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# Simultaneous removal of five triazole fungicides from synthetic solutions on activated carbons and cyclodextrin-based adsorbents

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## Abstract

In this study, an adsorption-oriented process for the removal of fungicides from polycontaminated aqueous solutions was applied. To remove triazole fungicides from aqueous mixtures of propiconazole (PROPI), tebuconazole (TEBU), epoxiconazole (EPOXI), bromuconazole (BROMU) and difenoconazole (DIFENO), several materials used as adsorbents were compared using batch experiments, namely two conventional activated carbons (ACs) and five nonconventional cross-linked cyclodextrin (CD)-based materials ( $\alpha$ -CDP,  $\beta$ -CDP,  $\gamma$ -CDP,  $\alpha\beta\gamma$ -CDP mixture, and hydroxypropyl- $\beta$ -CDP). This article presents the abatements obtained. As expected, ACs exhibited the highest levels of triazole fungicide removal: the treatment lowered the five azoles by more than 99%, and adsorption was non-selective. Concerning CD-based materials employed for the first time for the removal of fungicides from polycontaminated aqueous solutions, results were interesting in particular for hydroxypropyl- $\beta$ -CDP: 1 g of

adsorbent placed in 1 L of solution containing 1 mg of each of five triazoles (5 mg in total) was able to remove over half of the fungicide amount (2.97 mg). The order obtained was the following: BROMU << PROPI  $\cong$  EPOXI < TEBU << DIFENO. This indicates that, in the mixture studied, strong competition prevailed among fungicides for the binding sites.

Keywords: Materials Science, Materials Chemistry

## 1. Introduction

Cyclodextrins (CDs) are synthetic substances obtained from the enzymatic degradation of starch [1]. These non-toxic, biodegradable molecules are produced on an industrial scale. They have a remarkable capacity to form inclusion complexes in solution and in the solid state with other molecules through host-guest interaction [1, 2, 3, 4]. Due to these numerous characteristics, these molecules have a wide variety of practical applications, including pharmacy, medicine, foods, cosmetics, chemistry, textile industry, and biotechnology [5, 6, 7, 8, 9, 10, 11]. Recent research on CD is also very active in environmental fields such as water and wastewater treatment. Different comprehensive reviews [12, 13, 14, 15, 16] have been reported on this topic.

CD-based materials have been suggested by several workers for the removal of pollutants from synthetic solutions as well as real effluent and wastewater. Some of the reported pollutants include dyes [5, 14, 17, 18, 19], phenol and derivatives [20, 21, 22, 23, 24], bisphenol A [25], 1-naphthol and 2-naphthol [26, 27], benzene and derivatives [24, 28], aniline [29], volatile organic compounds [12, 30], toluene [31], naphthenic acids [32], dibenzofuran derivatives [33], aromatic amines [34], polycyclic aromatic compounds [5, 35], polychlorobiphenyls [36], surfactants [37, 38], pharmaceutical residues [39, 40], metals [35, 41, 42, 43, 44], and rare earth elements [45]. However, there are few studies on the removal of fungicides using CD-based materials [5, 46, 47].

In Europe, numerous pesticides including fungicides have been listed as priority substances because they are considered to be toxic, bio-accumulative, and persistent (Directives 75/440/EC, 76/464/EC, 2000/60/EC, 2008/105/EC, 2013/39/EU). Among them, five triazole fungicides, namely propiconazole (PROPI), tebuconazole (TEBU), epoxiconazole (EPOXI), bromuconazole (BROMU) and difenoconazole (DIFENO), deserve particular attention. Due to their wide action spectra, these substances are commonly used in the wood industry, vegetable cultivation, horticulture, and agriculture to protect various products against fungal decay. However, their application may lead to their release into soil, air, and water, and this poses environmental problems. In France, triazole fungicides are on the list of priority pollutants defined by the French Water Agency because their presence also poses health problems. They could induce cross-resistance to azole

antifungals used in medicine for the treatment of some human pathogen fungi [48, 49, 50, 51].

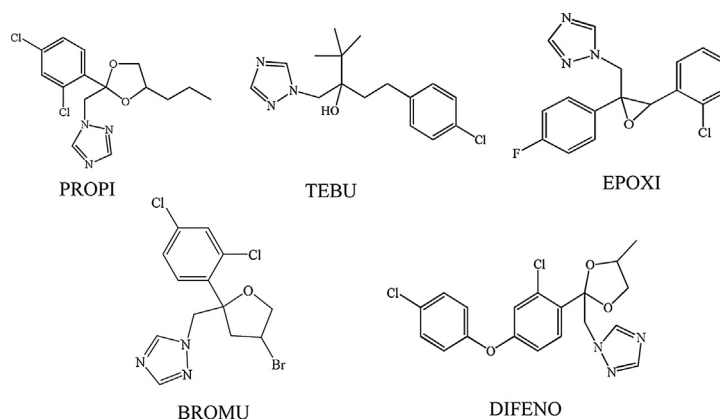
The main objective of this study was to investigate the adsorption capacities of (i) conventional materials such as activated carbons (ACs) under commercial form or modified with NaOH and (ii) nonconventional CD-based materials as adsorbents for treating poly-fungicide aqueous solutions, containing a mixture of five fungicides (PROPI, TEBU, EPOXI, BROMU and DIFENO). Here, studies concerning the effects of adsorbent dose and contact time on adsorption capacity were evaluated using the batch method.

## 2. Materials and methods

### 2.1. Materials

Acetonitrile Distol<sup>®</sup>, a range of products for organic trace analysis, was obtained from Fisher Scientific (Illkirch, France). Sodium chloride (99.5%) was purchased from Sigma Aldrich, Saint Quentin Fallavier (France). Five triazole fungicides (PROPI, TEBU, EPOXI, BROMU and DIFENO), analytical standard grade, were purchased from Sigma Aldrich, Saint Quentin Fallavier (France) and used without purification (see Fig. 1 and Table 1 for their chemical structure and characteristics). Aqueous synthetic solutions were prepared at concentrations of 1 mg L<sup>-1</sup> of each triazole in mixture (total of 5 mg L<sup>-1</sup>), or at concentrations of 5 mg L<sup>-1</sup> individually, with ultra-pure water produced by a Millipore Milli-Q Integral 3 system (Molsheim, France). Initial solution pH was 5 ± 0.1.

Commercial activated carbons (Panreac powdered form (PAC) and Chemviron CA201 granular form (GAC)) were selected for the adsorption studies and kindly supplied by Quimica SA (Spain) and Chemviron Carbon (Belgium), respectively. The main characteristics are described in Table 2. For the activation of the raw material, a previous procedure published by our group was used [52]: 5 g of the



**Fig. 1.** Chemical structure of 5 triazole fungicides.

**Table 1.** Characteristics of studied triazole fungicides.

	Molar weight <sup>a</sup>	CAS number	Solubility <sup>b</sup>	Log K <sub>OW</sub>
PROPI	342	60207-90-1	150	3.72
TEBU	307	107534-96-3	32	3.70
EPOXI	329	133855-98-8	6.63	3.30
BROMU	377	116255-48-2	500	3.24
DIFENO	406	119445-68-3	15	4.36

<sup>a</sup> In g mol<sup>-1</sup>.

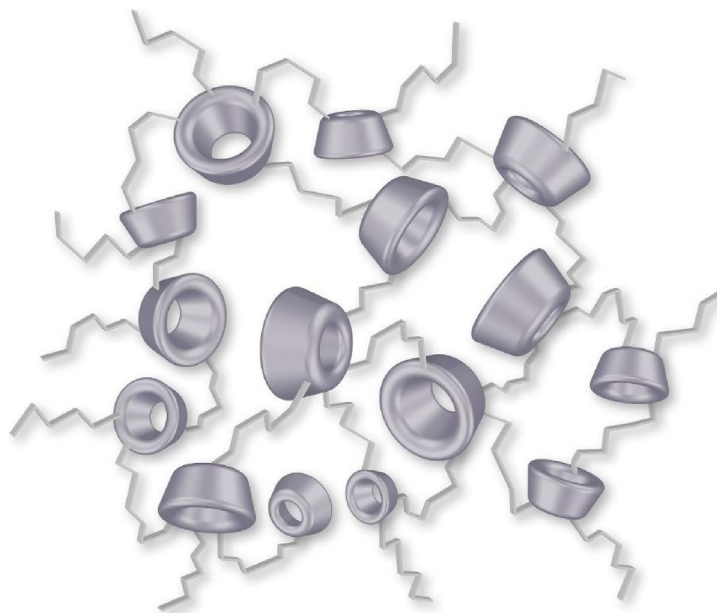
<sup>b</sup> In water at 20 °C; in mg L<sup>-1</sup>.

carbon were heated to boiling for 2 h in 100 mL of a concentrated NaOH solution (1 M), then cooled, filtered, extensively washed with water (NaOH ions in excess in the solution neutralized by HCl), dried under vacuum at 110 °C for 24 h and finally stored in a desiccator until used. The resulting materials were designated M-PAC and M-GAC (Table 2).

The cross-linked polymers were prepared by crosslinking  $\alpha$ -CD,  $\beta$ -CD,  $\gamma$ -CD, a mix of  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD, or hydroxypropyl- $\beta$ -CD (HP- $\beta$ -CD) using epichlorohydrin (Janssen Chimica, Beerse, Belgium). Epichlorohydrin is a bifunctional cross-linking agent containing two reactive functional groups that can form bonds with CD molecules and/or other epichlorohydrin molecules. The resulting polymers were a mixture containing CD units joined by repeating glyceryl linkers. A number of CD rings are interconnected, and a three-dimensional polymer network is formed as showed in Fig. 2. The synthesis and general description of CD-based materials have already been described in detail by our group [53]. A typical polymerization reaction was carried out as follows: in a thermostated reactor

**Table 2.** Characteristics of raw (PAC and GAC) and modified (M-PAC and M-GAC) activated carbons.

	PAC	M-PAC	GAC	M-GAC
Origin	wood		coal	
Activation mode	chemical		chemical	
Form	powder		granules	
Surface area (m <sup>2</sup> g <sup>-1</sup> )	1050	1055	1050	1027
pH of point of zero charge	7.6	10.8	7.2	10.9
Character		basic		basic
Composition (%)	C: 97.41	C: 88.43	C: 94.3	C: 91.21
*: obtained by difference	H: 0.59	H: 0.75	H: 0.57	H: 0.88
	N: 0.32	N: 0.31	N: 0.39	N: 0.31
	O*: 1.91	O*: 10.51	O*: 1.9	O*: 7.6



**Fig. 2.** Possible structure of insoluble materials containing cyclodextrins.

vessel, NaOH (40 mL, 50% w/w) containing NaBH<sub>4</sub> (5 mg) was heated to 50 °C. In this solution, CD powder (25 g) was dissolved. A desired amount of epichlorohydrin [53] was vigorously stirred with a magnetic stirrer. The viscosity of the solution started to increase and 2 h later a solid could be observed. Acetone (80 mL) was added and stirring and heating were continued for 10 min. After cooling, the insoluble polymer was poured into a beaker of cold water, filtered and the resulting solid was purified by several Soxhlet extractions with acetone and water. The polymer was then filtered and dried under vacuum at 60 °C for 24 h, crushed, and finally granulated to particles size of 150–250 μm in diameter (other characteristics: surface area 2.4 m<sup>2</sup> g<sup>-1</sup>, swelling capacity 5 cm<sup>3</sup> g<sup>-1</sup>, CD content 200 mg g<sup>-1</sup>; all the polymers used in this study possess similar characteristics). The resulting polymer materials were designated αCDP, βCDP, γCDP, mixCDP and HPβCDP.

## 2.2. Batch procedure

The experiments, conducted in triplicate, were realized using the batch method, for which kinetics and maximal adsorption capacities were determined. In each adsorption experiment, a given mass of adsorbents was added to triazole fungicide solutions in a tightly closed flask at 25 ± 1 °C. The solutions were stirred using a thermostatic mechanical shaker operating at 250 rpm. The adsorbent was removed after sedimentation for GAC and M-GAC, by filtration with a 12 μm paper filter for PAC and M-PAC, and by a 0.45 μm syringe filter for CD-based materials. To correct any adsorption of molecules on container and filters, control experiments

(without adsorbent) were also carried out in the same conditions. As a first step, a mixture of PROPI, TEBU, EPOXI, BROMU and DIFENO, at  $1 \text{ mg L}^{-1}$  each, was stirred with each adsorbent for 4 h in order to define the most efficient materials. (Preliminary experiments showed that this time was sufficient for removal of the fungicides.) Then, the effects of adsorbent dose (0.25, 0.5, 1, and  $2 \text{ g L}^{-1}$ ) for the selected AC and cross-linking polymer were evaluated for a contact time of 4 h, for triazoles in mixture at  $1 \text{ mg L}^{-1}$  each ( $5 \text{ mg L}^{-1}$  in total). The kinetics of adsorption was also determined for these two selected adsorbents at  $1 \text{ g L}^{-1}$  doses and an initial concentration of  $1 \text{ mg L}^{-1}$  pollutants. Studies were conducted for various time intervals (ranging from 1 to 240 min) to determine adsorption equilibrium time. Finally, the effect of triazole fungicides present alone (at a concentration of  $5 \text{ mg L}^{-1}$ ) or in the mixture (at a concentration of  $1 \text{ mg L}^{-1}$  each) was evaluated at the adsorbent dose of  $1 \text{ g L}^{-1}$ , for a contact time of 4 h. As the containers used for the batch were closed, no pH modification occurred. However, for both single and multi-fungicide solutions, it was noted that during the adsorption process with the materials, a slight pH variation did occur at the end of each experiment (an increase of between 0.2 and 0.5). The removal of triazoles, i.e., the adsorption performance that represents the ratio between the amount of adsorbed pollutant and its initial amount, is expressed as abatement percentage. This was calculated individually for each triazole.

### 2.3. Sample extraction and analysis

We recently developed an analytical methodology for the extraction and quantification of the five triazole fungicides in water [54]. The extraction method employed was based on liquid-liquid extraction and adapted from the one proposed by Wang et al. [55]. 10 mL of water sample (treated by adsorbents or untreated) were transferred into a 50 mL flat bottom flask and 20 mL acetonitrile and 3 g sodium chloride were added. The solutions were stirred by a magnetic plate for 10 min. The supernatant organic layers were recovered using a separating funnel and transferred to evaporation flasks for concentration, which was carried out with a 12-vessel Syncore Analyst (Büchi, Rungis, France). The volume of concentrated extracts was adjusted to 1 mL with acetonitrile in a volumetric flask. Then sample extracts were analyzed in the GC-MS/MS apparatus (Agilent, Massy, France), which was composed of a 7890A GC system, a 7000 GC triple quadrupole mass spectrometer, and an 80 GC CombiPAL autosampler. 1  $\mu\text{L}$  of the extract was injected at a temperature of  $300 \text{ }^\circ\text{C}$  in splitless mode under a constant flow of He (purity 99.9999%) at  $1.5 \text{ mL min}^{-1}$ , followed by a purge flow to split vent after 0.5 min. We used a (5% phenyl)-methylpolysiloxane HP5MS column (30 m  $\times$  0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness, Agilent 19091J-433). Total run time was 42.27 min. The temperatures of the transfer line, ion source and quadrupoles were 300, 300, and  $150 \text{ }^\circ\text{C}$  respectively. An electron-impact ion source at 70 eV was required.

**Table 3.** GC–MS/MS optimized parameters of the triazoles studied.

	Precursor ion	Product ion	Collision energy <sup>a</sup>	Retention time <sup>b</sup>	Limit of detection <sup>c</sup>
PROPI	173	146	18	26.361; 27.066	0.11
	173	109	30		
TEBU	125	99	20	27.353	0.07
	125	89	20		
EPOXI	192	138	12	26.648; 27.918	0.03
	192	111	32		
BROMU	173	145	26	28.312; 29.016	0.05
	173	109	30		
DIFENO	265	202	36	34.366; 34.485	0.28
	265	139	40		

<sup>a</sup> In V.<sup>b</sup> In min.<sup>c</sup> In  $\mu\text{g L}^{-1}$ .

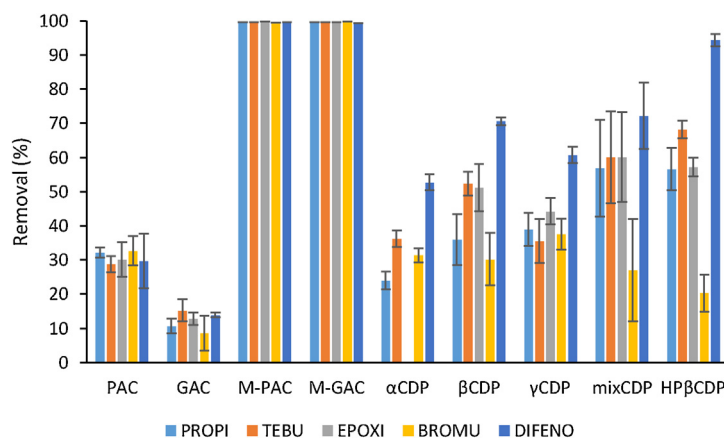
Nitrogen with a purity of 99.9% was produced by a NiGen LC-MS 40–1Claird generator (Gengaz, Wasquehal, France) and used as collision gas at  $1.5 \text{ mL min}^{-1}$ . Table 3 shows the optimized parameters in Multiple Reaction Monitoring mode.

### 3. Results and discussion

#### 3.1. Nature of the adsorbent

Fig. 3 compares the removal of PROPI, TEBU, EPOXI, BROMU and DIFENO, in mixture at  $1 \text{ mg L}^{-1}$  each, in water (initial pH = 5), by nine adsorbent materials (fixed conditions: adsorbent dose  $1 \text{ g L}^{-1}$ , contact time 4 h,  $T = 25 \text{ }^\circ\text{C}$ ). It clearly shows that the modified forms of activated carbon (M-PAC and M-GAC) were more efficient than their raw forms (PAC and GAC) and the CD-based materials (mean of  $99.7 \pm 0.1\%$  against  $21.5 \pm 9.9\%$  and  $47.0 \pm 20.1\%$  respectively, whatever the triazole). These results suggest that the adsorption capacities of modified AC, as compared to non-modified AC, is mainly due to the basic surface properties introduced by the NaOH treatment. Moreover, adsorption on M-PAC and M-GAC was non-selective (for example, abatement situated in the range  $99.5 \pm 0.0\%$  (BROMU) –  $99.8 \pm 0.0\%$  (EPOXI) on M-PAC), whereas competition occurred between molecules for adsorption on CD-based materials (abatement situated in the range  $0\%$  (EPOXI) –  $52.7\%$  (DIFENO) on  $\alpha\text{CDP}$  for example). The order of performance for CD-polymers were:  $\alpha\text{CDP} \ll \gamma\text{CDP} \sim \beta\text{CDP} < \text{mixCDP} < \text{HP}\beta\text{CDP}$ . CD-based materials also produced interesting results:  $1 \text{ g}$  of adsorbent placed in  $1 \text{ L}$  of solution containing  $1 \text{ mg}$  of each of five triazoles ( $5 \text{ mg}$  in total) was able to remove  $2.97 \text{ mg}$  of fungicide. Preliminary results also showed that, for both materials, the results were almost independent of pH between 4 and 7.





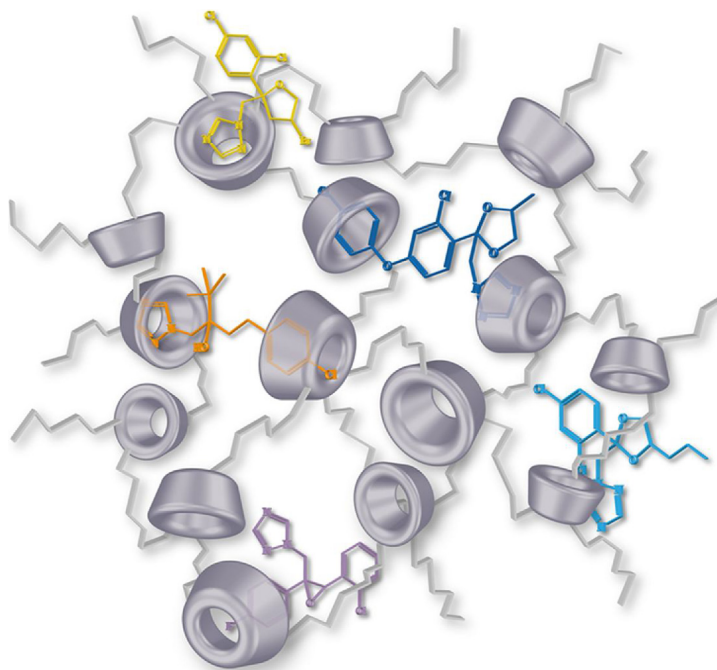
**Fig. 3.** Comparison of triazole adsorption capacities (% of removal) of various adsorbents (adsorbent dose  $1 \text{ g L}^{-1}$ ; initial triazole concentration:  $1 \text{ mg L}^{-1}$  each in mixture; contact time 4 h;  $n = 3$ ;  $T = 25 \text{ }^\circ\text{C}$ ).

For further experiments, the two most effective materials were selected: these were M-GAC for activated carbon, which produced results similar to M-PAC, but had the advantage of being easier to use (separation of the aqueous phase by sedimentation instead of filtration), and HP $\beta$ CDP for CD-based materials. Indeed, HP $\beta$ CDP material presented the best performance compared to the other polymers (mean of abatement for the 5 fungicides of  $59 \pm 27\%$ ), especially for DIFENO removal.

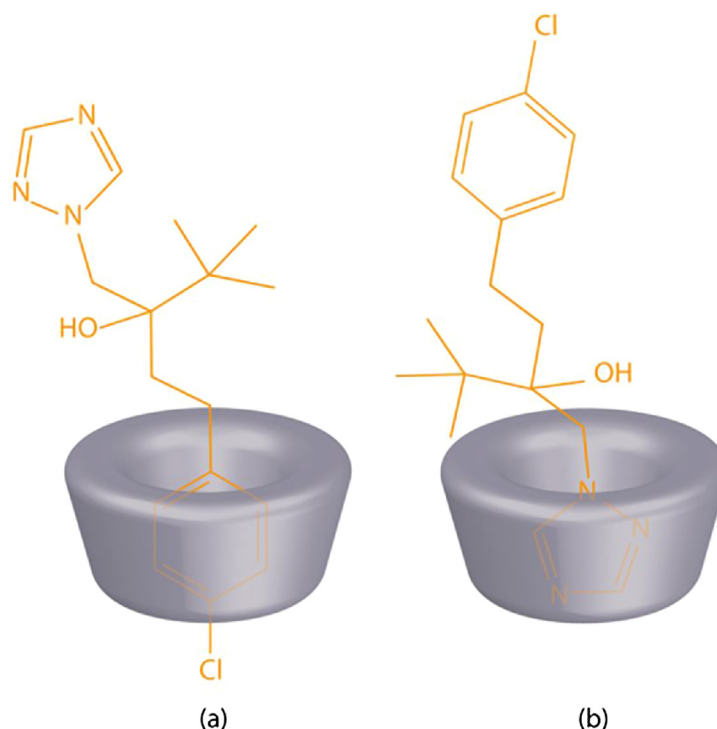
Several interactions could explain these results. Adsorption of organics by AC is a complex process, and there are still debates over how to fully explain the mechanisms involved during the adsorption process [56, 57, 58]. This is due to the fact that several forces and variables are involved, including the intrinsic properties of carbon (surface area, porosity, pore size distribution, point of zero charge, surface chemistry), the properties of the pollutants (solubility, molecular mass, etc.), and also solution properties (pH, temperature, etc.). In general, the forces include electrostatic, dispersive, and chemical interactions. As has been previously established by our group in another work [52], pesticide adsorption on AC is produced by dispersive interactions between the  $\pi$  electrons in the aromatic ring of the pollutant and the  $\pi$  electrons in the carbons, by physical adsorption in the carbon network, and by hydrogen bonding. In our study, the untreated carbons were modified by NaOH in order to introduce various oxygen functional groups on the carbon surface. Table 2 shows the elemental analysis of the samples of untreated and treated carbons (the oxygen content was obtained by difference). The results reported in this Table showed that modified carbons M-PAC and M-GAC had a higher amount of oxygen than untreated samples PAC and GAC. The oxidations also yielded carbons with the greatest  $\text{pH}_{\text{PZC}}$ . This suggested that samples treated with NaOH had a less acidic character than the untreated carbon, which favored adsorption process. In addition, no major differences in the specific surface areas of untreated

and treated samples were observed. This result suggested that the differences in the removal obtained by the samples were mainly due to their basic surface properties. Similar conclusions were proposed by Wang et al. [59].

For CD-based materials, the adsorption mechanism was also complex, probably simultaneously dominated by surface adsorption (due to the presence of interactions between  $\pi$  electrons from aromatic fungicides and the hydroxyl group of the polymer), diffusion into the polymer network, and chemisorption via the formation of an inclusion complex due to the presence of the CD sites (Fig. 4) [14, 20, 27, 35, 60]. In order to verify the role of the hydrophobic CD cavities in the adsorption process, the CD moieties have been replaced by sucrose units (sucrose possesses similar dimensions and chemical composition to those of the CD moieties) or starch, using the same experimental conditions for the synthesis. These polymers were not able to remove fungicides (< 10% and <20% for sucrose and starch polymers, respectively), suggesting that for EPI-linked CD the main adsorption mechanism of fungicides in these polymers was the inclusion within the CD cavities. In addition, we observed that an increase in the amount of CD in the material corresponded to an increase in the removal (unpublished data), which corroborated the idea that inclusion phenomena played a most important role in the mechanism. Recently, Fifere et al. [61] and Stepniak et al. [62] demonstrated that  $\beta$ -CD molecules were able to form inclusion complexes in solutions with propiconazole and tebuconazole, respectively. Fig. 5 shows two possible inclusion complexes between CD and tebuconazole.



**Fig. 4.** Schematic illustration for the removal of fungicide molecules by CD-based materials.



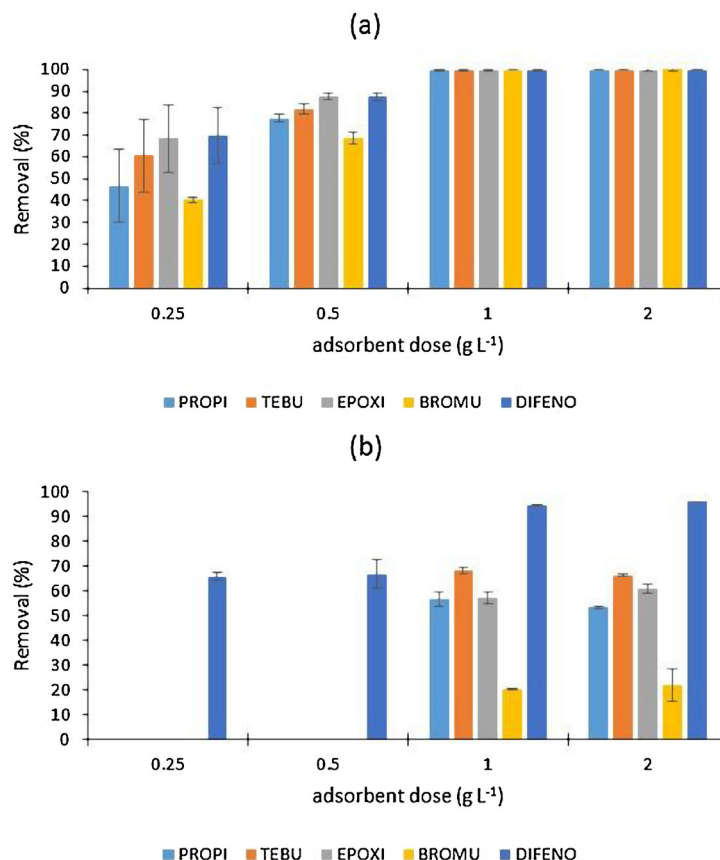
**Fig. 5.** Two possible inclusion complexes between CD and tebuconazole.

### 3.2. Effects of adsorbent dose

**Fig. 6** shows the results of the adsorption of a triazole mixture (at  $1 \text{ mg L}^{-1}$  each) on the two selected adsorbents by varying their concentration between  $0.25$  and  $2 \text{ mg L}^{-1}$  whilst maintaining a 4 h contact time. Whatever the adsorbent, increasing its concentration increased the removal of each triazole, due to the availability of more adsorption sites and the increase in adsorbent surface contact. For M-GAC, all triazole fungicides were retained, whatever the adsorbent dose employed, and maximal removal was achieved above  $1 \text{ g L}^{-1}$  (a plateau was reached around 100% for each triazole). For HP $\beta$ CDP, low doses retained only DIFENO (abatement  $>65\%$ ), and it was necessary to increase the adsorbent dose to  $1 \text{ g L}^{-1}$  to observe adsorption of all the fungicides. Nevertheless, the abatements were very different between triazole fungicides: DIFENO was the triazole molecule the best retained (maximal abatement  $>95\%$ ) in each experiment, and BROMU the least adsorbed (maximal abatement  $>20\%$ ).

### 3.3. Effect of contact time

**Fig. 7** shows the time-dependent removal behavior of triazole fungicides in mixture at  $1 \text{ mg L}^{-1}$  each, in relation to the adsorbents used (adsorbent dose:  $1 \text{ g L}^{-1}$ ). Although similar trends were observed in all plots, notable differences were only found in equilibrium time. Indeed, removal increased with time of contact for all

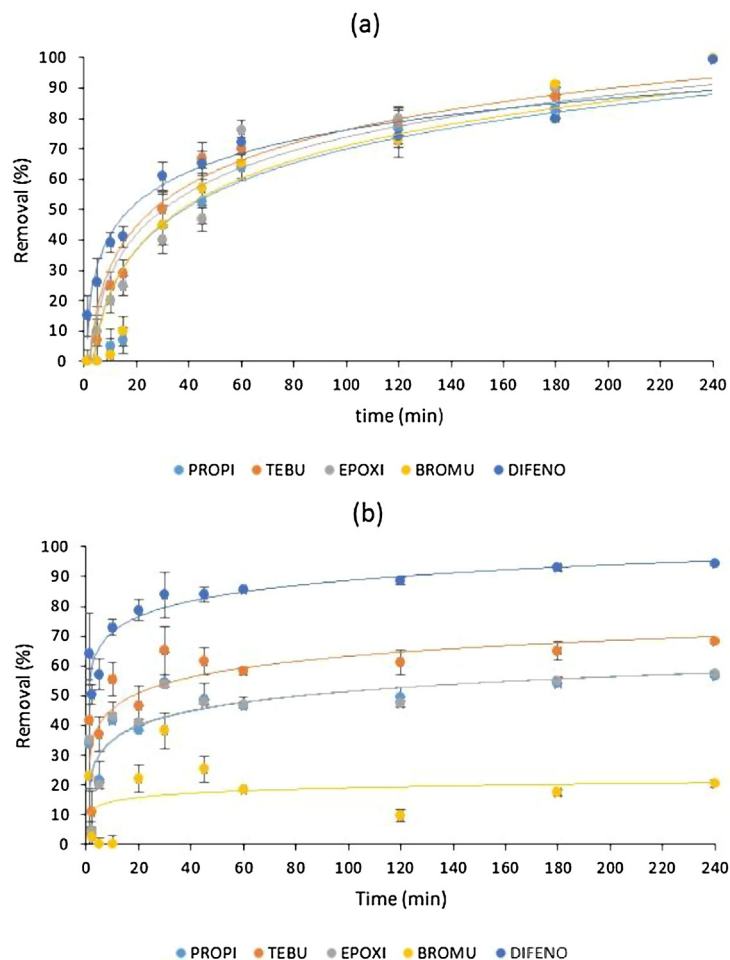


**Fig. 6.** Comparison of triazole fungicide removal (in %) between M-GAC (a) and HPβCDP (b) at different doses (initial concentration of 1 mg L<sup>-1</sup> of each fungicide in mixture; contact time 4 h; n = 3; T = 25 °C).

triazoles, reaching an equilibrium within 3 h for M-GAC (Fig. 7a) and only 20 min for HPβCDP (Fig. 7b). However, while all the triazole curves were superimposed for M-GAC, suggesting that no selectivity occurred between molecules for adsorption, this was not the case for HPβCDP. For the removal, the following order was obtained: BROMU  $\ll$  PROPI  $\cong$  EPOXI  $<$  TEBU  $\ll$  DIFENO. This indicates differences between fungicides for access to the CD cavity and formation of inclusion complexes. The differences in the degree of adsorption can be also attributed to the chemical structure of each fungicide (Fig. 1) and/or to the contribution of different interactions in the mechanism, such as hydrophobic interactions. Substituents on the aromatic ring can either withdraw or release electrons, thereby affecting the interactions between the fungicide and the material.

### 3.4. Individual solutions of triazole fungicides

Table 4 presents the removal of fungicides in a mixture at 1 mg L<sup>-1</sup> each (5 mg L<sup>-1</sup> in total) or alone at 5 mg L<sup>-1</sup> on M-GAC and HPβCDP. The results confirm



**Fig. 7.** Effect of contact time on triazole fungicide adsorption (removal in %) using (a): M-GAC and (b): HP $\beta$ CDP (adsorbent dose = 1 g L<sup>-1</sup>, concentration = 1 mg L<sup>-1</sup> for each fungicide in mixture; n = 3; T = 25 °C).

that no competition effect occurred with the use of M-GAC: globally, the same order of magnitude was obtained for each triazole alone or in presence of the others. For HP $\beta$ CDP, there were differences, especially for EPOXI and BROMU, which had opposite behaviors: BROMU, which was the least hydrophobic compound among the triazoles studied (see log  $K_{OW}$  values in Table 1), was retained better alone than in mixture, suggesting that the competition effects were greatest for this compound: other compounds tend to include preferentially in the apolar cavity of HP $\beta$ CDP. Indeed, Stepniak et al. [62] has shown that  $\beta$ -CD exhibits an affinity for apolar functional groups of fungicides such as TEBU, which was also better retained alone in our study. EPOXI was better retained in mixture than alone, suggesting not only the possible formation of inclusion complexes with CD, but also adsorption supported by  $\pi$ - $\pi$  interactions between the aromatic cycles of EPOXI and those of the other fungicides, favored by the presence of fluorine, a very electronegative element, on one of the aromatic cycles (see structure in

**Table 4.** Removal (in %) of triazole fungicides in a mixture (concentration of each molecule = 1 mg L<sup>-1</sup> i.e., 5 mg L<sup>-1</sup> in total) or in single solution (concentration = 5 mg L<sup>-1</sup>) onto M-GAC and HPβCDP (other conditions: adsorbent dose = 1 g L<sup>-1</sup>, contact time = 4 h; T = 25 °C).

	PROPI	TEBU	EPOXI	BROMU	DIFENO
	M-GAC				
in mixture	99.7 ± 0.3	99.7 ± 0.3	99.7 ± 0.2	99.8 ± 0.5	99.4 ± 0.3
alone	99.6 ± 0.9	94.8 ± 0.9	90.6 ± 0.7	82.8 ± 0.9	99.8 ± 0.2
	HPβCDP				
in mixture	56.6 ± 1.7	68.2 ± 2.6	57.2 ± 1.5	20.3 ± 1.3	94.3 ± 1.9
alone	50.0 ± 2.1	81.0 ± 0.6	25.4 ± 2.3	60.7 ± 3.2	99.1 ± 1.4

Fig. 1). This led to multilayer adsorption by creating  $\pi$ - $\pi$  bonds on the adsorbent surface between triazole fungicides already adsorbed and those yet in solution. The size of each molecule can determine its accessibility to the CD-based network. Thus, steric effects can also be advanced to explain the differences of adsorption observed for HPβCDP between triazoles when they were in mixture. Indeed, due to the presence of a voluminous atom of bromine, an element with an ionic radius of 196 pm, BROMU can represent a greater steric hindrance than other triazoles (ionic radius: 181 pm for the chlorine atom present in the five triazoles studied, 133 pm for the fluorine atom in EPOXI). This can decrease its ability to access the CD cavity in the presence of other triazoles.

#### 4. Conclusion

Results of adsorption in batch mode showed that both activated carbons and cyclodextrin-based materials are efficient adsorbents for the removal of fungicides present in polycontaminated solutions. Interesting affinities were found toward the mixture propiconazole + tebuconazole + epoxiconazole + bromuconazole + difenoconazole. As expected, activated carbons exhibited the highest levels of triazole fungicide removal, but adsorption onto carbons was non-selective. For hydroxypropyl-β-cyclodextrin-based materials at an adsorbent dose of 1 g L<sup>-1</sup>, the order obtained for the removal was the following: bromuconazole << propiconazole ≅ epoxiconazole < tebuconazole << difenoconazole. This indicates that, in the mixture studied, strong competition prevailed among fungicides for binding sites.

#### Declarations

#### Author contributions statement

Grégorio Crini: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Adeline E. Saintemarie, Audrey Jeanvoine: Performed the experiments.

Steffi Rocchi, Marc Fourmentin, Laurence Millon: Contributed reagents, materials, analysis tools or data.

Nadia Morin-Crini: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

### Competing interest statement

The authors declare no conflicts of interest.

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### Additional information

No additional information is available for this paper.

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