commented on previous versions of the manuscript.

Funding This work has been supported (N.M.M.) by the European Institute of Innovation and Technology obtained through EIT Climate-KIC Alumni ‘Participatory Grant-making’ Programme and in part (N. M., J.K., B. Nj. Dž. and D. K.) by Croatian Science Foundation under the project (IP-2013-11-5055).

Declarations

Conflict of interest All authors declare that they have no conflict of interest.

Consent for publication All authors read and approved the final manuscript.

References

Abdurahman A, Cui K, Wu J et al (2020) Adsorption of dissolved organic matter (DOM) on polystyrene microplastics in aquatic environments: kinetic, isotherm and site energy distribution analysis. Ecotoxicol Environ Saf 198:110658–110664. https://doi.org/10.1016/j.ecoenv.2020.110658

Andersen FA, Brečević L (1991) Infrared spectra of amorphous and crystalline calcium carbonate. Acta Chem Scand 45:1018–1024. https://doi.org/10.3891/acta.chem.scand.45-1018

Białowąs M, Jonko-Sobuś K, Pawlak J, et al (2022) Plastic in digestive tract and gills of cod and herring from the Baltic Sea. Sci Total Environ 822:153333. https://doi.org/10.1016/j.scitotenv.2022.153333

Birarda G, Buosi C, Caridi F et al (2021) Plastics, (bio)polymers and their apparent biogeochemical cycle: an infrared spectroscopy study on foraminifera. Environ Pollut 279:116912–116924. https://doi.org/10.1016/j.envpol.2021.116912

Brewer A, Dror I, Berkowitz B (2021) The mobility of plastic nanoparticles in aqueous and soil environments: a critical review. ACS ES&T Water 1:48–57. https://doi.org/10.1021/acsestwater.0c00130

Cai L, Hu L, Shi H, et al (2018) Effects of inorganic ions and natural organic matter on the aggregation of nanoplastics. Chemosphere 197:142–151. https://doi.org/10.1016/j.chemosphere.2018.01.052

Chapron L, Peru E, Engler A et al (2018) Macro- and microplastics affect cold-water corals growth, feeding and behaviour. Sci Rep 8:15299–15307. https://doi.org/10.1038/s41598-018-33683-6

Chen C-S, Le C, Chiu M-H, Chin W-C (2018a) The impact of nanoplastics on marine dissolved organic matter assembly. Sci Total

Environ 634:316–320. https://doi.org/10.1016/j.scitotenv.2018.03.269

Chen W, Ouyang ZY, Qian C, Yu HQ (2018b) Induced structural changes of humic acid by exposure of polystyrene microplastics: a spectroscopic insight. Environ Pollut 233:1–7. https://doi.org/10.1016/j.envpol.2017.10.027

Chin YP, Alken G, O'Loughlin E (1994) Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ Sci Technol 28:1853–1858. https://doi.org/10.1021/es00060a015

Ersts PJ (2016) [Internet] DotDotGoose (version 1.5.3). American Museum of Natural History, Center for Biodiversity and Conservation. Available from http://biodiversityinformatics.amnh.org/open_source/dotdotgoose. Accessed on [01.02.2022]

Fang J, Xuan Y, Li Q (2010) Preparation of polystyrene spheres in different particle sizes and assembly of the PS colloidal crystals. Sci China Technol Sci 53:3088–3093. https://doi.org/10.1007/s11431-010-4110-5

Feng S, Zeng Y, Cai Z et al (2021) Polystyrene microplastics alter the intestinal microbiota function and the hepatic metabolism status in marine medaka (Oryzias melastigma). Sci Total Environ 759:143558. https://doi.org/10.1016/j.scitotenv.2020.143558

Gorrasi G, Sorrentino A, Lichtfouse E (2021) Back to plastic pollution in COVID times. Environ Chem Lett 19:1–4. https://doi.org/10.1007/s10311-020-01129-z

Guzzetti E, Sureda A, Tejada S, Faggio C (2018) Microplastic in marine organism: environmental and toxicological effects. Environ Toxicol Pharmacol 64:164–171. https://doi.org/10.1016/j.etap.2018.10.009

Häder DP, Banaszak AT, Villafañe VE et al (2020) Anthropogenic pollution of aquatic ecosystems: emerging problems with global implications. Sci Total Environ 713:136586–136596. https://doi.org/10.1016/j.scitotenv.2020.136586

Hankins C, Duffy A, Drisco K (2018) Scleractinian coral microplastic ingestion: potential calcification effects, size limits and retention. Mar Pollut Bull 135:587–593. https://doi.org/10.1016/j.marpolbul.2018.07.067

Hierl F, Wu HC, Westphal H (2021) Scleractinian corals incorporate microplastic particles: identification from a laboratory study. Environ Sci Pollut Res 28:37882–37893. https://doi.org/10.1007/s11356-021-13240-x

Hoch AR, Reddy MM, Aiken GR (2000) Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. Geochim Cosmochim Acta 64:61–72. https://doi.org/10.1016/S0016-7037(99)00179-9

John J, Nandhini AR, Velayudhaperumal Chellam P, Sillanpää M (2021) Microplastics in mangroves and coral reef ecosystems: a review. Environ Chem Lett. https://doi.org/10.1007/s10311-021-01326-4

Kim YY, Ribeiro L, Maillot F et al (2010) Bio-inspired synthesis and mechanical properties of calcite–polymer particle composites. Adv Mater 22:2082–2086. https://doi.org/10.1002/adma.200903743

Kim YY, Darkins R, Broad A et al (2019) Hydroxyl-rich macromolecules enable the bio-inspired synthesis of single crystal nanocomposites. Nat Commun 10:5682–5697. https://doi.org/10.1038/s41467-019-13422-9

Kniggendorf AK, Nogueira R, Lorey C, Roth B (2021) Calcium carbonate deposits and microbial assemblages on microplastics in oligotrophic freshwaters. Chemosphere 266:128942–128952. https://doi.org/10.1016/j.chemosphere.2020.128942

Kulak AN, Semsarilar M, Kim YY et al (2014) One-pot synthesis of an inorganic heterostructure: uniform occlusion of magnetite nanoparticles within calcite single crystals. Chem Sci 5:738–743. https://doi.org/10.1039/c3sc52615a

Lu S, Zhu K, Song W et al (2018) Impact of water chemistry on surface charge and aggregation of polystyrene microspheres suspensions. Sci Total Environ 630:951–959. https://doi.org/10.1016/j.scitotenv.2018.02.296

Mahadevan G, Ruifan Q, Hian Jane YH, Valiyaveettil S (2021) Effect of polymer nano- and microparticles on calcium carbonate crystallization. ACS Omega 6:20522–20529. https://doi.org/10.1021/acsomega.1c02564

Mann S (2001) Biomineralization: principles and concepts in bioinorganic materials chemistry. Oxford University Press on Demand, New York

Moulin P, Roques H (2003) Zeta potential measurement of calcium carbonate. J Colloid Interface Sci 261:115–126. https://doi.org/10.1016/S0021-9797(03)00057-2

Othman AR, Hasan HA, Muhamad MH et al (2021) Microbial degradation of microplastics by enzymatic processes: a review. Environ Chem Lett 19:3057–3073. https://doi.org/10.1007/s10311-021-01197-9

Perminova IV, Frimmel FH, Kudryavtsev AV et al (2003) Molecular weight characteristics of humic substances from different environments as determined by size exclusion chromatography and their statistical evaluation. Environ Sci Technol 37:2477–2485. https://doi.org/10.1021/es0258069

Pirsaheb M, Hossini H, Makhdoumi P (2020) Review of microplastic occurrence and toxicological effects in marine environment: experimental evidence of inflammation. Process Saf Environ Prot 142:1–14. https://doi.org/10.1016/j.psep.2020.05.050

Pokroy B, Fitch AN, Marin F et al (2006) Anisotropic lattice distortions in biogenic calcite induced by intra-crystalline organic molecules. J Struct Biol 155:96–103. https://doi.org/10.1016/j.jsb.2006.03.008

Prata JC, Venâncio C, Girão AV et al (2021) Effects of virgin and weathered polystyrene and polypropylene microplastics on Raphidocelis subcapitata and embryos of Danio rerio under environmental concentrations. Sci Total Environ 816:151642. https://doi.org/10.1016/j.scitotenv.2021.151642

Raghu AV, Jeong HM (2008) Synthesis, characterization of novel dihydrazide containing polyurethanes Based on N1, N2-Bis[(4-hydroxyphenyl)methylene]ethanedihydrazide and various diisocyanates. J Appl Polym Sci 107:3401–3407. https://doi.org/10.1002/app

Reichert J, Arnold AL, Hammer N et al (2022) Reef-building corals act as long-term sink for microplastic. Glob Chang Biol 28:33–45. https://doi.org/10.1111/gcb.15920

Sharma VK, Ma X, Guo B, Zhang K (2021) Environmental factors-mediated behavior of microplastics and nanoplastics in water: a review. Chemosphere 271:129597–129605. https://doi.org/10.1016/j.chemosphere.2021.129597

Singh N, Tiwari E, Khandelwal N, Darbha GK (2019) Understanding the stability of nanoplastics in aqueous environments: effect of ionic strength, temperature, dissolved organic matter, clay, and heavy metals. Environ Sci Nano 6:2968–2976. https://doi.org/10.1039/C9EN00557A

Štajner L, Kontrec J, Njegić Džakula B et al (2018) The effect of different amino acids on spontaneous precipitation of calcium carbonate polymorphs. J Cryst Growth 486:71–81. https://doi.org/10.1016/j.jcrysgro.2018.01.023

Stevenson FJ (1982) Humus chemistry: genesis, composition, reactions. Wiley, New York