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Partition of biocides between water and inorganic phases of renders with organic binder

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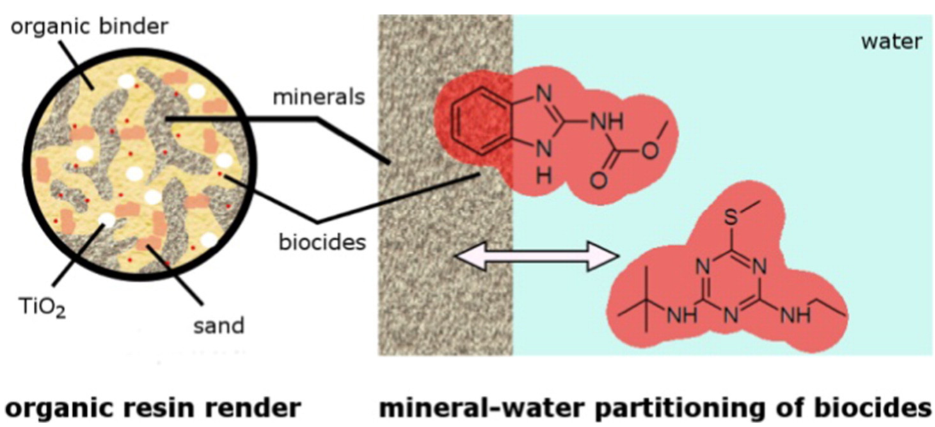
HIGHLIGHTS

- Partition constants obtained for main mineral phase ($CaCO_3$) were low.
- Partition constants obtained for talc were the highest among all minerals analyzed.
- Distribution constants can be estimated as a sum of single ingredients.
- The minerals are not the dominant phase for the sorption of biocides in renders.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of biocides as additives for building materials has gained importance in the recent years. These biocides are applied, e.g., to renders and paints to prevent them from microbial spoilage. However, these biocides can leach out into the environment. In order to better understand this leaching, the partition of biocides between water and inorganic phases of render with organic binder was investigated.

The partition constants of carbendazim, diuron, iodocarb, isoproturon, cybutryn (irgarol), octylisothiazolinone, terbutryn, and tebuconazole towards minerals typically used in renders, e.g. barite, calcium carbonate, marble, kaolinite, and talc were determined. Partition constants for calcium carbonate varied between 0.2 mL g^{-1} (diuron) and 5.2 mL g^{-1} (iodocarb), respectively. The results for barite and kaolinite were in a similar range and usually the compounds with high partition constants for one mineral also had high values for the other mineral. No sorption to marble at all was found. From all minerals investigated, only talc showed high partition for all studied biocides. Partition constants for talc varied from 21.3 mL g^{-1} (iodocarb) to 683.7 mL g^{-1} (tebuconazole), respectively. The comparison with render-water distribution constants of two artificially made renders showed that the distribution constants can be estimated based on partition constants of compounds for individual components of the render.

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1. Introduction

The use of biocides as additives for building materials such as enhanced thermal insulation composite systems (ETICS) has gained importance in the recent years. The final top-coatings used in those materials contain organic polymers as binders as well as inorganic components as fillers. The whole systems are vulnerable to infestations of bacterial, algal, and fungal biofilm growth. Once a surface is colonized by microorganisms, it may lose its integrity, show color changes and loss of adhesion (Gaylarde et al., 2011). In order to protect these materials from microbial spoilage, biocides are applied. To raise the effectiveness, biocides must be present at or near the upper surface on the respective material (Burkhardt et al., 2009). Because the render is exposed to the natural environment, biocides that are added in their free state tend to leach, i.e., wash off during wet weather together with the rain water or degrade (thermal and UV degradation) (Burrows et al., 2002; Bollmann et al., 2016). To counter the effects of such losses, relatively high initial loadings of biocides are applied (Karsa and Ashworth, 2002). The leached compounds may reach separated or combined sewer systems or leach directly into soil (Bollmann et al., 2014; Burkhardt et al., 2009; Coutu et al., 2012; Wittmer et al., 2010). Even in wastewater treatment, biocides are not fully removed and are discharged into surface waters where they may affect aquatic organisms (Singer et al., 2010; Mohr et al., 2008).

The leaching process is a subject of interests of many scientists. It has been studied using both: big systems with artificial rain as controlled rain exposure (Burkhardt et al., 2011, 2012; Wangler et al., 2012), and small systems (Schoknecht et al., 2009). Additionally, Gromaire et al. (2015) have tested emission of quarternary ammonium salts from roof materials under natural rainfall. Results show, that biocides leach out in significant amounts, leading in some cases to entire loss of active biocidal compounds from the materials within a year (Burkhardt et al., 2009).

Schoknecht et al. (2009) hypothesized, that the leaching is a diffusion-controlled process and can be associated with the octanol-water partition constant. Desorption studies performed by Styszko et al., 2014 showed that the acrylate and silicone content of the render can influence the partition of biocides (such as isothiazolinone, carbamates or triazines) to some extent, but no significant correlation with the octanol-water partition constant for the resulting render/water distribution constants has been found.

Render with organic binder are complex mixtures, which are described in standard EN 15824:2009. Typically, they consist of carbonates (30–60% weight percentage), polymeric binder (10–15%, such as acrylate or silicone), sand in different grain sizes and other additives. While partitioning of one ingredient of the render can easily be predicted (organic phases of the render show a significant correlation with K_{OW} values (Bollmann et al., 2015)), it is difficult to predict the distribution constants for a render considered as a whole. Schwarzenbach et al., 2002 developed methods to approach complex systems like soils by assuming the whole system acts like the sum of the single phases that are involved when each part acts independently and comes to equilibrium with all other parts. It can thus be expected that the total biocide amount adsorbed to render can be calculated as the sum of the biocide amount in each phase. In that case, the render/water distribution constant (D_{render}, Eq. (1)) may be described as the sum of the partitioning to mineral phases, sand particles, organic binding phase and other render ingredients, where D describes the distribution of the respective biocide between bulk render and water while K_d will be used for single phase partitioning; f describes the fraction of the respective phases in the bulk and C the concentration of the biocide in each phase (Bollmann et al., 2015).

$$D_{render} = \frac{C_{mineral} \cdot f_{mineral} + C_{organic\,binding\,phase} \cdot f_{organic\,binding\,phase} + f_{sand} \cdot C_{sand} + \dots}{C_{water}} \quad (1)$$

Bollmann et al. (2015) calculated the relation between the acrylate-water partition constant and the desorption constant from acrylate composite render normalized to the organic matter content based on her own study as well as results from (Styszko et al., 2014). The calculations were performed for six biocides cybutryn, iodocarb, diuron, isoproturon, tebuconazole, and carbendazim indicating a significant positive linear correlation between the two constants ($r = 0.79$). Only carbendazim was not following the trend, hence it was excluded from the consideration. It was concluded that acrylate is the dominant phase for the partition of most biocides in the render-water system. However, there were significant deviations between the partition of biocides between acrylate and water, and render and water. It was hypothesized that the mineral phases of the acrylate composite render significantly contribute to the partition of biocides.

Thus, in the present work it was studied how much biocide would sorb to the mineral phases of renders and how much this could contribute to the partition of biocides between render and water. The partition constants were determined experimentally and used to calculate the distribution constant for the simple render model. The calculations were then compared with the experimental data from two artificially prepared renders.

2. Materials and methods

2.1. Chemicals and minerals

Compounds used in these experiments (Table 1; Supplementary material S1): carbendazim, diuron, iodocarb, isoproturon, cybutryn (irgarol 1051), octylisothiazolinone, terbutryn, and tebuconazole as well as isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, and carbendazim-D4 as internal standards for quantitation with HPLC-MS/MS. Minerals included in this study were: barite, calcium carbonate, marble, kaolinite, and talc. Suppliers and purities of the used

Table 1
Physical-chemical properties of the biocides covered within this paper: *$logK_{OW}$*: octanol-water partition constant, WS: water solubility, pKa: acid dissociation constant.

Group common name	Physico-chemical properties
Carbamates	
Carbendazim	$\log(K_{ow})$ 1.55[a] pKa: 10 (acid) 4.5 (base)[b] WS: 8 mg L^{-1}[a]
Iodocarb	$\log(K_{ow})$ 2.45[a] pKa: 11.8 (acid)[b] WS: 168 mg L^{-1}[a]
Isothiazolinones	
Octylisothiazolinone	$\log(K_{ow})$ 2,61[a] pKa: −0.4 (base)[b] WS: 480 mg L^{-1}[a]
Phenylureas	
Diuron	$\log(K_{ow})$ 2,67[a] pKa: 13.8 (acid) −1.6 (base)[b] WS: 35 mg L^{-1}[a]
Isoproturon	$\log(K_{ow})$ 2,84[a] pKa: 14.3 (acid) 0.1 (base)[b] WS: 65 mg L^{-1}[a]
Triazines	
Cybutryn (Irgarol 1051)	$\log(K_{ow})$ 4,07[a] pKa: 4.1 (base)[b] WS: 7 mg L^{-1}[a]
Terbutryn	$\log(K_{ow})$ 3,77[a] pKa: 4.1 (base)[b] WS: 25 mg L^{-1}[a]
Triazoles	
Tebuconazole	$\log(K_{ow})$ 3,89[a] pKa: 13.7 (acid) 1.8 (base)[b] WS: 36 mg L^{-1}[a]

[a] Calculated by use of the EPI suite model from the US EPA (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm).
[b] pKa: estimated with (ACD, 2013).