

Exposure of microplastics to water organic matter poses an imminent threat to biomineralization

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Abstract

Plastic pollution in water ecosystems creates problems for wildlife, compromising survival and ultimately leading to many deaths. Calcium carbonate biominerals are crucial materials that play a vital role in skeletal formations in many species. Recent findings showed microplastic encapsulation into calcium carbonate biomineralized tissues. We hypothesize that microplastic, present in water ecosystems, changes due to exposure to dissolved organic matter and affects the formation and characteristics of calcium carbonate biominerals. More precisely, we predict that dissolved organic matter adsorbed onto microplastic particles enhances their encapsulation into calcium carbonate. To assess the influence of organic matter on microplastic encapsulation, we performed calcium carbonate precipitation experiments with humic acid as the reactive fraction of dissolved organic matter and polystyrene microspheres as model microplastic particles. In this way, we simulated the effect of the microplastic on the biomineralization process under the influence of dissolved organic matter. The results of scanning electron microscopy and electrokinetic potential measurements showed that the encapsulation of polystyrene microspheres is more pronounced after the treatment with humic acid. We showed for the first time that adsorbed humic acid favours the microplastic encapsulation into calcium carbonate. The new findings raise concern regarding the influence of long-term exposure of microplastics to the dissolved organic matter in water ecosystems resulting in encapsulation into exoskeleton and endoskeleton and causing changes in the skeletal structure under high amounts of encapsulated microplastic in biomineralized tissues of numerous species.

Key words

Microplastic, polystyrene, humic acid, calcium carbonate precipitation, biomineralization

1. 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 mineralized 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. Each year 8 million tons of plastic waste is disposed into water ecosystems and causes the death of whales, birds, turtles and fish (Häder et al. 2020). During time plastic waste disintegrates and forms microplastic which can be digested by smaller organisms like corals, sponges, and even foraminifera (Guzzetti et al. 2018). In 2021, researchers found microplastic

encapsulated into the calcite shell of foraminifera but also in the aragonite skeleton of corals (Birarda et al. 2021; Hierl et al. 2021; Reichert et al. 2021). Interestingly, older findings showed that microplastic was not encapsulated in the mineralized tissues of water organisms (Chapron et al. 2018; Hankins 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 observed encapsulation of microplastic into growing calcium carbonate mineralized tissues, leading us to speculate that with time the situation will only get worse. 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). In freshwaters, seas, and oceans dissolved organic matter is ubiquitous and it consists of amino acids, peptides, proteins, polysaccharides and 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 most of the organisms producing calcium carbonate can be found (Kniggendorf et al. 2021). This novel study aimed to investigate the difference between the encapsulation of fresh microplastic particles and those exposed to the dissolved organic matter into calcium carbonate. It was hypothesized that over time the microplastic encapsulation into calcium carbonate can enhance due to inevitable organic matter adsorption onto microplastic. Any obtained change may indicate a significant alteration in biomineralization processes and consequently exoskeleton formation in numerous species. We used batch laboratory precipitation experiments and calcium carbonate systems to experimentally verify this hypothesis. 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.

2. Experimental

Analytical grade chemicals sodium carbonate (Na_2CO_3) (Sigma Aldrich), calcium chloride ($\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$) (Acros Organics), polystyrene microspheres (size $1.6 \pm 0.2 \mu\text{m}$, Tianjin Baseline Chromtech Research Centre), humic acid (Sigma Aldrich) and deionized water (conductivity $< 0.055 \mu\text{S cm}^{-1}$) were used. The precipitation experiments were performed by using equal volumes (200 cm^3) of CaCl_2 and Na_2CO_3 reactant solutions in a thermostated (298 K) double-walled glass vessel with continuous stirring at a constant rate using a Teflon-coated magnetic stirring bar. The initial concentrations were $c(\text{CaCl}_2) = c(\text{Na}_2\text{CO}_3) = 2.5 \text{ mmol dm}^{-3}$. In the reference systems (systems without polystyrene microspheres and without humic acid) calcium carbonate precipitation was performed by fast and simultaneous mixing of CaCl_2 solution into the Na_2CO_3 solution. Precipitation systems containing 1 ppm of humic acid or 20 mg/dm^3 nontreated/ treated polystyrene microsphere were prepared by adding the humic acid or nontreated/ treated polystyrene microsphere to Na_2CO_3 solution before mixing the reactant solutions. The treated polystyrene microspheres were prepared by rotating 8 mg of microspheres in $300 \mu\text{L}$ of humic acid solution (4000 ppm) for 10 minutes and then centrifuged and washed with distilled water. The precipitation process was followed by measuring pH versus time (pH/ion meter, Radiometer PHM 240). After two hours of precipitation, the suspensions were filtered through a membrane filter ($0.22 \mu\text{m}$) and the precipitate was dried at $50 \text{ }^\circ\text{C}$ for one hour. The composition of the dry samples has been determined by FT-IR spectroscopy. IR spectra were recorded on the FT-IR TENSOR II (Bruker) using the ATR module in the $400 - 4000 \text{ cm}^{-1}$ region, using 16 scans and 4 cm^{-1} resolution. The morphology of the calcium carbonate samples was determined by JEOL JSM-7000F (Jeol Ltd.) without coating. The particle size distribution and electrokinetic potential of obtained samples were determined in water at $25 \text{ }^\circ\text{C}$ ($\text{pH} \approx 6$) using electrophoretic (ELS) and dynamic (DLS) light scattering. The analysis was performed on Litesizer 500 (Anton Paar) equipped with a semiconductor laser diode (40 mW) operating at 658 nm. The measurement was repeated 3 times and the obtained data was evaluated with Kalliope 1.2.0 software. Atomic force microscopy imaging was performed in the AC mode (simultaneously acquiring topography, amplitude,

and phase images) using the NanoWizard 4 ULTRA AFM. Multi75Al-G AFM probes were obtained from BudgetSensors. The volume of 1 μL of the prepared solution was deposited on a freshly exfoliated HOPG substrate and dried using a hot plate set to 60 $^{\circ}\text{C}$. Obtained images were subsequently processed using the JPKSPM data processing software, and root mean square surface roughness was determined using Gwyddion software (Nečas and Klapetek 2012).

3. Results and discussion

3.1. Characterization 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 deposited untreated polystyrene microspheres is shown in Fig. 1a. Further processing was conducted on the smaller scale images to remove the curvature of the sphere. For this, a fourth-order polynomial fit was used. Obtained images of the surface features are shown in Fig. 1b and 1c, 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 ($1.40 \pm 0.03 \text{ nm}$) than the untreated sample ($0.9 \pm 0.2 \text{ nm}$). This can also be seen from the profiles of the surfaces, as visualized in Fig. 1d, where profiles along lines are indicated in the 1b and 1c. These results clearly show that due to humic acid adsorption the treated polystyrene microspheres have a higher surface roughness and distinct high features not found on the untreated samples.

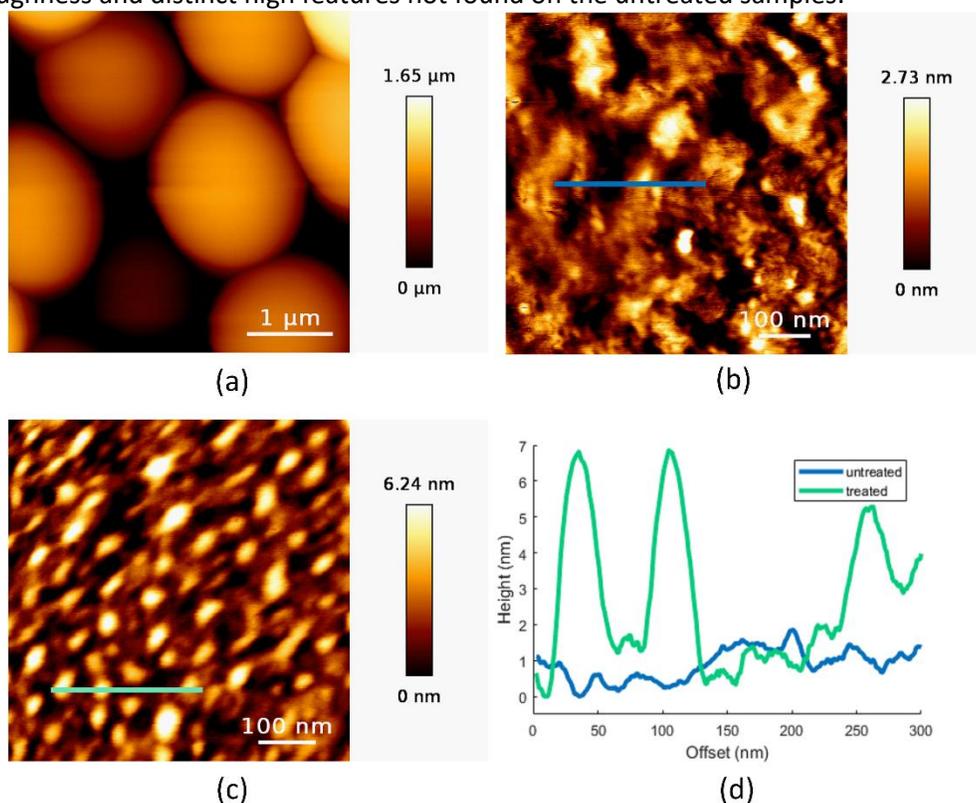


Fig. 1 Atomic force microscopy measurement of polystyrene microspheres. Large scale topography of untreated microspheres. (a) Topography image of surface features on a smaller scale: untreated polystyrene microsphere (b) humic acid treated polystyrene microsphere (c). Profiles of untreated and treated polystyrene surfaces (d) (indicated with blue and green lines in (b) and (c))

Moreover, dynamic light scattering showed that the size of the untreated polystyrene microspheres was $1.63 \pm 0.17 \mu\text{m}$ which was in accordance with the information from the supplier. For polystyrene microspheres treated with humic acid particle size was $1.84 \pm 0.03 \mu\text{m}$. The microspheres were coated with humic acid molecules with a layer of an approximate thickness of $0.10 \mu\text{m}$, which increased the overall particle size. Literature shows the increase of particle size occurs due to humic acid coating the polystyrene microspheres (Chen et al. 2018b; Liu et al. 2020). 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 as well. To determine the impact of the organic matter adsorbed on microplastic on biomineralization processes calcium carbonate precipitation experiments with polystyrene microspheres were conducted.

3.2. Precipitation and characterization 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 humic acid, treated or untreated polystyrene microspheres was performed. Supersaturation is the key parameter that controls precipitation. In this work initial supersaturation, in all investigated systems, was identical and was expressed as the saturation ratio, S_c , defined as a square root of the quotient of the calcium carbonate ion activity product, $a(\text{Ca}^{2+}) \times a(\text{CO}_3^{2-})$, and thermodynamic solubility product of calcite, K_{sp}^0 : $S_c = [(a(\text{Ca}^{2+}) \times a(\text{CO}_3^{2-})) / K_{sp}^0]^{1/2}$. The initial supersaturation with respect to calcite was $S_c \approx 19.0$. Relatively high initial supersaturation of the chosen reference system, which resulted in instantaneous precipitation, as well as precipitation of pure calcite, allowed us to obtain measurable effects on morphology and encapsulation into calcite. Fig. 2a shows supersaturation changes in time during calcium carbonate precipitation, calculated from measured pH. In all experiments, the precipitation started immediately after mixing the reactant solutions, which can be seen as a sudden drop of supersaturation and also by instantaneous turbidity of the solution. When comparing progress curves the change in the slope of the curves can be observed. A change in the slope of progress curves indicates a change in crystal growth rate. In comparison to the reference system (system without humic acid and polystyrene microspheres) (Fig. 2a, black line), lowering of the slope of the progress curve of the precipitation in the presence of 1 ppm of humic acid (Fig. 2a, red line) indicates crystal growth inhibition. As was previously observed by Hoch et al. (Hoch et al. 2000) crystal growth inhibition occurred as a consequence of the adsorption of humic acid onto the surface of growing calcite crystals. 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, the slope of the progress curves for the precipitation in the presence of untreated (Fig. 2a, green line) or even treated (Fig. 2a, blue line) polystyrene microspheres increased in comparison to the reference system indicating, in both cases, crystal growth rate enhancement. Similarly, Mahadevan et al (Mahadevan et al. 2021) reported that micro and nanoplastic particles induced precipitation of calcium carbonate.

The phase composition of samples isolated from precipitation experiments was determined by infrared spectroscopy (Fig. 2b). In the reference system as well as in the system with 1 ppm of humic acid only peaks corresponding to calcite were present: $\nu(\text{CO}_3)_{\text{out of plane}}$ at 872.9 cm^{-1} and $\nu(\text{O}-\text{C}-\text{O})$ at 712.5 cm^{-1} (Andersen and Brečević 1991). In the precipitation systems with untreated and treated polystyrene microbeads, infrared spectra showed the same peaks and only calcite precipitated. Also, in these systems, the infrared spectra showed peaks corresponding to polystyrene: $\nu_s(\text{C}=\text{C})$ at $1601.1, 1493.2, 1452.0 \text{ cm}^{-1}$ and $\nu(\text{C}-\text{H})_{\text{out of plane}}$ at 758.3 and 699.1 cm^{-1} (Fang et al. 2010). Peaks assigned to humic acid were not observed.

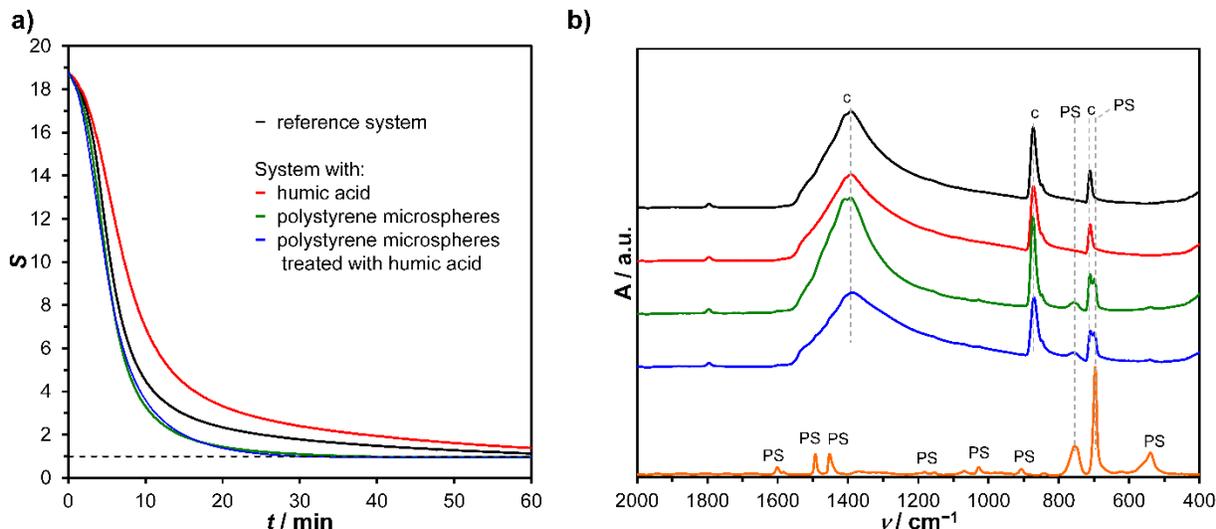


Fig. 2 a) Change of solution supersaturation in time during calcium carbonate precipitation. The dashed lines in the graph correspond to calculated values of solubility of stable calcite ($S = 1$). **b)** FTIR spectra of untreated polystyrene microspheres (orange line) and calcium carbonate precipitates obtained in the reference system (system without humic acid and polystyrene microspheres, black line) and the systems with: 1 ppm humic acid (red line); polystyrene microspheres treated with humic acid (blue line) and with untreated polystyrene microspheres (green line). Characteristic peaks for calcite (C) and polystyrene (PS)

Scanning electron microscopy images of calcium carbonate samples isolated from the reference system, system with the addition of 1 ppm humic acid and system with untreated and treated polystyrene microspheres are shown in Fig. 3. The precipitated sample in the reference system consisted of typical rhombohedral calcite crystals with expressed {104} faces (Fig. 3a). The addition of 1 ppm of 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 polystyrene microspheres was not dramatically affected and the crystals had smooth and sharp edges without noticeable microsphere encapsulation (Fig. 3c). In the sample prepared with polystyrene microspheres treated with humic acid, the calcite crystals showed the development of truncations on the edges of rhombohedral calcite due to the effect of humic acid released from the surface of polystyrene microspheres (Fig. 3d). Compared to the sample with untreated polystyrene 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 and can interact with calcium ions on the surface of calcite crystals. This effect was observed in the interaction of dissolved organic matter, microplastic and metal cations. They can aggregate and adsorb onto minerals as a consequence of electrostatic attraction (Brewer et al. 2020; Sharma et al. 2021). The untreated polystyrene microspheres were randomly dispersed throughout the sample and they were not attracted toward calcite crystals. The untreated polystyrene microbeads do not have functional groups, such as carboxylic groups, which are present on the surface of treated microbeads. The microspheres treated with humic acid were encapsulated in the growing calcite crystals and as estimated from SEM the number of free microspheres was dramatically lower compared to the sample with untreated polystyrene microspheres. The characterization 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). We predict that encapsulated microspheres in living organisms can cause significant change and possible

structural problems and the recent research, showing that up to 2.82 % of bioavailable microplastic accumulates in reef-building corals, highlights the problem of plastic pollution (Reichert et al. 2021).

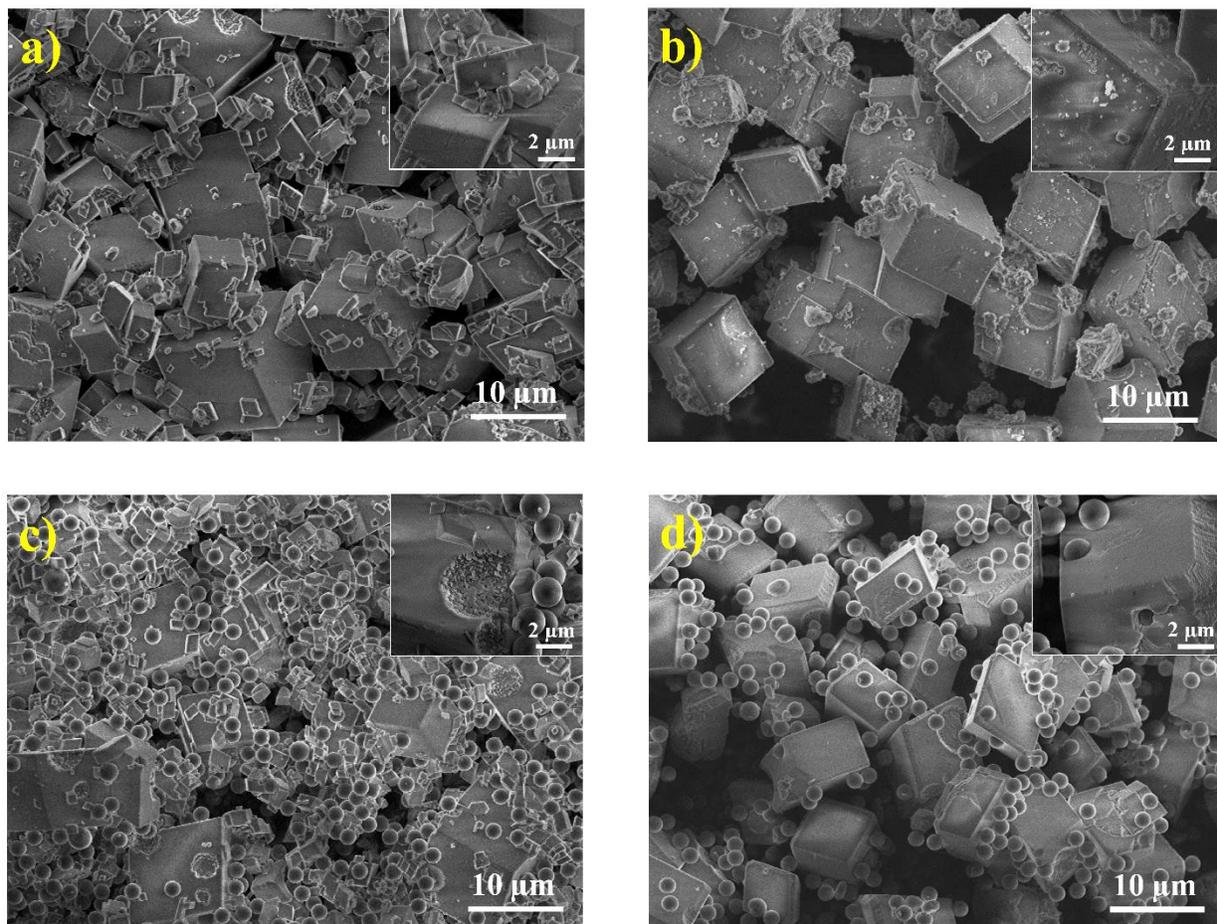


Fig. 3 Scanning electron microscopy images of calcium carbonate samples in the reference system (a) and in the system with: 1 ppm humic acid (b), polystyrene microspheres (c) and polystyrene microspheres treated with humic acid (d)

The obtained scanning electron microscopy results are in good correlation with the results of the electrokinetic potential measurements. Fig. 4 shows the electrokinetic potential of untreated polystyrene microspheres and polystyrene microspheres treated with humic acid, as well as the electrokinetic potential of precipitated calcium carbonate alongside untreated and treated polystyrene microspheres. 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. This was expected since humic acid is negatively charged at the used measurement conditions and literature shows that the electrokinetic potential of humic substances is lower than -10 mV, depending on the concentration (Esfahani et al. 2015). The electrokinetic potential of samples isolated from systems, where calcium carbonate precipitated alongside polystyrene microspheres and microspheres treated with humic acid, increased in comparison with electrokinetic potential values of pure polystyrene microspheres and microspheres treated with humic acid. In the system containing calcite crystals and untreated polystyrene the electrokinetic potential was -5.04 ± 0.99 mV and it further increased to -3.44 ± 1.09 mV in the system with treated polystyrene microspheres. For comparison at similar pH ($\text{pH} \approx 6$), the electrokinetic potential for calcite is -2.88 mV (Moulin and Roques 2003). Since in each experiment, the number of polystyrene

microspheres was constant as well as the solution composition, regarding calcium and carbonate ions and temperature, the largest increase in electrokinetic potential can be attributed to more pronounced calcium carbonate encapsulation of microspheres treated with humic acid.

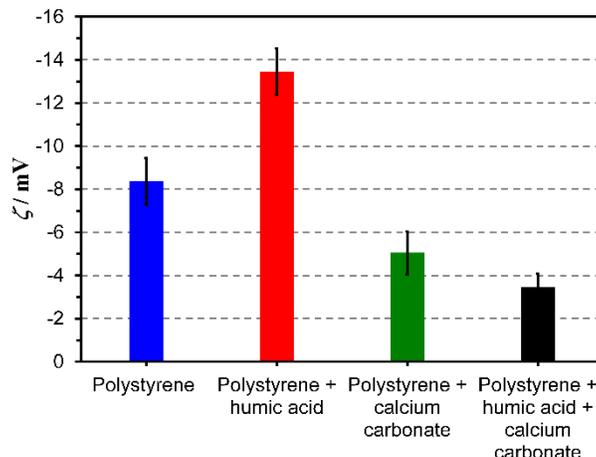


Fig. 4 The electrokinetic potential of samples in water. Polystyrene microspheres untreated and treated with humic acid and calcium carbonate with polystyrene microspheres untreated and treated with humic acid

Until now extensive research has been done to determine the ecological and toxicological effect of microplastics on the living organisms producing calcium carbonate (Lee and Hur 2020; Pirsahab et al. 2020; Birarda et al. 2021; Hierl et al. 2021; John et al. 2021; Reichert et al. 2021). Up to date, no research has investigated how the adsorbed organic matter influences the microplastic encapsulation into calcium carbonate. Adsorbed organic matter affects the microplastic transfer and transport to the sediment in the aquatic environment (Kniggendorf et al. 2021) leading to inevitable organism exposure to microplastic. This novel research shows that organic matter changes the surface characteristics of the polystyrene microspheres and facilitates the encapsulation of polystyrene microspheres into growing calcite crystals. The results presented in this paper undeniably show the risk for biomineralization processes indicating that prolonged microplastic exposure to the dissolved organic matter could in the next couple of decades cause higher microplastic encapsulation in calcium carbonate resulting in the change of the skeletal structure under high amounts of encapsulated microplastic. To develop conservation strategies, and to mitigate the effects of microplastic on biomineralized tissues, more detailed studies on the influence of dissolved organic matter, and different microplastic types is necessary.

4. 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 exoskeleton of different species. In our study, the research conducted for the first time shows pronounced polystyrene microspheres encapsulation in growing calcite crystals due to surface changes of microspheres after treatment with humic acid. The new findings raise concern regarding the influence of long term exposure of microplastics to the dissolved organic matter in water ecosystems resulting in encapsulation into exoskeleton and endoskeleton of species producing calcium carbonate and causing a possible change in the skeletal structure under high amounts of encapsulated microplastic.

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

Authors' contributions All authors contributed to the study 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.

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