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# Removal of Hydrophobic Organic Pollutants and Copper by Alginate-Based and Polycaprolactone Materials

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**Abstract:** Organic pollutants (OPs) and heavy metals are environmental toxicants associated with great concerns. Decontamination processes are urgent for both, and the possibility to achieve their simultaneous removal from polluted waters is highly interesting. Additionally, in many cases, the effect of organic matter in the removal process is overlooked and must be considered. This work aimed to study the potential of alginate-based and polycaprolactone (PCL) materials to remove OPs and copper ions in the absence and presence of organic matter. The OPs investigated were the polycyclic aromatic hydrocarbons anthracene and benzo[a]pyrene, and the pesticide chlorpyrifos, both hydrophobic compounds. Copper (II) ions were used as a model of heavy metals. Alginate-based spheres were prepared by gelation, and PCL microparticles were obtained by oil/water emulsion solvent evaporation. The materials with the highest efficiencies for OP removal from aqueous solutions were those with activated carbon and PCL. Furthermore, the spheres with activated carbon could remove anthracene and copper simultaneously, even in the presence of humic acid. This work points to activated carbon–alginate spheres as a multifunctional adsorbent able to remove different pollutants and to PCL for potential applications in OP decontamination processes.

**Keywords:** anthracene; benzo[a]pyrene; chlorpyrifos; copper; organic pollutants; polycaprolactone; alginate; organic matter; adsorption

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## 1. Introduction

Every form of life on earth depends on water. However, according to World Health Organization (WHO), 2 billion people cannot access safe drinking water [1]. Yet, water used by industry, mining, agriculture, or other activities is a place for wastewater discharge. From these human activities, water contamination by organic pollutants (OPs) and heavy metals is described [2]. Various OPs are resistant to degradation, presenting a persistent toxicological risk to wildlife and people.

Anthropogenic activities like residential heating, asphalt production, and diesel exhausts are some of the most impacting activities generating polycyclic aromatic hydrocarbons (PAHs) [3]. Moreover, the presence of PAHs in drinking water has been described by different authors [4–6]. In parallel, chlorpyrifos is a worldwide used organophosphorus pesticide that aims to control agricultural pests and to which individuals are becoming more exposed [7].

The presence of PAHs and organophosphorus pesticides in water and their health effects remains a worrying issue. For example, benzo[a]pyrene (BaP) is a PAH present in drinking water, associated with different tumors, and considered by the Environmental Protection Agency of the United States (EPA) and by the International Agency for Research on Cancer as carcinogenic to humans [8]. Chlorpyrifos has also been reported in drinking water. EPA underlines its damaging effects related to acetylcholinesterase inhibition and its potential for neurodevelopmental effects [9]. Additionally, autoimmunity biomarkers were found in human trials of exposure to chlorpyrifos (or other pesticides) and diesel exhausts [10].

Other pertinent players in environmental pollution are heavy metals which greatly impact the environment at the toxicological level [11]. These pollutants are common in water, and exposure to heavy metals and metalloids is associated with cancer and cardiovascular disorders [12,13].

The bioaccumulation of pollutants like OPs and heavy metals in living systems is of great concern. Likewise, the decontamination of these pollutants in the environment is of high priority, and new approaches are required. Three reviews suggest updates on this topic [2,14,15]. The strategies include physical, chemical, and biological remediation methods [14]. Nevertheless, the enzymatic detoxification of organophosphorus compounds is challenging [16], and adsorption remains an attractive technique for water treatment.

Developing a good adsorbent material includes its cost-effectiveness, reusability, and biodegradability. The polysaccharide alginate and the synthetic polymer polycaprolactone (PCL) are biodegradable materials with multifunctional applications in the environmental and biomedical fields [17–22]. Alginate binds copper ions [23], and calcium alginate beads remove heavy metals from water media [18,19]. Applied to metal-plating industrial effluent, alginate beads could simultaneously uptake zinc, nickel, and iron ions [19]. Additionally, PCL materials have been described by other authors to adsorb PAHs and heavy metals [20,21]. However, it is not clear if the adsorbing capabilities of these materials are effective with a more soluble organic pollutant such as chlorpyrifos, in comparison with classic adsorbents such as activated carbon, and how they perform in competition with organic matter commonly present in waters.

It is undeniable that a decontamination strategy targeting different pollutants is a very attractive process. However, the complex composition of natural water and wastewater matrices is a challenge to decontamination processes [14]. For example, the presence of organic matter may interfere with the pollutants' dynamics, such as adsorption and degradation [24]. Indeed, a study revealed that humic acid—a humus component—greatly inhibits the adsorption of OPs to carbon materials [25]. Many OPs, such as PAHs and some pesticides, present low solubility and high hydrophobicity that favor binding to humic acid and other forms of organic matter in water and soil, hindering the elimination of these pollutants [26,27]. The sequestration of OPs by humic acid is related to the hydrophobicity of the solute. Data suggest it to be more effective with pollutants of medium- to high-hydrophobicity, with a log octanol-water partition coefficient (log Kow) >4.5 [27]. PAHs and some pesticides are hydrophobic pollutants, and for example anthracene, BaP, and chlorpyrifos present a log Kow = 4.45, 6.13, and 4.96, respectively [28–30]. In fact, humic acid has been described to bind to PAHs and copper ions [26,31].

This work aimed to evaluate the adsorbent potential of alginate- and PCL-based materials to address the need for multi-target adsorbents and withstanding the competition of organic matter in the media. The efficiency of the materials was investigated for the removal of individual OPs or the simultaneous removal of OPs and copper ions from an aqueous solution in the absence and presence of organic matter. To the best of our knowledge, this is the first study investigating alginate- and PCL-based materials for their multi-target removal capacity for anthracene, chlorpyrifos, and copper ions.

## 2. Materials and Methods

### 2.1. Reagents

The OPs were obtained from Sigma-Aldrich (St. Louis, MO, USA), anthracene (cat. no. A89200, purity $\geq$ 97%), BaP (B1760, purity $\geq$ 96%), and chlorpyrifos (45395, purity $\geq$ 98%). Activated carbon was obtained from MERCK (Darmstadt, Germany) (102186). Polycaprolactone, potassium hydrogen phthalate, sodium alginate, and sodium dodecyl sulfate (SDS) were supplied by Sigma-Aldrich (704105, 33325, A2033, and L3771), graphene was obtained from TCI (G0499), and calcium chloride was purchased from Panreac (1023820500). Copper

(II) chloride was obtained from Acros (206345000, purity ≥ 98%) as well as humic acid (120861000). All other chemicals used were HPLC or analytical reagent grade and purchased from Fisher Chemical (Geel, Belgium) or Chem-Lab/Honeywell (Seelze, Germany).

### 2.2. Preparation of Alginate-Based Materials

The alginate-based materials consisted of alginate spheres (AS), alginate spheres containing activated carbon (AS-AC), and alginate spheres containing graphene (AS-G).

Alginate spheres were prepared by calcium-induced gelation as described before [18,19]. Briefly, sodium alginate (2% *w*/*v*) solutions were prepared by powder dissolution in distilled water under agitation for at least 12 h. Subsequently, alginate solution was added drop-by-drop to a 200 mM $CaCl_2$ solution, where spheres were kept until complete gelation. Before use, spheres were oven-dried at 35–40 °C. For AS-AC and AS-G, activated carbon 1% (*w*/*v*) or graphene 0.1% (*w*/*v*) were dissolved in water in the first step with sodium alginate.

For microscopic observation, the spheres were transferred for the microscopic stage using a clamp.

### 2.3. Preparation of PCL Microparticles

PCL microparticles were prepared by the oil/water emulsion solvent evaporation method described in [22]. Briefly, PCL 5% (*w*/*v*) was dissolved in dichloromethane and poured in water containing 0.5% (*w*/*v*) SDS. Continuous agitation for 1 h at 1000 rpm at room temperature allowed complete evaporation of dichloromethane. Particles were collected using filter paper, washed three times with distilled water (a volume double of the pre-evaporation step), and dried at room temperature.

For microscopic analysis, the spheres were immersed in a droplet of methylene blue, dried overnight, and transferred with a brush into a Neubauer chamber. Next, the chamber was placed at the microscopy stage, and the spheres observed and captured with phase contrast at 40× magnification.

### 2.4. Humic Acid Preparation

Solutions of humic acid were prepared by adapting the method described in [32]. The humic acid powder was dissolved in 100 mM of NaOH and stirred at room temperature, then centrifuged at 7000 rpm, 4 °C for 20 min by using a Heraeus Biofuge Stratos Centrifuge. The supernatant was collected, 0.5 M of phthalate buffer was added, and the pH was adjusted to 4.5. Another identical centrifugation was performed, and the supernatant was collected. Before use, the humic acid solutions were filtered through a 0.2 μm pore filter. The concentration was determined by completely drying at 100 °C and subtracting the dried blank weight from the weight of the dried humic acid solution.

Considering that surface waters contain natural organic matter in the range of 0.1–20 mg/L [33], we decided to use a concentration of 100 mg/L for humic acid in the removal assays ensuring a higher concentration found in water but also mimicking the treatment of wastewater with high organic loads.

### 2.5. Removal Assays

The removal experiments addressed the removal of different classes of compounds, namely PAHs, organophosphorus pesticides, and heavy metals. To select pollutants, we looked for different parameters. Anthracene was selected as a more typical model for PAHs. The interest for BaP was related to its toxicity and presence in drinking water [34]. Chlorpyrifos was selected as one of the most used pesticides worldwide, and copper was selected due to its easy laboratory management.

The removal efficiency of the different materials was studied using batch removal assays with aqueous solutions containing PAHs, chlorpyrifos, and copper (II) ions. The concentrations selected for each pollutant were based on concentrations reported by other authors in similar studies [35–37]. Anthracene and BaP were tested at an initial concentration of 1 mg/L, chlorpyrifos at 25 mg/L, and copper (II) ions at 4 mg/L. Since the stock solutions of the OPs were in acetonitrile, the assay media contained 1% acetonitrile. Each tested material was weighed to reach an adsorbent dose of 12 mg/mL in the assay, except when stated differently. The adsorption assays were performed with a volume of 1 mL when investigating the removal of a single pollutant which was increased to 1.5 mL when investigating the simultaneous removal of different pollutants. This procedure was performed due to the need for higher volumes for copper quantification using flame atomic absorption spectroscopy. The assays were conducted in the dark, at room temperature, and with continuous agitation. At the end of the assays (24 h), pH was measured to ensure no significant changes occurred relative to the initial pH 6.

### *2.6. Chemical Quantification*

PAHs and chlorpyrifos were quantified by a reverse-phase HPLC C18 column in an Agilent 1100 system. Samples were manually injected using a syringe (injection volume 20 μL), and the mobile phase consisted of acetonitrile:water (85:15) with a flux of 1 mL/min. The UV detection wavelengths were 251 nm for anthracene, 266 nm for BaP, and 225 nm for chlorpyrifos. The retention time of chlorpyrifos, BaP, and anthracene was 7.7, 13.8, and 6.7 min, respectively. Representative chromatograms of each compound are shown in Supplementary Figure S1. Calibration curves for each pollutant were obtained using standards with an acetonitrile concentration of 1% corresponding to the concentration in the samples injected. The chromatographic areas obtained for the different pollutants during the removal assays fitted within the corresponding calibration curves. The limit of detection for anthracene, BaP, and chlorpyrifos was 13, 4, and 150 μg/L, respectively. Due to the hydrophobicity and volatility of the hydrophobic compounds tested, the removal ratios were calculated in comparison to control assays (OPs without any adsorbent). Additionally, blank tests were also performed with the adsorbents but without OPs to check if any compound was released by the materials that could interfere with the pollutants' quantification.

Quantification of copper was attained by using the Varian SpectrAA 55B model of flame atomic absorption spectrometer equipped with an air/acetylene burner. At 24 h, the samples were filtered or centrifuged to separate the adsorbent materials from the liquid phase. Then, the supernatant was introduced into the atomic absorption system through an inlet tube into the nebulizer. A hollow cathode lamp was used for a selected wavelength of 327.6 nm, and the additional parameters were adjusted according to the manufacturer's recommendations. Prior to quantification, a calibration curve was obtained with copper (II) nitrate standards.

## 3. Results and Discussion

The materials developed in this work are represented in the following figures. Figure 1 shows representative images of alginate-based spheres obtained after drying and their microscopic visualization, and Figure 2 shows representative images of PCL microparticles. These materials were initially tested for the removal of the hydrophobic OPs chlorpyrifos and BaP, both highly hydrophobic compounds (log Kow between 5 and 6). Then, the materials showing the best removal performance were selected and tested for the removal of anthracene, a more typical model for PAHs, with a three-ring structure and less hydrophobic (log Kow 4.45) than BaP. Next, for testing the competition with humic acid in the media, two materials showing the best removal efficiency were assayed for the simultaneous removal of anthracene and copper (II) ions. Finally, the material showing the highest multi-target capacity was selected, and the simultaneous removal of chlorpyrifos, anthracene, and copper was investigated in the presence of humic acid.

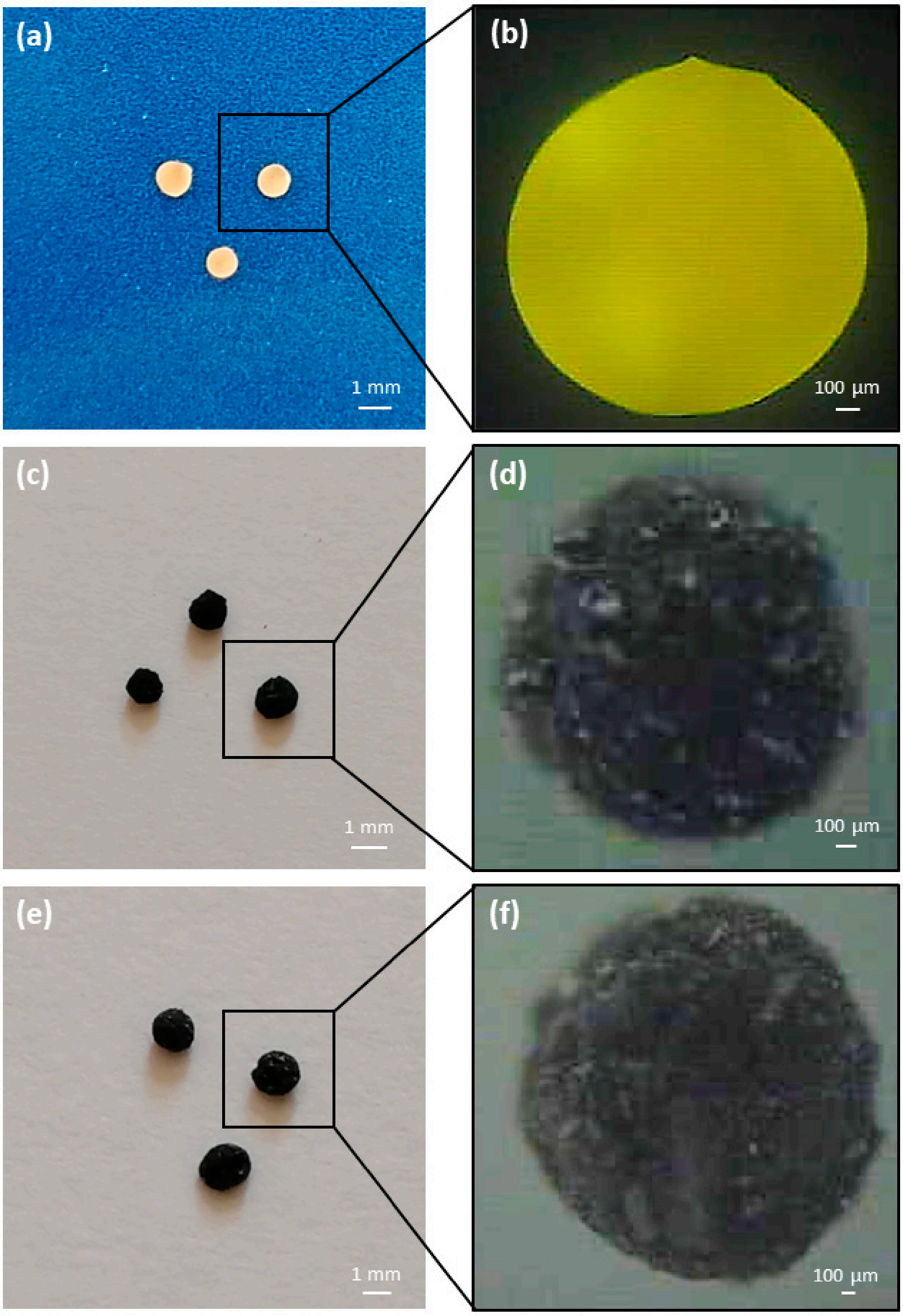
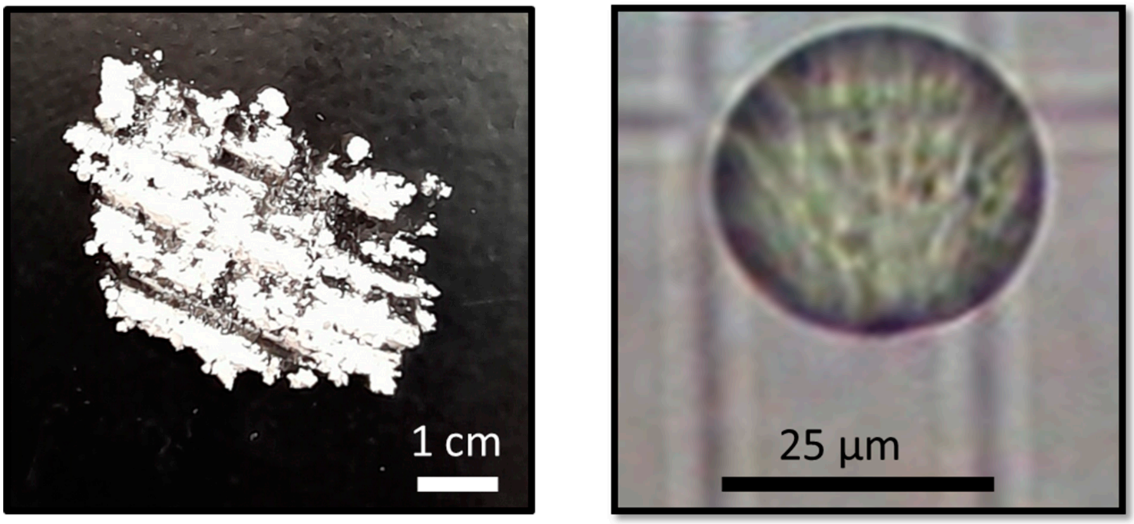


**Figure 1.** Representative photographs (**a**,**c**,**e**) and micrographs (**b**,**d**,**f**) of the alginate-based materials prepared: (**a**,**b**) Alginate spheres, diameter = 991 ± 72 µm (*n* = 30); (**c**,**d**) Alginate spheres with encapsulated graphene, diameter = 1200 ± 98 µm (*n* = 30); (**e**,**f**) Alginate spheres with encapsulated activated carbon, diameter = 1722 ± 115 µm (*n* = 30). Micrographs were obtained using a Canon PowerShot A640 camera coupled to a Zeiss Axiotech microscope and analyzed for diameter length using Axionvision software (version 4.8).

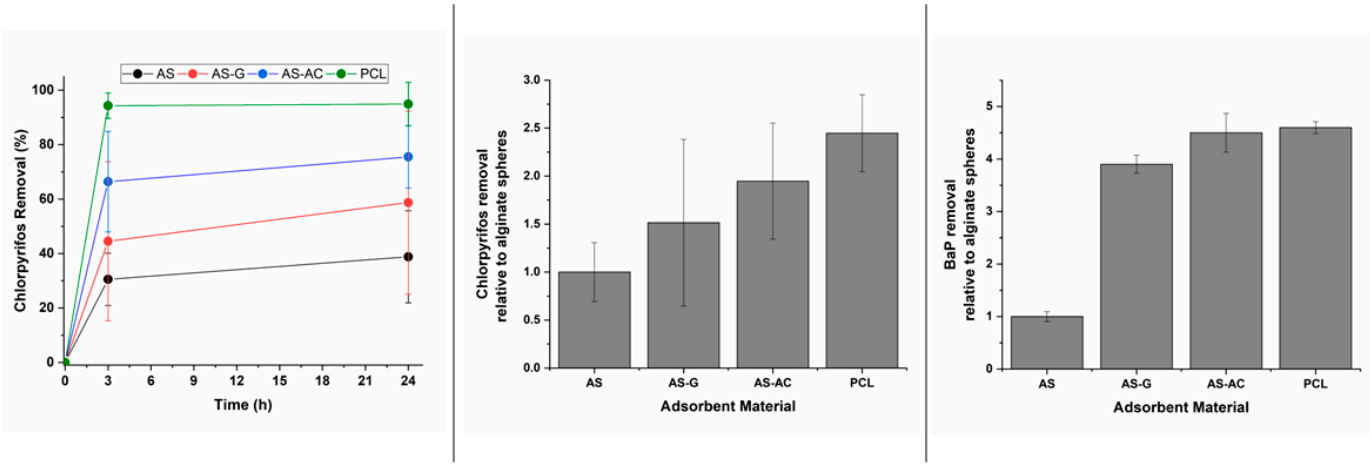


(**a**) (**b**)

**Figure 2.** Representative images of polycaprolactone (PCL) microparticles. (**a**) Photograph of PCL microparticle powder visible to the naked eye, and (**b**) micrograph of a PCL microparticle using phase contrast. The diameter of PCL microparticles was 30 ± 12 µm (*n* = 27). Micrograph obtained using a Nikon Coolpix 995 camera coupled to a Nikon Eclipse E200 microscope.

### *3.1. Efficacy of the Different Materials in the Removal of Hydrophobic Organic Pollutants from Aqueous Solutions*

The pollutant removal efficacy of the different materials was initially studied with the pesticide chlorpyrifos (Figure 3a,b). The tested materials were alginate-based spheres AS, AS-AC, AS-G, and PCL microparticles.



(**a**) (**b**) (**c**)

**Figure 3.** Removal of chlorpyrifos and BaP from aqueous solutions by the different adsorbent materials: alginate spheres (AS), alginate spheres with graphene (AS-G) or with activated carbon (AS-AC), and polycaprolactone microparticles (PCL). (**a**) Kinetics of the removal of chlorpyrifos; (**b**) Comparison of the efficiency of removal of chlorpyrifos by the different materials, relative to the removal provided by AS, in 24 h assay; (**c**) Comparison of the efficiency of removal of BaP by the different materials, relative to the removal provided by AS, in 24 h assay. The results shown are the mean ± SE from triplicate experiments.

Experiments started with kinetic assays. However, the volatility of the OPs dictated the difficulty of following the kinetics with detail, and it was decided to evaluate the removal of the pollutants at shorter and longer time points, 3 h and 24 h. These time points afforded information on the beginning of the removal process with already significant removal rates and identifying the materials achieving higher removal rates for extended periods. The data obtained provided helpful information on the kinetics of the process and unequivocally demonstrated the ability of the adsorbents to uptake the pesticide.

Spheres of alginate per si (AS) removed chlorpyrifos from the aqueous solution at 3 h and 24 h with a removal percentage of 30 ± 10% and 39 ± 17%, respectively (Figure 3a). The alginate spheres also removed 19 ± 6% BaP at 24 h (Supplementary Table S1). These results showed that the calcium alginate spheres could remove hydrophobic OPs from aqueous media. However, the removal capacities were low compared to those described for heavy metals [18,19]. Indeed, the ability of plain alginate to uptake the OPs was limited (<50%), so new materials were developed: AS-AC, AS-G, and PCL. These new materials were more efficient at removing chlorpyrifos from the aqueous solution at 3 h and 24 h (Figure 3a). To better comprehend this relation, the relative removal efficiency for chlorpyrifos by the different materials was compared to AS and is represented in Figure 3b. The AS-G, AS-AC, and PCL materials were 1.5, 1.9, and 2.4 times more efficient in removing chlorpyrifos, respectively, when compared to AS. This trend was not unique to chlorpyrifos since it was also observed in the removal of BaP from aqueous solutions (Figure 3c). In this case, AS-G, AS-AC, and PCL were 3.9, 4.5, and 4.6 times more efficient in removing BaP, respectively, when compared to calcium alginate alone.

The similar results obtained for chlorpyrifos and BaP, with a removal capacity represented AS < AS-G < AS-AC < PCL, led to the subsequent studies on the removal of anthracene, which is a more generalized model of PAHs. However, based on the previous results, the focus was on the most efficient materials, i.e., AS-AC, AS-G, and PCL. The removal kinetics was followed and, also in this case, it was observed that all materials tested were able to remove anthracene. Moreover, the removal efficiency followed the previous capacity observed for chlorpyrifos and BaP, i.e., AS-G < AS-AC < PCL. The kinetics of anthracene removal is depicted in Figure 4. Once again, the PCL microparticles enabled the faster uptake of anthracene. A complete PAH removal from the aqueous solution at 3 h was observed (Figure 4), similar to what was observed for chlorpyrifos (Figure 3a).

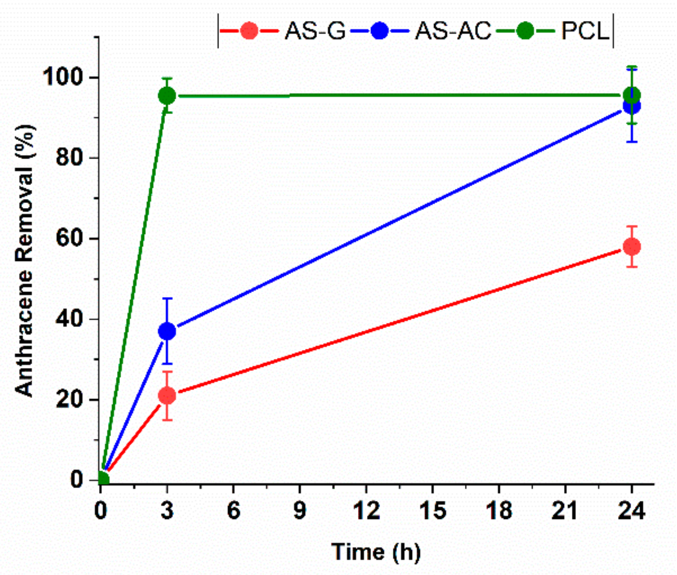


**Figure 4.** Kinetics of the removal of anthracene from aqueous solutions by the different materials: alginate spheres with encapsulated graphene (AS-G) or activated carbon (AS-AC) and polycaprolactone microparticles (PCL). The results shown are the mean ± SE from triplicate experiments.

The removal efficiencies of the new-developed materials tested for the different OPs are resumed in Supplementary Table S1. AS-AC and PCL were the most efficient adsorbents of all OPs tested. AS-AC showed a removal efficiency for PAHs close to 90% or higher.

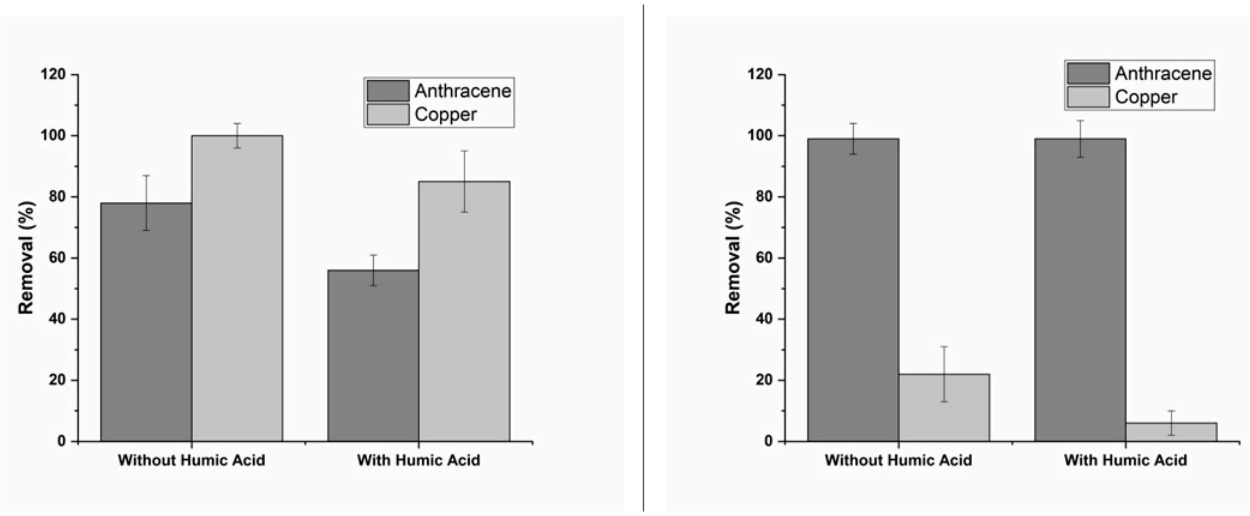
Interestingly, these values are similar to those recently reported for an activated carbon-based magnetic composite [38]. The PCL spheres achieved removal efficiencies superior to 90% for both chlorpyrifos and the PAHs tested. Moreover, in terms of kinetics, it is possible to see that PCL microparticles ensure the fastest removal of OPs from the media (Figures 3a and 4).

The higher efficiency of the AS-AC and PCL materials to remove OPs was considered to follow the subsequent studies where simultaneous removal of OPs and copper ions was investigated in the absence and presence of organic matter.

### *3.2. Simultaneous Removal of Anthracene and Copper Ions in the Absence and Presence of Humic Acid*

For these experiments, the PAH anthracene and the heavy metal copper were simultaneously present in the aqueous solutions treated with the adsorbents. As a model of heavy metals, copper (II) was used due to its easy laboratory management and because its binding to humic acid is recognized [31]. Additionally, the presence of organic matter in natural waters and wastewater was mimicked using humic acid as described in the methods. A lower adsorbent dose (6 mg/L) was used in these competitive conditions.

The AS-AC spheres were selected to start the multi-target removal capacity experiments due to the alginate spheres' excellent capacity for heavy metal uptake [18,19]. As represented in Figure 5, the AS-AC spheres maintained their capacity to remove anthracene from aqueous media containing copper ions, even in the presence of humic acid. However, it is noticeable that humic acid affects the removal capacity of AS-AC, provoking a decrease in anthracene removal from 78 ± 9% to 56 ± 5% (Figure 5a). Regarding the uptake of copper by AS-AC, it was observed that 100 ± 4% removal was attained in the presence of anthracene and that 85 ± 10% removal was attained in the presence of anthracene plus humic acid (Figure 5a). Nevertheless, the metal removal performance of AS-AC was higher than the removal of anthracene. Comparatively, the presence of humic acid also interfered with copper adsorption, leading to a decrease in the percentage of removal by 15% (Figure 5a).



(**a**) (**b**)

**Figure 5.** Simultaneous removal of anthracene and copper (II) ions in the absence and presence of humic acid by: (**a**) alginate spheres with activated carbon; and (**b**) polycaprolactone microparticles. The assays were carried out with aqueous solutions containing the two pollutants at initial concentrations of 1 mg/L anthracene and 4 mg/L copper ions. In the assays with humic acid, the concentration was 100 mg/L. An adsorbent dose of 6 mg/mL was applied, and the removal was measured at 24 h. The results are the mean ± SE from triplicate experiments.

The results demonstrate the ability of AS-AC to uptake both anthracene and copper ions from aqueous media. However, a higher adsorbent dose might be necessary to achieve complete removal of the PAH. It is also clear that humic acid competes for anthracene and copper, as expected from the well-established ability of humic acid to bind hydrophobic and cationic solutes [27,31]. Indeed, the binding of PAHs and heavy metals to humic acid has been previously described [26,31].

However, despite the high concentration of humic acid present in the assays (100 mg/L), AS-AC provided remarkable uptake of both pollutants from aqueous solutions.

The PCL microparticles showed to be highly efficient in removing anthracene. Its removal capacity regarding anthracene was not affected by the presence of copper or humic acid. As represented in panel B of Figure 5, the anthracene removal capacity of PCL microparticles was 99 ± 5% in the presence of copper and 99 ± 6% in the presence of copper and humic acid. Next, PCL microparticles were tested for their capacity to remove copper ions. It is possible to observe that PCL can remove this heavy metal model at a lower degree when compared to the removal of anthracene. PCL adsorbed only 22 ± 9% of the copper ions available in the solution (Figure 5b).

Moreover, the presence of organic matter affects the low capacity of PCL to remove copper from aqueous solution provoking a decrease in the percentage of removal to 6 ± 4% (Figure 5b). These results indicate that for heavy metals, PCL is not the preferred material to be applied. Nevertheless, their fast and efficient removal of anthracene should not be ignored (Figures 3–5).

Comparing both materials, PCL is more robust in removing hydrophobic OPs, including anthracene, in complex media containing copper ions and organic matter. Another work showed the efficiency of PCL electrospun nanofibrous membranes to adsorb PAHs [20]. The study identified the sorption mechanism to occur through hydrophobic interactions [20], and the binding of PAHs to activated carbon is described to occur through $\pi$-$\pi$ or H-$\pi$ interactions [39]. Regarding PCL adsorption of heavy metals, a recent study reported copper adsorption from water by an electrospun nanofiber membrane containing PCL attaining an adsorption capacity at the equilibrium of 22.8 mg/g of adsorbent [21]. The results of this work suggest an improvement in attaining a removal of 170 mg/g of PCL microparticles at 24 h. Nevertheless, compared to AS-AC, the PCL microparticles were revealed to be much less adequate for copper uptake.

On the contrary, AS-AC demonstrated a solid capacity to simultaneously remove anthracene and copper. Despite this removal being affected by humic acid, it was maintained with a removal percentage value considered extremely useful. Both materials are of great interest for water treatment. To choose between the application of PCL and AS-AC, water composition regarding OPs and heavy metals must be known. For water treatment where PAHs are abundant but contain low concentrations of copper/heavy metals, the PCL microparticles are the most suitable material to use. For waters presenting PAHs and copper, then AS-AC is a better option.

Since many polluted waters going for treatment contain different organic pollutants and heavy metals, the ability of AS-AC to face a more complex system was investigated.

### *3.3. Simultaneous Removal of Hydrophobic Organic Pollutants and Copper Ions in the Presence of Humic Acid*

The AS-AC adsorbent was challenged for its multi-target removal capacity with aqueous solutions containing the three pollutants (pesticide, PAH, and heavy metal) and humic acid. The results are presented in Table 1. AS-AC maintained its capacity to simultaneously remove all the pollutants from media, although at different percentages. The results show that indeed AS-AC spheres highly adsorb copper, followed by anthracene and chlorpyrifos, even in the presence of humic acid.

**Table 1.** Simultaneous removal of chlorpyrifos, anthracene, and copper (II) ions by alginate spheres with activated carbon in the presence of humic acid. The assays were carried out with aqueous solutions containing the three pollutants at the indicated concentrations and humic acid at 100 mg/L. An adsorbent dose of 6 mg/mL was applied, and the removal was measured at 24 h. The results are the mean ± SE from triplicate experiments.

| Pollutant | Initial Concentration (mg/L) | Removal (%) |
|---|---|---|
| Chlorpyrifos | 25 | 47 ± 6 |
| Anthracene | 1 | 64 ± 11 |
| Copper (II) ions | 4 | 79 ± 8 |

These results and those presented in Figure 5 are relevant for understanding the influence of humic acid on the adsorbent performance. To the best of our knowledge, this is the first study testing the adsorbent efficiency of AS-AC and PCL materials in the presence of organic matter, in this case, humic acid.

## 4. Conclusions

The present work evolves from previous research on the capacity of alginate materials to remove heavy metals from aqueous media, including from industrial effluent [18,19]. By incorporating other materials, graphene or activated carbon, capable of adsorbing organic compounds, multifunctional adsorbents were produced. Moreover, the biodegradability of alginate-based and PCL materials supports the potential applications in decontamination processes. Among the different alginate-based materials tested, the simple calcium–alginate spheres (AS) presented lower efficiency in removing chlorpyrifos and BaP (<50% removal). Nevertheless, the new alginate-based materials developed in this work showed increased efficiency compared to alginate alone.

The chlorpyrifos and BaP removal capacity of the materials are in the order AS < AS-G < AS-AC < PCL. The AS-AC and PCL microparticles were the materials showing the highest ability to remove anthracene, BaP, and chlorpyrifos, and were then challenged for their multi-target removal potential.

PCL revealed a higher consistency for removing hydrophobic pollutants in different conditions compared to AS-AC. For example, as shown in this work, the removal of anthracene by PCL was not affected either by the presence of copper (II) ions or by the presence of copper ions and humic acid, probably due to the hydrophobic interactions described by other authors [20]. This consistency can be highly valuable when considering applying this material to the removal of PAHs from waters.

In addition, the AS-AC spheres were more attractive regarding their multi-target capacity related to the simultaneous removal of chlorpyrifos, anthracene, and copper ions, as tested in the presence of organic matter. These types of multi-pollutant decontamination processes may attract great attention in the near future due to their versatility and economic advantages.

Finally, the new materials AS-AC and PCL proposed in this study were demonstrated to be efficient in removing chlorpyrifos, anthracene, and copper ions in the presence of organic matter. If the AS-AC spheres are a multifunctional adsorbent for different pollutants on one side, the PCL revealed a potential application in environmental decontamination processes that deserves further studies.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10112300/s1, Figure S1. Representative HPLC chromatograms of hydrophobic organic compounds: (**a**) 25 mg/L chlorpyrifos with a retention time (RT) of 7.7 min; (**b**) 1 mg/L BaP with an RT of 13.8 min; and (**c**) 1 mg/L anthracene with an RT of 6.7 min; Table S1. Removal of the hydrophobic organic pollutants by the different adsorbent materials. An adsorbent dose of 12 mg/mL was applied to the assays, and the removal was measured at 24 h. The results are the mean ± SE from triplicate experiments.

**Author Contributions:** Conceptualization, D.M.-d.-S. and R.L.; methodology, D.M.-d.-S.; formal analysis, D.M.-d.-S.; investigation, D.M.-d.-S., J.M.L., I.C. and J.S.S.; resources, R.L.; data curation, D.M.-d.-S.; writing—original draft preparation, D.M.-d.-S.; writing—review and editing, D.M.-d.-S. and R.L.; visualization, D.M.-d.-S. and I.C.; supervision, D.M.-d.-S.; project administration, D.M.-d.-S.; funding acquisition, D.M.-d.-S. and R.L. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** Data is contained within the article or Supplementary Material.

**Conflicts of Interest:** The authors declare no conflict of interest.

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