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Smectite clay pillared with copper complexed polyhedral oligoisilsesquioxane for adsorption of chloridazon and its metabolites

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Chloridazon has been a widely used herbicide during the past decades, especially in sugar-beet cultivation. UV-induced degradation of chloridazon leads to the formation of the relevant desphenyl-counterparts, i.e. desphenyl-chloridazon and methyl-desphenyl-chloridazon. Even if accumulation of these residues in natural waters is far from alarming, a low-cost effective and environmentally friendly adsorbent, capable of binding chloridazon and its degradation products is desirable to reduce their concentration in water even further below legal limits. Here we show that pillared smectite clay, prepared by cation exchange of sodium with copper complexed, cage-shaped polyhedral oligomeric silsesquioxane (Cu^{2+}@POSS) could be a promising candidate for this purpose. X-ray diffraction and high resolution transmission electron microscopy evidenced a homogeneous layered structure where the interlayer spacing is enlarged by 7.1±0.2 Å (the diameter of Cu^{2+}@POSS) with respect to the pristine clay. Exposure of this pillared smectite clay to chloridazon and its metabolites in water showed that Cu^{2+}@POSS intercalation significantly improved the adsorption capacity. In addition, after several thermal regeneration cycles Cu^{2+}@POSS_SWy-2 still exhibited excellent adsorption properties. These findings demonstrate that smectite clay pillared with copper complexed polyhedral oligoisilsesquioxane is a promising environmentally friendly and relatively low cost material for herbicide waste remediation.

Environmental significance

Chloridazon, a herbicide largely employed in European agriculture, and its metabolites have accumulated in environment to a level where their elimination from drinking water is recommended to safeguard human health but a recyclable and relatively inexpensive remediation technology for such herbicides has not been developed yet. This work proposes smectite clay pillared with copper-complexed polyhedral oligoisilsesquioxane as an adsorbent, and demonstrates the efficacy of this material in extracting chloridazon and its metabolites from water. The design of this adsorbent can be adapted to other contaminants by choosing appropriate ligands for the polyhedral oligoisilsesquioxane and metal ions for the complexation as to optimize the pore size and affinity for trapping the chosen molecule.

Introduction

Addressing the lack of adequate and safe water is among the most important challenges of the last few decades. Groundwater, an important source of drinking water in most countries, has been threatened by herbicide/pesticide contamination due to runoff from the soil surface and plants to rivers and lakes. Studies on groundwater contamination have reported increasing amounts of herbicides/pesticides and their metabolites. Chloridazon, a selective systemic herbicide used for the control of annual broad-leaved weeds, has been widely employed especially in sugar-beet cultivation since it was considered to be a relatively non-harmful herbicide. Its degradation leads to the formation of desphenyl-chloridazon and methyl-desphenyl-chloridazon; the former, produced by aerobic degradation in the soil, is predominant. According to European regulations, the maximum residue limit for herbicides is 0.1 µg L^{-1} for single compounds and 0.5 µg L^{-1} for the sum of all herbicides. As reported by Schuhmann et al., in some parts of Europe, chloridazon was detected at concentrations up to 3.5 µg L^{-1}, whereas the metabolites desphenyl-chloridazon and methyl-
In this work, we report the intercalation of Cu$^{2+}$-complexed POSS into smectite clay. POSS is accessible, active sites for adsorption. Moreover, the chemical affinity of the nanopores created by pillaring can tune the functionalization to achieve desired properties. POSS is particularly flexible organic-inorganic cage-like polyhedral oligomeric silsesquioxanes as a complexed metal because of its affinity to nitrogen-containing groups that promises well for enhancing the adsorption capacity of chloridazon and its metabolites. POSS was selected because it presents three important advantages: i) the eight nitrogen containing organic ligands (-NH$_2$ and -NH) on each POSS allow to complex 4 Cu ions; ii) POSS’ cubic shape separates the complexed copper ions from each other and avoids aggregation during the synthesis process, which would reduce the activity of copper ions, and iii) creates the appropriate interlayer space between the smectite layers and the right porosity for chloridazon to interact.

Characterization of the nanocomposite included X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption measurements, thermogravimetric and differential thermal analysis (TGA/DTA) and X-ray photoelectron spectroscopy (XPS). The pillared clay exhibited a high specific surface area; compared to pristine smectite clay it showed a significant enhancement of adsorption capacity for chloridazon and its metabolites.

**Experiment**

**Materials**

Wyoming montmorillonite (SWy-2, (Na, Ca)$_{0.3}$ (Al, Mg)$_{2}$ Si$_{10}$O$_{28}$ (OH)$_{2}$ • nH$_2$O), with a cation exchange capacity (CEC) of 78 meq/100 g and flake size ~200 µm, was obtained from the Source Clay Minerals Repository, Columbia. 3-(2-aminoethylamino)-propyltrimethoxysilane (EDAPTMS) was acquired from Fluka Chemicals, chloridazon (C$_{10}$H$_8$ClN$_2$O, AR) from Sigma-Aldrich, desphenyl-chloridazon (C$_{9}$H$_7$ClN$_2$O, AR) and methyl-desphenyl-chloridazon (C$_{9}$H$_8$ClN$_3$O, AR) from Enamine Ltd. All chemicals were used as received.

**Synthesis of the Cu$^{2+}$@POSS_SWy-2 nanocomposite**

In this work, we report the intercalation of Cu$^{2+}$-complexed POSS into smectite clay towards the synthesis of a novel type of pillared structure suitable for environmental remediation. Copper was chosen as a complexed metal because of its affinity to nitrogen-containing desphenyl-chloridazon were present in concentrations of 24.0 µg L$^{-1}$ and 6.1 µg L$^{-1}$, respectively.

In order to limit exposure to chloridazon and its metabolites, their elimination from natural water by the use of an innovative adsorbent with high selectivity and sorption capacity, but available at relatively low cost, would be an important step forward. Since the beginning of civilization, natural clay minerals have been employed by mankind and because of their low cost, abundance in most continents, high sorption properties and potential for ion exchange, clay materials are also a good option for the present purpose. Due to their layered structure, clays can host adsorbates and counter ions in the space between the platelets. They exhibit a strong affinity for both cationic and anionic moieties, whereas the sorption capacity for basic molecules is much higher than that for acidic ones because of the negative charge inherent to the clay structure. However, not solely the chemical affinity of the interlayer space of clays can limit the adsorption capacity for chloridazon, the size of the interlayer space also plays an important role and it is therefore crucial to modify the structure of the clay in order to improve its adsorption capacity.

Pillaring is a well-known technique for engineering the interlayer space in clays by increasing the specific surface area and providing accessible, active sites for adsorption. Molecules, ions, or complexes can be used as pillaring agents. Among them, organinorganic cage-like polyhedral oligomeric silsesquioxanes (POSS) are particularly flexible because different organic ligands can tune the functionalization to achieve desired properties. Moreover, the chemical affinity of the nanopores created by pillaring with POSS can be tailored through complexation of metal ions.

In this work, we report the intercalation of Cu$^{2+}$-complexed POSS into smectite clay towards the synthesis of a novel type of pillared structure suitable for environmental remediation. Copper was chosen as a complexed metal because of its affinity to nitrogen-containing...
Milli-Q water (resistivity 18 MΩ cm, 25 °C) was used in the synthesis. SWy-2 was purified with the standard method in clay science, as described in our previous paper.22 Sodium exchanged montmorillonite was prepared by immersing the pristine clay into 1 N solution of sodium chloride, washed with distilled-deionized water and transferred into dialysis tubes in order to obtain chloride free clays.22 The synthesis of cage-shaped POSS was based on a hydrolytic polycondensation reaction; EDAPTMS was diluted in ethanol/water (v/v = 14/1) to give a 0.45 M solution of POSS, which was shaken for a few minutes before bottling for further use.23,24 20 mL of 0.15 M CuCl₂ aqueous solution (3 mmol) was complexed with 14 mL POSS solution (6 mmol) through sonication and stirred for 30 min. The complexation of the copper cations with the amino and imino groups on the R branches of POSS was evident from the colour change of the complex solution, which turned from light blue to dark blue. The Cu²⁺@POSS_SWy-2 nanocomposite was prepared by cation exchange of sodium with copper-complexed POSS (Cu²⁺@POSS) as indicated in Scheme 1. A suspension of 0.5 wt.% of SWy-2 in water was mixed with Cu²⁺@POSS in a weight ratio [Cu²⁺@POSS]/[SWy-2]=3, which ensures that there are sufficient siloxane complexes to exchange for the sodium ions in the clay interlayer space. After stirring for 24 h, the Cu²⁺@POSS_SWy-2 nanocomposite was separated by centrifugation at 5000 rpm and washed three times with ethanol/water (v/v = 1:1), before being spread onto glass plates for air drying.

In order to study the role of Cu²⁺, POSS-pillared clay without the complexed metal was also prepared by the same synthetic route; this nanocomposite will be identified as POSS_SWy-2 in the following.

Characterization of the pillared nanocomposite Cu²⁺@POSS_SWy-2

FTIR spectra were recorded on a SHIMADZU 8400 infrared spectrometer in the range 4000-500 cm⁻¹; each spectrum was the average of 200 scans, collected with a resolution of 2 cm⁻¹. The samples were KBr pellets that contained 2 wt.% of Cu²⁺@POSS_SWy-2. XRD spectra were acquired using a D8 Advance Bruker diffractometer with Cu Kα radiation (λ=1.5418 Å) employing a 0.25° divergent slit and a 0.125° anti-scattering slit; the patterns were recorded in the 2θ range from 20° to 80°, in steps of 0.02° and a counting time 2 s per step. The nitrogen adsorption-desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2420 V2.05 (V2.05 J) porosimeter. Prior to analysis, all three samples were degassed overnight at 120 °C under vacuum. The specific surface area was evaluated with Brunauer-Emmet-Teller (BET) model by fitting N₂ adsorption isotherm, the pore volume was determined at P/P₀ = 0.995 and the Non-Local Density Functional Theory (NLDFT) method25 was applied to the N₂ adsorption data to obtain the pore size distribution. TGA/DTA was performed using a Perkin Elmer Pyris Diamond TG/DTA. Samples of approximately 5 mg were heated in N₂ from 25 °C to 700 °C, at a rate of 5 °C min⁻¹. TEM images were obtained by using a FEI Tecnai T20, operating at 200 kV. Images were recorded under low-dose conditions with a slow-scan CCD camera. SEM images were recorded with a FEI-Philips FEG-XL30s microscope, with which also energy dispersive X-ray spectroscopy (EDS) was performed with the help of an EDAX Octane Silicon Drift Detector with an accelerating voltage of 20 kV. XPS was performed with a SSX-100 (Surface Science Instruments) spectrometer equipped with a monochromatic Al Kα X-ray source (hv=1486.6 eV). The measurement chamber pressure was maintained at 1×10⁻⁹ mbar during data acquisition; the photoelectron take-off angle was 37° with respect to the surface normal. The samples were dispersed in ethanol/water (v/v = 30/70) by sonication and stirring for 30 min, and a small drop of the suspension was left to dry in air on a homemade 150 nm thick gold film supported on mica. Spectral analysis included a Shirley background subtraction and fitting with peak profiles taken as a convolution of Gaussian and Lorentzian functions, with the help of the least squares curve-fitting program WinSpec (LISE, University of Namur, Belgium). Binding energies (BEs) were referenced to the Si2p peak at 103.3 eV and are accurate to ±0.1 eV when deduced from the fitting procedure. All measurements were carried out on freshly prepared samples; three different spots were measured on each sample to check for homogeneity.

Batch adsorption experiments

10 mg of Cu²⁺@POSS_SWy-2, POSS_SWy-2 or SWy-2 was swelled in 10 mL of ethanol/water (30/70, v/v) for 24 h under stirring and sonication in a glass vial. Stock solutions of 50 ppm chloridazon, desphenyl-chloridazon and methyl-desphenyl-chloridazon were prepared in ethanol/water (30/70, v/v). Batch adsorption experiments were conducted at ambient temperature. Chloridazon, desphenyl-chloridazon or methyl-desphenyl-chloridazon was added, at concentrations adjusted from 5 ppm to 25 ppm, to 10 mg of swelled suspensions of the Cu²⁺@POSS_SWy-2, POSS_SWy-2 or SWy-2; the suspensions were stirred for 24 h. After the adsorption equilibrium was reached, the suspensions were centrifuged and filtered with 0.45 µm nylon filters. The concentrations of the herbicide and its metabolites were measured with high performance liquid chromatography (Prominence HPLC, Shimadzu) using a diode array detector and data station and analysed at 283 nm, the wavelength of maximum absorption of these compounds. All of the experimental data reported were the average of triplicate determinations. The adsorption capacities of the organic solute by Cu²⁺@POSS_SWy-2, POSS_SWy-2 and SWy-2 were calculated with the equation:

\[ Q_e = \frac{(C_0 - C_e)/m} \times V \]

where \( C_0 \) and \( C_e \) are the initial and the adsorption equilibrium concentration, respectively; \( m \) is the mass of the adsorbent and \( V \) represents the volume of the suspension.

The adsorption isotherms were analysed with the Freundlich isotherm model, commonly used for aqueous phase adsorption:

\[ \ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \]

where \( K_f \) represents Freundlich constant, \( n \) is the Freundlich linearity index and \( C_e \) represents the adsorption equilibrium concentration.

Thermal regeneration experiments

250 mg of Cu²⁺@POSS_SWy-2 was added to 250 mL of ethanol/water (30/70, v/v) in a glass vial and stirred for 24 h. Stock solutions of 50 ppm chloridazon were prepared in ethanol/water (30/70, v/v). 250 mL of the stock solution of chloridazon was added to the
Fig. 1 (a) FTIR spectra and (b) XRD spectra of SWy-2, POSS_SWy-2 and Cu$^{2+}$@POSS_SWy-2, X-ray photoelectron spectra of Cu$^{2+}$@POSS_SWy-2 (c) N1s and (d) Cu2p3/2 core level regions.

Cu$^{2+}$@POSS_SWy-2 suspension and the mixture was stirred for 24 h. The adsorbent was separated by centrifugation and dried in the oven (Thermol Scientific Heraeus) overnight at 40 °C, followed by heating in a different oven (Nabertherm Box Furnace) at 290 °C for 4 h. After that, the cooled sample was carefully weighed and used for the second cycle. The adsorption experiments were carried out with an adsorbent concentration of 0.5 mg mL$^{-1}$, and a chloridazon concentration of 25 mg L$^{-1}$; four cycles were performed.

Results and Discussion

Material Characterization

The samples were analysed by FTIR to confirm the successful incorporation of the POSS derivative in the layered structure. The spectra of pristine SWy-2, POSS_SWy-2 and Cu$^{2+}$@POSS_SWy-2 are shown in Fig. 1(a). One recognizes the characteristic peaks of smectite clay at 1060 cm$^{-1}$ (Si-O stretching), 695 cm$^{-1}$ and 642 cm$^{-1}$ (Si-O-Si bending vibrations). In addition, in the spectrum of pristine SWy-2 the -OH stretching vibration around 3630 cm$^{-1}$ is ascribed to the presence of -OH on the aluminosilicate skeleton, while the stretching modes at 3400-3600 cm$^{-1}$ and the bending vibration at 1645 cm$^{-1}$ can be attributed to physisorbed water. A confirmation of the presence of POSS in the hybrid material comes from the bands centred at 2863 cm$^{-1}$ and 2921 cm$^{-1}$, which correspond to C-H stretching vibrations, as well as from the peak at 1520 cm$^{-1}$, due to the N-H stretching mode.

The successful intercalation of POSS derivatives in SWy-2 can be proved by XRD, which allows estimating the interlayer distance between the clay platelets. The XRD spectra of SWy-2, POSS_SWy-2 and Cu$^{2+}$@POSS_SWy-2 are displayed in Fig. 1(b). By applying the Bragg equation, one can derive the basal d$_{001}$-spacing, which in pristine smectite clay amounts to 12.0±0.3 Å, but becomes 16.3±0.3 Å after intercalation with POSS. The latter basal plane spacing corresponds to an interlayer separation Δ = (16.3±0.3) Å - 9.6 Å = 6.7±0.3 Å, where 9.6 Å represents the thickness of single clay layer. This value is in accordance with the size of POSS. For Cu$^{2+}$@POSS_SWy-2, the basal plane spacing is even larger, namely 16.7±0.4 Å, and the corresponding interlayer separation of (16.7±0.2) Å - 9.6 Å = 7.1±0.2 Å points to successful Cu$^{2+}$ complexation with POSS and intercalation of Cu$^{2+}$@POSS between the smectite clay layers.

To verify the presence and integrity of Cu$^{2+}$@POSS within the layered nanostructure, as well as to analyse the chemical environment of Cu$^{2+}$ and POSS, we employed XPS. The overview spectrum attests to the presence of all the expected elements (see Supporting information, Figure S1). The XPS spectrum of the N1s core level region of Cu$^{2+}$@POSS_SWy-2, shown in Fig. 1(c), requires four contributions in the fit: the spectral signatures of -NH$_2$ and -NH
bonds of the POSS are centred at BEs of 399.9 eV and 400.8 eV respectively and make up 19.4±4% and 37.1±3% of the total N1s intensity. The contributions at BEs of 403.4 eV and 402.0 eV are respectively due to the NH--Cu²⁺ and NH₂--Cu²⁺ and represent 17.6±4% and 25.8±3% of the total N1s intensity. Hence the spectral intensities of the total amounts of -NH₂ (-NH₂ and -NH₂--Cu²⁺) and -NH--NH, the relatively electron poor amino Cu²⁺--NH, the relatively electron poor amino Cu²⁺--NH₂ and Cu(II)O; the small peak at 947.0 eV is the shake-up satellite. The ratio between Cu²⁺--NH and Cu²⁺--NH₂ in the Cu₂p½ spectrum agrees with the N1s spectrum. Taken together the XPS spectra confirm that Cu²⁺@POSS was successfully intercalated into SWy-2.

Undeniable proof for the successful intercalation of Cu²⁺@POSS into the interlayer space of SWy-2 is provided by the high-resolution transmission electron microscopy (HRTEM) images shown in Fig. 2, where the layered structure can be clearly observed in panel (a). The interlayer spacing can be retrieved by performing a fast Fourier transform (FFT) of the image, where the diffraction corresponding to (001) planes of SWy-2 structure is observed as shown in Fig. 2(b). Performing an inverse FFT on the marked area, the basal plane spacing d_002 is measured to be ~1.79 nm in agreement with the XRD result discussed above.

In order to get further insight on the morphology of the composite material, SEM was performed. A well-defined porous structure, which resembles the crumpled sheet, can be observed on the image in Fig. 3(a). In an enlarged view of the same spot, presented in Fig. 3(b), the exfoliated layers (white arrows) and the enlarged interlayer space (yellow arrows) of smectite clay can be clearly seen.

Furthermore, EDS elemental mapping was performed to verify whether the pillaring structures were uniformly distributed and to determine the relative ratio of Cu²⁺ in the Cu²⁺@POSS_SWy-2. As shown in Fig. 3, we collected EDS spectra in the area marked in dark red in the SEM image (Fig. 3(c)) and found identical spectra, of which one is reported in Fig. 3(d). We then imaged the distribution of Si, Al, N and Cu in the area enclosed in the red square area (Fig. 3(c)) and found a homogeneous distribution for all four elements, which indicates that the insertion of Cu²⁺ into smectite clay is uniform throughout the sample. In addition, Al and Si are the main components of the smectite layers, which are composed of an octahedral alumina layer and sandwiched between two tetrahedral silica layers. From the elemental composition deduced from the EDS spectra we can infer that the amount of Cu²⁺ in the nanocomposite is approximately 2.4 wt.%.

To estimate the amount of POSS and Cu²⁺@POSS introduced into SWy-2, TGA-DTA were performed on POSS_SWy-2 and Cu²⁺@POSS_SWy-2, as well as on the pristine clay; the results are shown in Fig. 4(a-c). For pristine smectite clay, the broad peak trace observed at 667 °C on the relevant DTA marks the dihydroxylation of structural -OH groups in SWy-2, which make up 3.0 % of the total mass.44 For POSS_SWy-2 and Cu²⁺@POSS_SWy-2, the region from 200 °C to 500 °C refers to the decomposition of POSS: between 200 °C and 300 °C amino groups detach from POSS,55 followed by the combustion of the alkane on the R group of POSS between 300 °C and 500 °C.56 The Si-O bond decomposition of the POSS-cage and the dehydroxylation of structural -OH group in SWy-2 occur between 500 °C to 700 °C.56 From these data we can estimate that for POSS_SWy-2, the amount of POSS intercalated...
Fig. 3 (a)(b) SEM image of Cu$_2^+$@POSS_SWy-2. (c) SEM image with the area selected for energy dispersive X-ray spectroscopy (EDS) spectra and EDS elemental mapping measurement marked in red. (d) SEM-EDS spectra of Cu$_2^+$@POSS_SWy-2. Insert: the elemental composition results. The bottom panels show the EDS elemental mapping results for Si, Al, N and Cu in Cu$_2^+$@POSS_SWy-2 based on the red square area in (c).

into SWy-2 equals 2.0 wt.% of the total mass, while for Cu$_2^+$@POSS_SWy-2, it reaches 8.0 wt.% of the total mass. In other words, Cu$_2^+$ favours the insertion of POSS between SWy-2 layers. If we calculate the amount of nitrogen based on the POSS structure, we find that nitrogen should make up about 2.5 wt.% of the total weight, in good agreement with the EDS result (2.6%).

Nitrogen adsorption-desorption measurements were performed on SWy-2, POSS_SWy-2 and Cu$_2^+$@POSS_SWy-2 to monitor the increase of surface area with intercalation and to retrieve information on the pore structure; the isotherms are presented in Fig. 4(d-f). As for the pristine smectite, a sudden release of N$_2$ at P/P$_0$ = 0.5 gives rise to a type H3 hysteresis loop, commonly ascribed to slit-shaped pores in layered materials, and the adsorption-desorption isotherm corresponds to a type II isotherm, attributed to the general microporous structure. After POSS and Cu$_2^+$@POSS intercalation, the hysteresis loop widens, implying an increase in pore volume from 0.093 cm$^3$ g$^{-1}$ in the pristine material to 0.230 cm$^3$ g$^{-1}$ in Cu$_2^+$@POSS_SWy-2 (Table 1). The specific surface area (SSA) and the pore volume calculated from the BET data are reported in Table 1. The SSA for SWy-2 was found to amount to 26 m$^2$ g$^{-1}$, but increased to 127 m$^2$ g$^{-1}$ after intercalation with Cu$_2^+$@POSS. This indicates that N$_2$ can only adsorb on the external surface and the interlayer space remains inaccessible in the pristine material, while the opening of the interlayer space in the nanocomposite allows for N$_2$ penetration. However, compared to POSS_SWy-2, a significant increase of SSA can be observed for Cu$_2^+$@POSS_SWy-2; this indicates that the Cu$_2^+$ enhanced POSS intercalation leads to the formation more mesoporous structures, which can result in a dramatically increased pore surface area.

To gain better insight into the structural characteristics of our materials, we determined the pore size distribution (PSD). For this the NLDFT method was employed since both micropores and mesopores are present in the structure of pillared smectite clays. The PSD results obtained from the NLDFT model are shown in Fig. S2(a), where one notes that the relative amount of micropores increased with the intercalation of POSS and Cu$_2^+$@POSS.
intercalation of POSS in SWy-2 has a limited effect on the internal and external pore distribution. However, when Cu$^{2+}$@POSS was used as pillaring agent, the microporosity as well as mesoporosity increased significantly (Fig. S2(b)). In the micropore range, the peaks in the pore diameter centred at 0.5 nm and 1.4 nm for Cu$^{2+}$@POSS_SWy-2 differ considerably from the broad peak at 0.7 nm observed when pillaring with POSS. The complexation of Cu$^{2+}$ with the nitrogen-containing ligands results in an increased rigidity of the POSS molecule, which might result in micropores, whose size is centred at 0.5 nm. Since Cu$^{2+}$@POSS is positively charged, the narrowly distributed pore sizes around 1.4 nm might be the result of electrostatic repulsion. Such an electrostatic repulsion could also be responsible for the larger amount randomly distributed mesopores, giving rise to the hierarchical micro-/mesoporous structure seen in TEM, which results in the increase in total pore volume reported in Table 1.

Adsortion isotherms and adsorption capacity for chloridazon and its metabolites

The adsorption isotherms of chloridazon on SWy-2, POSS_SWy-2 and Cu$^{2+}$@POSS_SWy-2 are shown in Fig. 5(a). In the Giles classification, these isotherms can be classified as L-type, which indicates that pristine and intercalated smectite clay have a medium affinity for chloridazon and there is no strong competition from the solvent. However, the slope of the initial part of the adsorption isotherms on Cu$^{2+}$@POSS_SWy-2 is much higher than on SWy-2, which illustrates Cu$^{2+}$@POSS_SWy-2 and POSS_SWy-2 have a higher affinity for chloridazon than SWy-2. For an initial concentration of 25 mg L$^{-1}$, the amount of chloridazon adsorbed on Cu$^{2+}$@POSS_SWy-2 (Q$_e$) is nearly 3 times of that on SWy-2 and 1.5 times that on POSS_SWy-2. To determine the adsorption capacity of the nanocomposites for chloridazon, the adsorption data were fitted with the Freundlich model and the result is shown in Fig. 5(b). The fit and the statistical analysis were performed with Origin software and the estimated parameters are given in Table 2. $K_f$ is an empirical constant related to the adsorption capacity (mg g$^{-1}$ L$^{-1}$), $n$ is the Freundlich exponent or a site energy heterogeneity factor, often used as a measure of isotherm nonlinearity, and the value of the correlation coefficient $R^2$ relates to the quality of isotherm fit: the closer the value is to 1, the better the fit. As can be seen from Table 2, $R^2$ values amounted to 0.992, 0.998 and 0.996 for SWy-2, POSS_SWy-2 and Cu$^{2+}$@POSS_SWy-2, confirming a good fit in all cases. The empirical constant $K_f$ increased 8 times for the adsorption of chloridazon on Cu$^{2+}$@POSS_SWy-2 compared to that for adsorption on the pristine clay. The higher adsorption capacity of Cu$^{2+}$@POSS_SWy-2 can be ascribed to two reasons: on the one
Fig. 5 Adsorption isotherms of (a) chloridazon (insert: structural model of chloridazon; grey = carbon, blue = nitrogen, red = oxygen and green = chlorine). (c) desphenyl-chloridazon (insert: structural model of desphenyl-chloridazon, colour code same as in (a)), (e) methyl-desphenyl-chloridazon (insert: structural model of methyl-desphenyl-chloridazon, colour code of the balls as in (a)), Freundlich model fitting for the adsorption of (b) chloridazon on Cu\(^{2+}\)@POSS_SWy-2, POSS_SWy-2 and SWy-2, Freundlich model fitting for the adsorption of (d) desphenyl-chloridazon and (f) methyl-desphenyl-chloridazon on Cu\(^{2+}\)@POSS_SWy-2 and SWy-2. X-ray photoelectron spectra of Chloridazon + Cu\(^{2+}\)@POSS_SWy-2: (g) Cu\(2p_{3/2}\) and (h) Cl\(2p\) core level regions.
hand, the significantly higher specific surface area of Cu\(^{2+}\)@POSS_SWy-2 provides more physisorption sites for chloridazon. On the other hand, the presence of Cu\(^{2+}\), which has a strong affinity for Cl- and N-containing organic molecules, enhances the chemisorption of chloridazon.

In order to check the adsorption mechanism of chloridazon on Cu\(^{2+}\)@POSS_SWy-2, XPS performed. As shown in Fig. 5(g), the Cu2p3/2 core-level region requires 5 components in the fit. The three components also present in the starting material, i.e. the first one due to Cu\(^{2+}\)--NH at a BE of 934.2 eV, the second one stemming from Cu\(^{2+}\)--NH\(_2\) at 936.0 eV and the third originating from Cu(II)O at 938.3 eV, contribute here differently to the Cu2p3/2 spectral intensity. The increased relative intensity of the Cu\(^{2+}\)--NH\(_2\) component (now 61.0%), and the decreased relative intensity of the Cu\(^{2+}\)--NH one (now 4.4%) confirm that the -NH\(_2\) group of chloridazon is very active towards the Cu\(^{2+}\) and replaces the weakly bounded -NH group. Additionally, the two new components at BE’s of 936.9 eV and 940.3 eV can be ascribed to the adsorption of Cl to Cu\(^{2+}\) and Cu(II)O, respectively. In fact, since the -Cl group of chloridazon is more electronegative than -NH\(_2\), Cu\(^{2+}\) to which it is attached becomes more electron poor, and hence appears at a higher BE.\(^{45}\) Likewise -Cl attached to Cu(II)O further decreases the electron density around the Cu\(^{2+}\), resulting in an additional component at higher binding energy.\(^{45}\) Correspondingly the Cl2p core-level region (Fig. 5(h)) can be fitted with three components at BE’s of 198.1 eV, 199.4 eV and 200.8 eV and originating respectively from Cl--Cu(II)O,\(^{46}\) Cl--Cu\(^{2+}\),\(^{45}\) and Cl-cyclic of chloridazon.\(^{47}\) The N1s core level region, reported in the Supporting Information, agrees with this interpretation.

Table 2 Parameters of Freundlich isotherm model \(Q_e = K_f \times C_1^{1/n}\) for the adsorption of chloridazon, desphenyl-chloridazon and methyl-desphenyl-chloridazon on SWy-2, POSS_SWy-2 and Cu\(^{2+}\)@POSS_SWy-2.

| Samples                   | \(K_f\)   | \(n\) | \(R^2\) |
|---------------------------|-----------|-------|---------|
| Chloridazon               |           |       |         |
| SWy-2                     | 58.22     | 0.900 | 0.992   |
| POSS_SWy-2                | 137.01    | 1.008 | 0.998   |
| Cu\(^{2+}\)@POSS_SWy-2    | 471.07    | 1.305 | 0.996   |
| Desphenyl-chloridazon     |           |       |         |
| SWy-2                     | 17.15     | 0.892 | 0.986   |
| Cu\(^{2+}\)@POSS_SWy-2    | 81.29     | 1.262 | 0.984   |
| Methyl-desphenyl-chloridazon |     |       |         |
| SWy-2                     | 10.55     | 0.861 | 0.991   |
| Cu\(^{2+}\)@POSS_SWy-2    | 25.68     | 0.934 | 0.984   |

Fig. 6 Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) data for (a) chloridazon, (b) Cu\(^{2+}\)@POSS_SWy-2 + chloridazon and (c) adsorption capacity for chloridazon of Cu\(^{2+}\)@POSS_SWy-2 after an increasing number of thermal regeneration cycles. (d) X-ray photoelectron spectrum of the Cu2p3/2 core level region of thermally regenerated Cu\(^{2+}\)@POSS_SWy-2.
The uptake of desphenyl-chloridazon on Cu\textsuperscript{2+}@POSS_SWy-2 was also found to be significantly higher than that on SWy-2, as seen from the adsorption isotherms shown in Fig. 5(c). At an initial concentration 25 mg L\textsuperscript{-1}, the Q\textsubscript{e} for desphenyl-chloridazon adsorbed on Cu\textsuperscript{2+}@POSS_SWy-2 is nearly 2 times of that on SWy-2. The Freundlich model fitting results are shown in Fig. 5(d) and the data listed in Table 2. Similarly to chloridazon, also for desphenyl-chloridazon the empirical constant \( K_f \) significantly increased for adsorption on Cu\textsuperscript{2+}@POSS_SWy-2 as compared to pristine SWy-2, and the Freundlich exponent \( n \) changed from 0.892 to 1.262, testifying to an improved adsorption capacity.

For the uptake of the other metabolite, methyl-desphenyl-chloridazon, the isotherms are shown in Fig. 5(e) and their fit with the Freundlich model in Fig. 5(f). Since methyl-desphenyl-chloridazon and desphenyl-chloridazon have a similar chemical structure, their adsorption behaviour is analogous. At an initial concentration of 25 mg L\textsuperscript{-1}, the Q\textsubscript{e} for methyl-desphenyl-chloridazon on Cu\textsuperscript{2+}@POSS_SWy-2 was determined to amount to 891 mg kg\textsuperscript{-1}, which is twice of that on SWy-2. The observed difference between the uptake of chloridazon, desphenyl-chloridazon and methyl-desphenyl-chloridazon is attributed to the different substituent group at the imino position. The significantly higher uptake capacity for chloridazon than for its two metabolites is presumably related to the phenyl group. On the one hand, the higher adsorption capacity can be ascribed to the hydrophobic effects because the siloxanes of the basal planes are considered to be hydrophobic, and therefore have a higher affinity for organic molecules containing aromatic rings.

This type of bonding is not present for desphenyl-chloridazon and methyl-desphenyl-chloridazon, where the phenyl group is replaced by hydrogen or by a methyl group. On the other hand, the phenyl group is electron richer than -CH\textsubscript{3} or -H, which means it can donate more electronic charge to -NH\textsubscript{2} and -Cl to make them more electronegative than in desphenyl-chloridazon and methyl-desphenyl-chloridazon. That results in Cu\textsuperscript{2+} having a relatively higher affinity for chloridazon.

### Thermal regeneration analysis

An important issue for assessing the potential of Cu\textsuperscript{2+}@POSS_SWy-2 as chloridazon adsorbent is to test its reusability; hence we regenerated the material thermally and followed the sorption behaviour over four adsorption/regeneration cycles. The TGA/DTA data for chloridazon, presented in Fig. 6(a), show that decomposition occurs around 290 °C. However, as discussed above (Fig. 6(b)), below 300 °C, the amino groups detach from POSS, while Cu\textsuperscript{2+} remains in the interlayer space of SWy-2. This means that after decomposition of the adsorbed chloridazon at 290 °C also the structure of Cu\textsuperscript{2+}@POSS_SWy-2 is slightly altered, but the pillaring Si-O cubes still remain intact. We therefore checked if the material still adsorbs chloridazon after this regeneration treatment. The adsorption capacity of Cu\textsuperscript{2+}@POSS_SWy-2 for chloridazon as a function of number of regeneration cycles is plotted in Fig. 6(c). While the pristine Cu\textsuperscript{2+}@POSS_SWy-2 adsorbs 4920±36 mg kg\textsuperscript{-1}, after four thermal regeneration cycles the adsorption capacity for chloridazon was 3260±61 mg kg\textsuperscript{-1}, i.e. reduced by 32.3%. To check whether this reduction is due to the oxidation of Cu\textsuperscript{2+} to Cu(I)O, which weakens the affinity to chloridazon, we checked the XPS spectrum of the Cu\textsuperscript{2+}_P2\textsubscript{3/2} core level region of thermally regenerated Cu\textsuperscript{2+}@POSS_SWy-2, as shown in Fig. 6(d). The spectrum clearly testifies to an important increase of Cu(I)O after the heat treatment. Despite this decrease in adsorption capacity after recycling, Cu\textsuperscript{2+}@POSS_SWy-2 can be considered as a potential adsorbent for chloridazon and its metabolites.

### Conclusions

We established a controllable and reproducible synthesis method for a new adsorbent of chloridazon and its metabolites, namely smectite clay pillared with copper complexed polyhedral oligosilsesquioxane. The successful intercalation of Cu\textsuperscript{2+} complexed POSS into the interlayer space of the clay was confirmed by FTIR, XRD and high-resolution TEM. X-ray photoelectron spectroscopy as well as thermogravimetric and differential thermal analysis illustrated the type of interaction between the host materials and the intercalated molecules, and also shed light on the intercalation yield. Porosimetry measurements revealed that pillared structures are created and gave the specific surface area of the hybrid nanostructures. The hybrid nanostructure obtained by intercalation Cu\textsuperscript{2+}@POSS into smectite clay showed a four times higher adsorption capacity for chloridazon, and a two times higher adsorption capacity for its metabolites, desphenyl-chloridazon and methyl-desphenyl-chloridazon, than the pristine SWy-2. This enhanced performance is attributed to the high specific surface area and the affinity of copper ions for nitrogen-containing herbicides. Cu\textsuperscript{2+}@POSS_SWy-2 maintains an excellent adsorption capacity even after several thermal regeneration cycles. These findings promise well for the potential of Cu\textsuperscript{2+}@POSS_SWy-2 as relatively low cost material for herbicides waste remediation.

### Author contributions

D. Gournis and P. Rudolf designed the experiments and finalized the manuscript. F. Yan conducted all the experiments and wrote the draft of the manuscript. K. Spyrou and E. Thomou participated in the synthesis, S. Kumar participated in the XPS experiments and in the analysis of the XPS data, H. Cao and Y. Pei participated in the SEM experiments, M. C. A. Stuart conducted the TEM experiments and participated in the analysis of the data. All authors discussed the results and commented on the manuscript.

### Conflicts of interest

There are no conflicts to declare.

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Copper complexed polyhedral oligomeric silsesquioxane pillared smectite clay (Cu^{2+}@POSS_SWy-2) exhibits excellent adsorption properties for chloridazon and its metabolites.