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Sustainable Solutions for Pollutants Removal with a Hybrid Multifunctional Adsorbent Based on Recycled Expanded Glass

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Abstract: The removal of the As(V) and Iprodione fungicide onto EGS@APTES-GT, obtained by amino-modified expanded glass spheres (EGS) modified with goethite, was studied in this work. Material characterization was performed using SEM/EDS, XRD, and FTIR techniques. The adsorption capacities of 51.01 and 94.28 mg g^{−1}, for As(V) and Iprodione removal at 25 °C, respectively, were achieved. A kinetic study indicated lower intraparticle diffusional transport resistance. Physisorption is the dominant mechanism for Iprodione removal, while surface complexation is for As(V). The disposal of effluent water after five adsorption–desorption cycles was attained through Iprodione photocatalytic degradation and arsenate precipitation. Exhausted EGS@APTES-GT, processed by goethite acidic dissolution and grinding, was used as a reinforcing filler in composites production based on commercial unsaturated polyester resin (UPe). An improvement in the mechanical properties was observed, with a gradual increase in the tensile strength, reaching a maximum of 25.9% for UPe with 10 wt.% of ground exhausted adsorbent compared to pure UPe. The overarching concept is defined by the aspiration to develop technologies that address all output flows of advanced processes. Thus, the combination of wastewater treatment technologies and the production of potentially marketable composites successfully achieved both a low environmental impact and the implementation of a circular economy.

Keywords: goethite; expanded glass spheres; desorbed pollutants disposal; photocatalysis; stabilization



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1. Introduction

The global glass output has reached 140 million tons per year in recent years [1,2]. Furthermore, figures reveal that major global economies, such as the United States and China, produce tens of millions of tons of waste glass annually [2], resulting in an increase in landfill usage and a serious threat to human health and the environment. Comparing various solid waste kinds, such as glass, wood, and plastic, reveals that glass is not biodegradable over an

extended period of time due to its chemical stability, making recycling extremely important. Only 21% of glass produced globally was recycled due to the complexity and potential high costs of the glass recycling process [2]. The production of infrastructure materials as a partial substitute for cement, sand, and/or coarse aggregates is gaining popularity globally as an alternate method of using waste glass and lowering recycling costs [3]. Since recycling glass waste guarantees the availability of inexpensive raw materials in large quantities, it is intriguing to consider the potential for further modification and environmental protection, as demonstrated by the instance of recycled glass material in the form of expanded glass spheres (EGS).

Rapid industrialization, which includes the rising agricultural output and waste discharges, has resulted in increased air, water, and soil pollution, endangering human health as well as the health of all living things [4–6]. To preserve ecosystems, it is crucial to remove pesticides and heavy metals from drinking water [7,8]. Given their poisonous and carcinogenic properties, the majority of heavy metals can damage mental and neurological functioning and create serious chronic health issues at low concentrations [7,9,10]. Due to their relative chemical stability [11], pesticides may enter living bodies and bioaccumulate there when used inappropriately for pest prevention, mitigation, and destruction. They may also be harmful due to the possibility of high pollutant loads in shallow water with a low dilution capacity [12] or contamination from rainfall, farm-land infiltration, and paddy field drainage. Due to their relative chemical stability, pesticides may enter living bodies and bioaccumulate there when used inappropriately for pest prevention, mitigation, and destruction. They may also be harmful due to the possibility of high pollutant loads in shallow water with a low dilution capacity or contamination from rainfall, farmland infiltration, and paddy field drainage.

Arsenic is commonly found in water due to a variety of natural and man-made activities, including mining, mineral dissolution, pesticides used in agriculture, and others [13]. Prolonged exposure to drinking and irrigation water contaminated with arsenic can cause major health concerns, including skin and lung cancer, angioedema, and cardiovascular disease [14]. As a result, groundwater contamination by arsenic has garnered international attention. Arsenite (As(III)) as well as arsenate (As(V)) are the two primary forms of arsenic that are present in natural water. However, compared to arsenite, arsenate is simpler to remove from water. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) have established a maximum permissible level of arsenic in drinking water of roughly 10 µg/L [15]. Adsorption is one of the simplest, most economical and effective ways to remove arsenic from water, which is why many natural or composite adsorbents have been created in recent years [16].

One common fungicide used in agricultural production is Iprodione. Fungal infections like Sclerotinia, Botrytis, Rhizoctonia, and Alternaria are well controlled by this dicarboximide contact fungicide, which has both curative and protective qualities. Iprodione has been found in surface and groundwater in recent investigations, mostly as a result of runoff from treated fields and leaching into groundwater sources. Iprodione is a steroidogenesis inhibitor that can have both immediate and long-term negative health effects, such as atrophy and hypertrophy. It has also been shown to be moderately hazardous to small animals, toxic to aquatic life, and possibly carcinogenic to humans [17].

A number of treatment technologies, such as flocculation, coagulation, oxidation processes, ultrafiltration, reverse osmosis, biological treatment, sedimentation, membrane processes, adsorption, and other combined techniques, have been developed to remove pollutants from wastewater and water [18,19]. The methods by which various adsorbents remove pesticides from waterways and the trends in pesticide concentrations in waterways worldwide are currently poorly understood [20].

There will always be a need for new adsorbents for wastewater treatment in addition to the many conventional ones that have been used historically in water treatment [21], such as commercial activated carbon, zeolite, clay minerals, and resins. This is because the removal capabilities of hundreds of different adsorbents, natural materials, carbon adsorbents, silica-based adsorbents, and aerogels have been studied [5].

Unmodified glass particles have polar functional hydroxyl groups Si–OH or charged Si–O[−] or Si–OH²⁺ groups in aqueous medium and this behavior is dependent on the pH value. The organo-silanes are substances commonly used for the modification of glass or silica surfaces, providing them with various properties [22–24]. Alkoxysilanes, like (3-aminopropyl) triethoxysilane (APTES), are of the most frequently used organo-silane agents for the preparation of amino-terminated films. Additionally, amine groups are available for further functionalization [25]. Organic functional groups including thiol, amino, carboxylic, and sulfur groups commonly possess stronger complexation or a chelating ability toward heavy metal ions and some organic species, and have been used to functionalize the inorganic adsorbents to improve their adsorption performance [7]. The ion exchange, π – π interaction, hydrogen bonding, and/or electrostatic attraction are the contributions to the fast and high-capacity removal.

Although activated carbons derived from carbonaceous precursors have found extensive usage as adsorbents, their usefulness may be limited by their high regeneration costs when using fossil fuels as a starting material [26]. While a lot of research has been carried out on alternative low-cost and environmentally friendly adsorbents (such as agricultural wastes, naturally occurring materials, and by-products like sludge, red mud, fly ash, etc.), relatively little research has been carried out on inorganic waste, like glass, for water treatment applications [27]. Nano-sized adsorbents cannot be used in fixed-bed columns due to their tiny particle size; instead, they must be granular in form or supported on porous materials of a comparatively greater size [28]. In light of this, researchers have looked into granular and supporting adsorbent materials, with some of them showing promising results [29,30]. The creation of hybrid materials has become a feasible alternative for preserving the advantageous qualities of ferric hydroxide materials.

One of the major issues in the adsorption process for pollutant removal from wastewater is the recovery and long-term management of spent adsorbents. The emphasis should be on how spent adsorbents can be recovered, regenerated, and reused or disposed of responsibly. Environmental impacts due to dangerous spent adsorbents could be mitigated through the creative path of using these waste products by repurposing in a stabilized hybrid material form [31]. There are various methods for recovering and regenerating spent adsorbents, including filtering, thermal desorption and breakdown, chemical desorption, and adsorbent regeneration utilizing microbes. Adsorbent regeneration for reuse also includes soil supplements, usage as a condenser, and catalyst/catalyst support, as well as safe disposal options such as incineration and landfill. The sustainable management of used adsorbents, including the processes involved in adsorbent recovery and regeneration for reuse, is investigated in light of resource recovery and the circular economy [32]. Rial et al. spent adsorbents based on polysaccharides with iron oxides that adsorbed organic pollutants and metal ions from wastewater used as additives in ceramics or cement production [33].

The main goals of the presented work relate to three complementary parts: (i) The synthesis of a new hybrid material using commercial recycled expanded glass spheres (EGS) modified with 3-aminopropyl-triethoxysilane (APTES), applied to introduce amino functionalities as an affinitive group for cation binding in the first step. The controlled deposition of iron oxyhydroxide in the goethite form (GT), in the second step, provided the EGS@APTES-GT adsorbent used for arsenate and Iprodione fungicide removal. The

detail characterization of the EGS@APTES-GT adsorbent and its adsorption performance testing in both the batch and dynamic mode was performed. (ii) The extension of adsorbent usability was achieved through five adsorption–desorption cycles. As(V) in effluent water was stabilized to obtain non-leaching precipitate, while Iprodione was subjected to photocatalytic decomposition to provide treated water with a Chemical Oxygen Demand (COD) lower than the one prescribed by the national regulation. (iii) The depleted adsorbent was transformed into value-added products by acidic washing and grinding into filler, used as reinforcement in unsaturated polyester resin (UPE). The obtained composites can be used for a variety of purposes, such as building, ceramics, or as filler in resin-based composites [33]. The overall idea relates to the development of the closed loop of environmentally friendly technologies from adsorbent production to end-of-life material recycling into added-value composites.

2. Materials and Methods

2.1. Materials

Data on chemicals and raw materials used for adsorbent preparation are given in Supplementary Material S2.1 (SM S2.1).

2.2. Hybrid Adsorbent Synthesis

Synthesis of hybrid material was performed in relation to procedure described in recent literature [34,35], with some modifications. Procedure for purification and surface activation of raw material, EGS, is described in SM S2.2.

2.3. Modification of EGS with APTES and Goethite

The modification steps were performed by treatment of etched glass spheres surface with amino-silane coupling agent (APTES) followed by iron oxyhydroxide (GT) precipitation (Figure 1). The freshly cleaned EGS material (10 g) was submerged in non-polar solvent, xylene, with simultaneous introduction of N_2 for 30 min. After that, APTES (10% w/w in xylene) was added drop-wise for 120 min. Reaction was carried out for 20 h at 25 °C in N_2 atmosphere, followed by dropping of 5 mL of 96% ethanol ten times in the course of last period of the modification procedure. Centrifugation and thorough rinsing with ethanol several times and then water was applied. The obtained material, denoted as EGS@APTES, was stored wet prior to impregnation with goethite (35 wt.% water content).

Final steps of hybrid adsorbent preparation was EGS@APTES modification via GT precipitation analogously to the procedure described elsewhere [36,37]. It involved three identical steps in order to distribute oxide as evenly as possible through porous EGS@APTES material without pores clogging. The first step of GT precipitation was carried out by following procedure: EGS@APTES material (50 g) was submerged in xylene. The reaction was conducted continuously with simultaneous introduction of up-flow N_2 stream to obtain a fine distribution of the iron solution over the spheres inner, i.e., interior porous structure, and outer surface for 30 min in suspension by drop-wise addition of 20 mL $FeSO_4 \cdot 7H_2O$ saturated solution (2.0 mol L^{-1}) for 30 min and simultaneous bubbling of N_2 . The oxidation was performed by changing the nitrogen with air introduction and neutralizing reaction by addition of 10 mL $NaHCO_3$ saturated solution (2.6 mol L^{-1}) for 30 min, which caused the precipitation of the oxide in goethite form. The reaction was conducted for 48 h under air flow until the green–blue color of the material changed to ocher shade. The synthesized material was rinsed three times with water and stored wet. The procedure for the precipitation of GT was repeated in an analogous manner (the second and the third step) to obtain ~19 wt.% of GT in relation to the EGS@APTES carrier. The final material, denoted as EGS@APTES-GT, was used wet (42 wt.% water content). On

the Figure 1 shows (step 3) differences of GT content in EGS@APTES-GT after the first, second, and third precipitation procedure step, where color changes from light brown to brown–red.

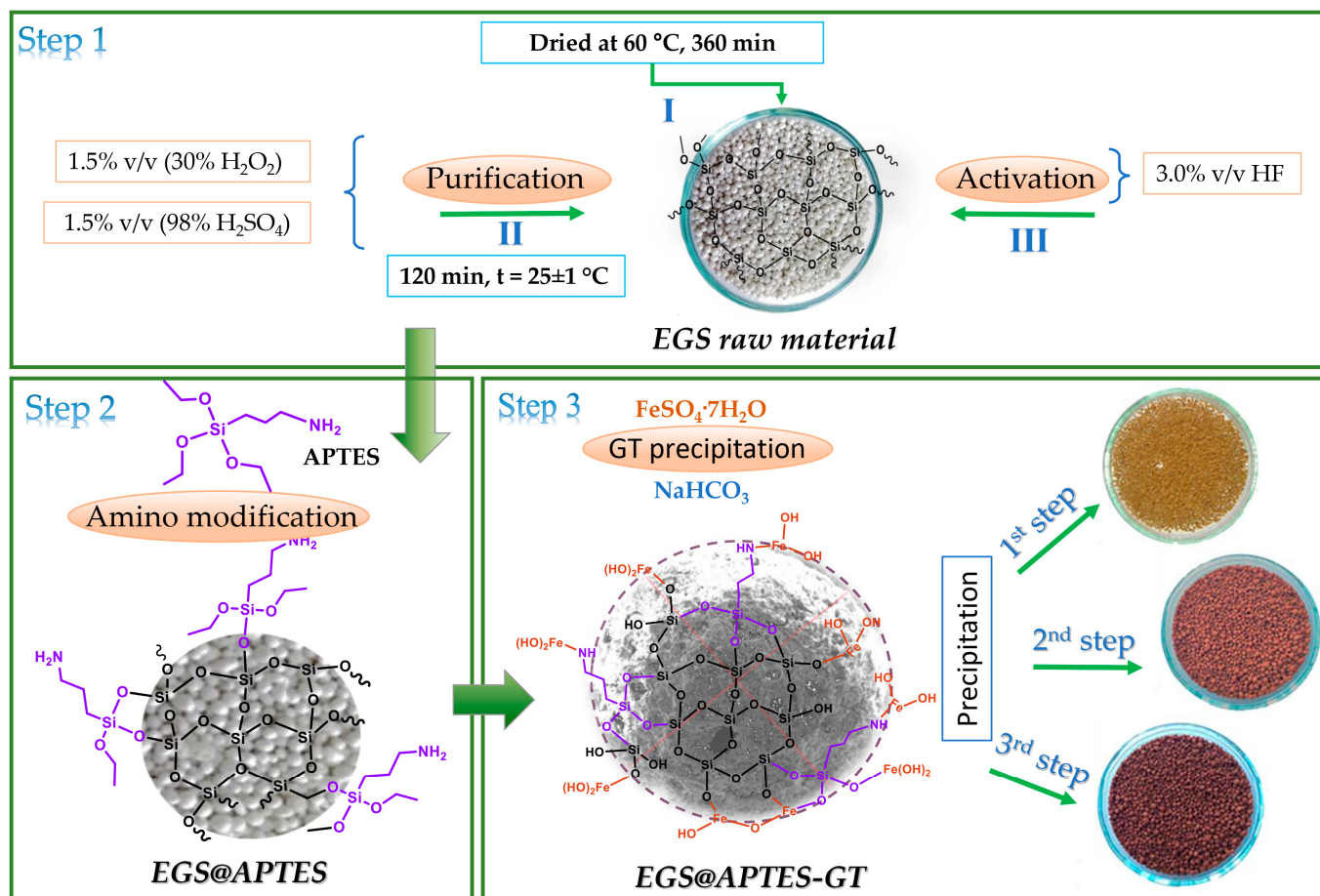


Figure 1. Schematic presentation of EGS@APTES-GT preparation.

2.4. Characterization of Hybrid Adsorbent

Characterization methods are described in detail in SM S2.4.

2.5. Batch Adsorption and Kinetics Studies

Details on adsorption experiments and analytical measurements used for determination of pollutants concentration before and after the adsorption process, adsorption models used for calculation of adsorption capacity, and kinetic and thermodynamic parameters are given in SM S2.5.

2.6. Fixed-Bed Column Breakthrough Studies

Description of column study under different operating conditions [38] were performed by using simplified multi-parameter fitting of the column adsorption data, i.e., Yoon–Nelson [39], Bohart–Adams [40], and Thomas [41] models, all described in SM S2.6.

2.7. Desorption, Regeneration, Exhausted Adsorbent and Pollutants Stabilization, and Degradation Studies

2.7.1. Desorption and Regeneration Studies

For desorption efficiency of EGS@APTES-GT, effluent water disposal and exhausted adsorbent treatment were examined. Considering that adsorbent performance can be reduced during the usage, a proper selection of desorption agent and overall adsorption–

desorption process parameters is of great importance. Since the prepared hybrid adsorbent is based on non-biodegradable recycled glass, from an economic and ecological point of view it is very important to determine its regeneration ability. Optimization of desorption procedure for arsenate and Iprodione was performed with respect to pH, concentration, and type of used regenerating agents according to the procedures as described in a previous study [42,43] (SM S2.7).

2.7.2. Inorganic Pollutants' Stabilization Studies

In line with broadly accepted idea about necessity of exhausted adsorbent disposal [27], the developed methodology for exhausted material processing is presented in SM2.7.2.

2.7.3. Photocatalytic Degradation of Fungicides

An alternative technique for water purification is photocatalytic Iprodione degradation using ZnO semiconductor photocatalysts [44,45], which is presented in SM S2.7.3. The efficiency of photocatalytic process was monitored using UV-Vis and HPLC methods.

2.7.4. Stabilization of Exhausted EGS@APTES-GT Hybrid Adsorbent in UPe Resin Composites

Safe disposal of pollutant-rich adsorbents is an issue of threatening concern in the era of sustainable development. So, after pollutant desorption, the possibility of further treatment and final disposal of the exhausted EGS@APTES-GT adsorbent, named exEGS, was performed in this study. exEGS was obtained by acid washing, drying, and finally, grinding of purified material to obtain fraction <20 μm . Composite materials were obtained by homogenization of 2.5, 5.0, 7.5, and 10 wt.% exEGS in commercial unsaturated polyester resin DION FR 7721-00 (UPe) (SM S2.7.4). Prepared materials were cured using methyl ethyl ketone peroxide (MEKP) as an initiator and cobalt octoate (Co-oct) as an accelerator. Obtained composites were used for determination of structural, mechanical, and dynamical-mechanical properties, as fully described in SM S2.7.4.

2.7.5. Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test was applied in relation to the stabilized forms of exEGS@APTES-GT in UPe-based composites in relation to the USEPA Method 1311 [46] (SM S2.7.5).

3. Results and Discussion

3.1. Characterization of the EGS@APTES-GT Hybrid Adsorbent

3.1.1. Particle Porosity, Amino-Group Content, and pH_{pzc}

The particle porosities of EGS, EGS@APTES, and EGS@APTES-GT were found to be 0.82, 0.79, and 0.74 $\text{cm}^3 \text{g}^{-1}$, respectively. Also, the high amino-group content of the synthesized EGS@APTES material, 1.7 mmol g^{-1} , provides an affinitive EGS surface for GT precipitation. A high particle porosity has a beneficial influence on the modification process and fast intra-particle mass transport. This consequently allows shorter mass transfer zones and empty-bed contact times (EBCT), which are advantageous for designing small point-of-use or point-of-entry systems capable of operating at high hydraulic loading rates [47]. The drift test used for the point-of-zero charge (pH_{pzc}) determination for EGS@APTES-GT, obtained by the cross-section of the $\text{pH}_{\text{initial}}/\text{pH}_{\text{final}}$ (pH_i/pH_f) relation and diagonal, indicates a charge equivalence of 8.04 (Figure S2).

3.1.2. Morphological Characterization

Scanning electron micrographs for EGS@APTES-GT in Figure 2a–c show the irregular spherical morphology of the EGS@APTES-GT adsorbent with a diameter up to 2 mm and a highly porous surface and interior structure. The EGS@APTES-GT particles exhibit different

morphologies ranging from spherical to a slightly irregular spherical shape. Figure 2c indicates that the surface contains connected open pores that make the material suitable for effective diffusional mass transport. The surface of the material consists of a mesoporous and microporous structure. It can be seen that goethite particles are homogeneously distributed, often clustered or aggregated on the external and internal porous surface (Figure 2c,e,f). It is visible that the formation of oxides in the pores, without material clogging or a diameter reduction, maintain material porosity with no interference to the diffusional processes, which are a good condition for pollutant adsorption onto the outer and interior surface.

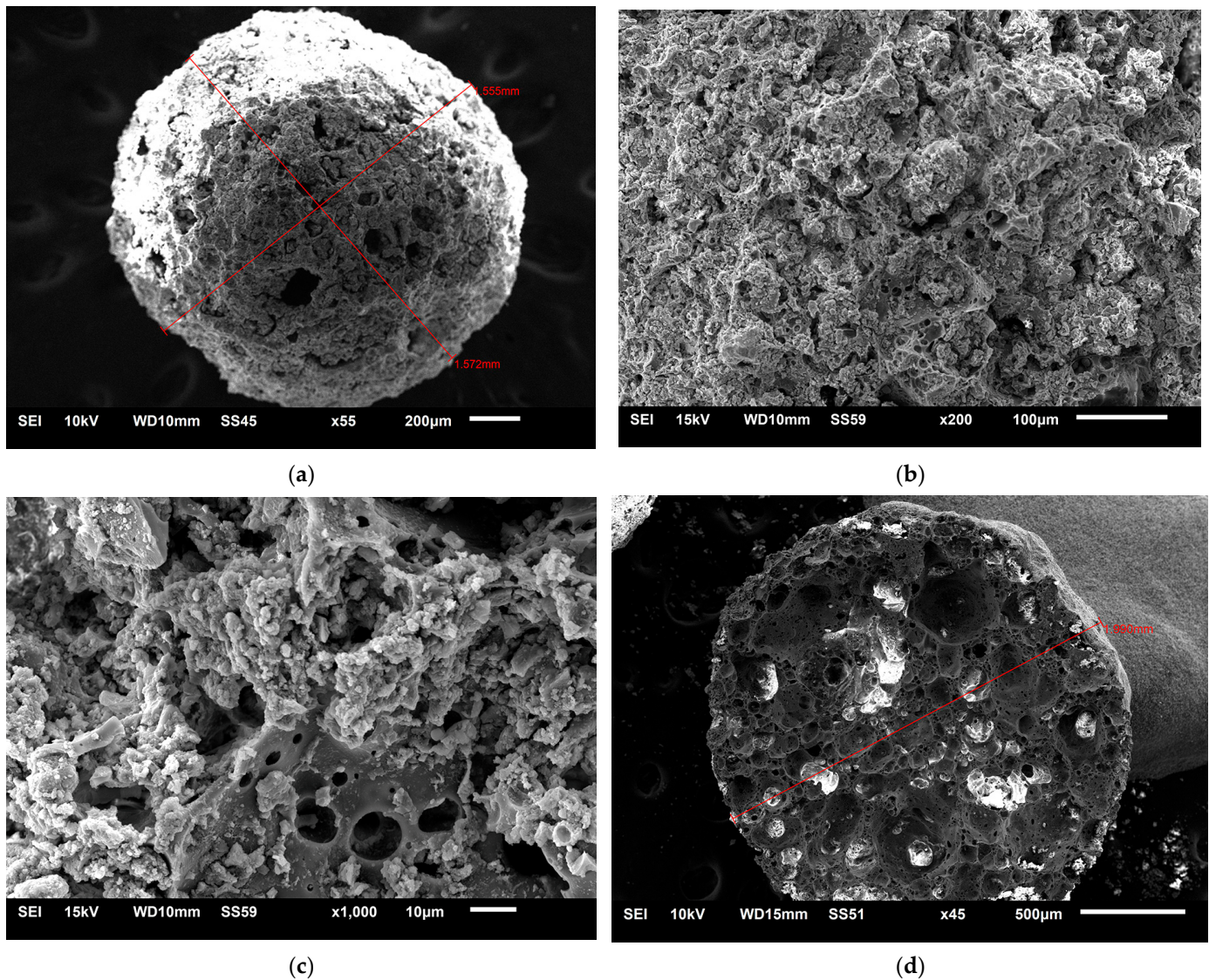


Figure 2. Cont.

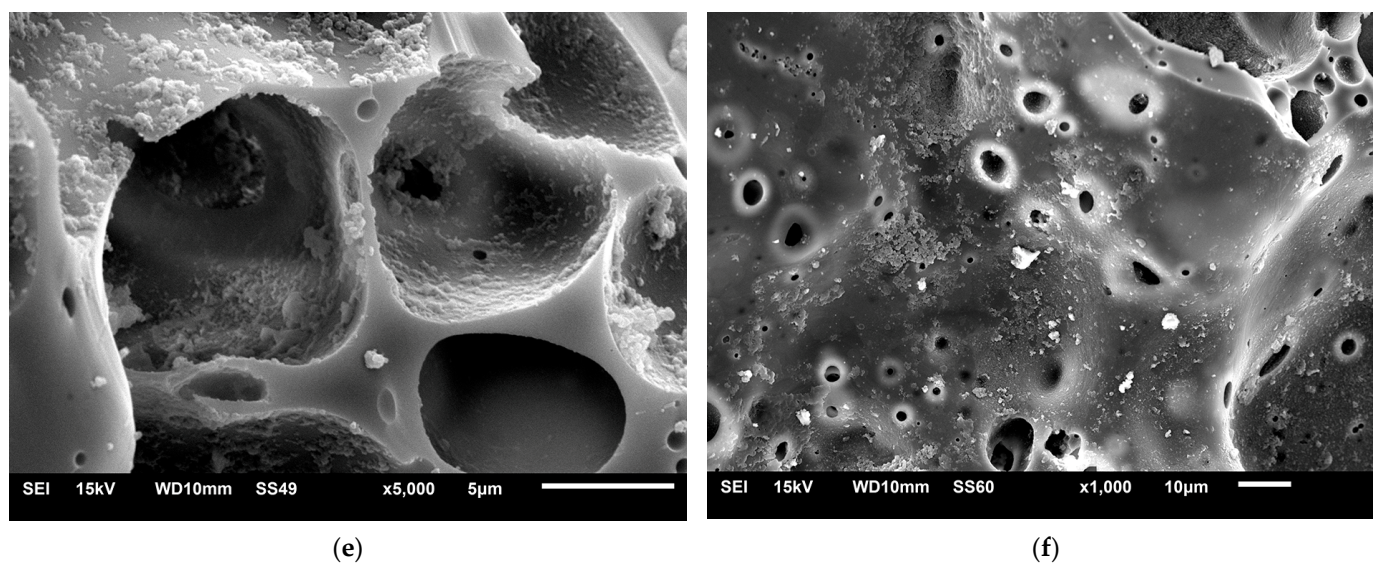


Figure 2. SEM images of EGS@APTES-GT (a), external surface at magnifications of 200 and 1000 $\times$ (b,c), cross-section, (d) and internal surface in cross-section of EGS@APTES-GT at different magnifications of 1000 and 5000 $\times$ (e,f).

The elemental content and its distribution on the adsorbent surface, the distribution through the inner structure of the porous material, were investigated by the EDS. Figure 3 (outer sphere surface) and Figure 4 (cross-section of the inner sphere surface) show a porous surface with an appropriate quantity of deposited iron.

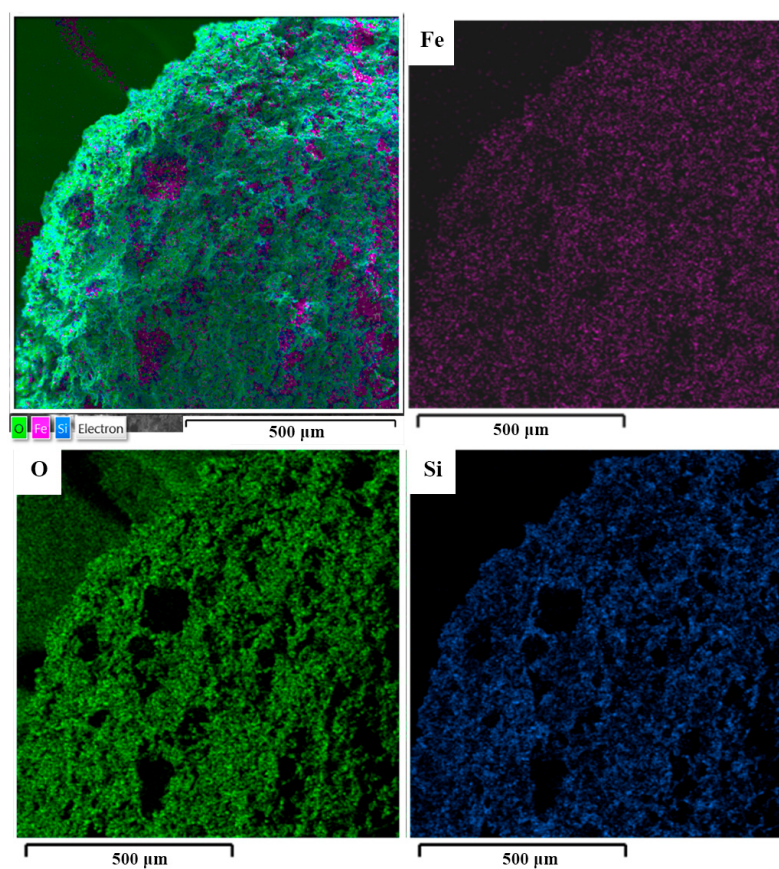


Figure 3. EGS@APTES-GT sphere outer surface EDS mapping with Fe, Si, and O concentration distribution.

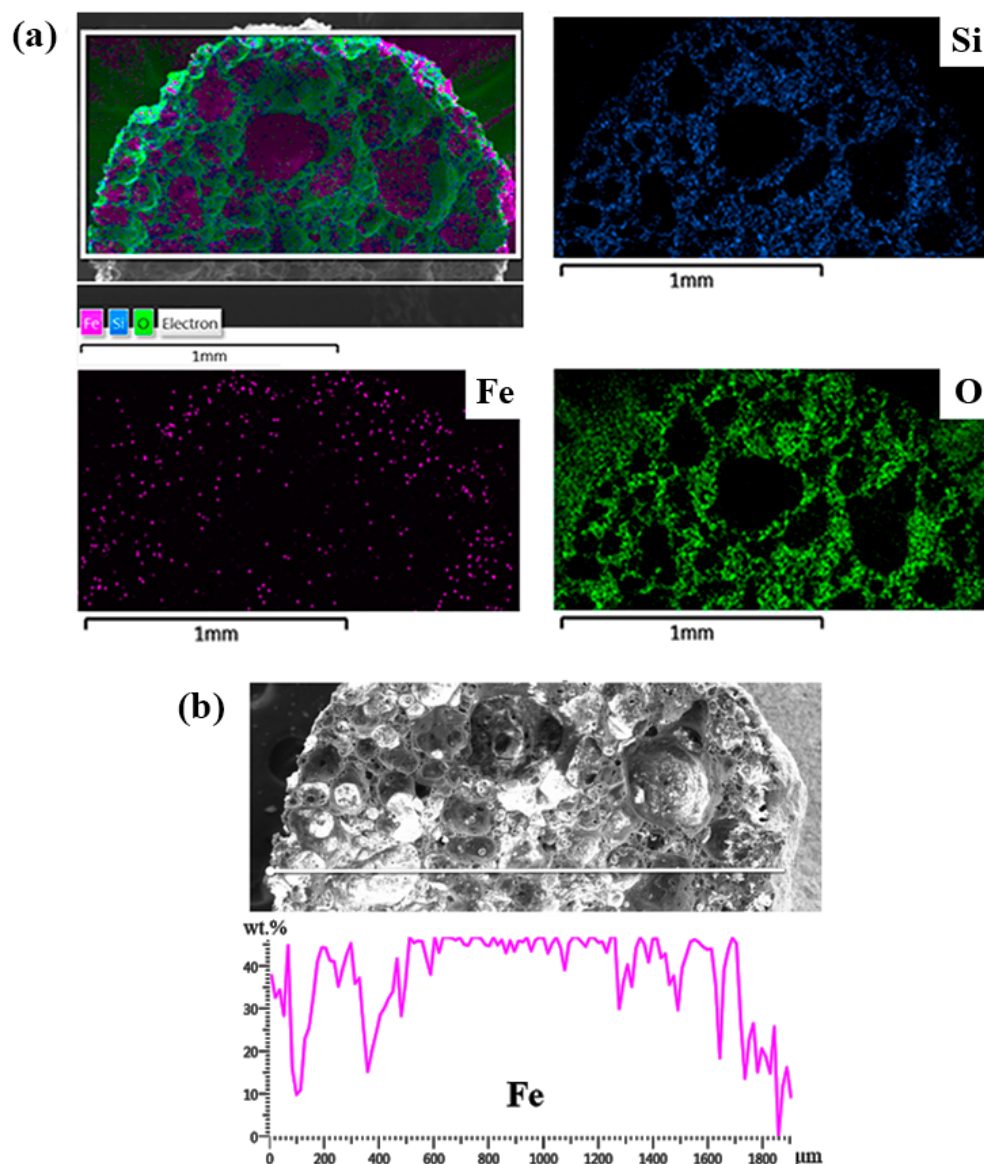


Figure 4. Mapping of element concentration distribution at the cross-section of the EGS@APTES-GT sphere (a) and iron concentration distribution at the intersection of sphere (b).

The mapping results from Figure 4a,b indicate that iron is dispersed along the cross-sectional area and it is obvious that the GT deposit entered in the pores and formed a lower quantity of GT in the region of the sphere's center. The iron concentration continually decreases from the external surface to the center of the spherical particle. The mapping results showed the presence of the GT deposit with a large number of active sites for As(V) and fungicides adsorption.

The EDS results, shown in Figures S3–S5 in SM S3.1.2, indicate that EGS@APTES-GT contains mainly Si, O, and Fe with a trace amount of Na, Ca, Mg, Mn, K, and Al since the EGS material was obtained in the recycling process.

3.1.3. Structural Characterization (FTIR and XRD Analysis)

The FTIR spectrum of the pure expanded glass spheres (EGS), amino-functionalized expanded glass spheres (EGS@APTES) and one with precipitated goethite (EGS@APTES-GT), before and after arsenate and Iprodione adsorption, are presented in Figure 5a.

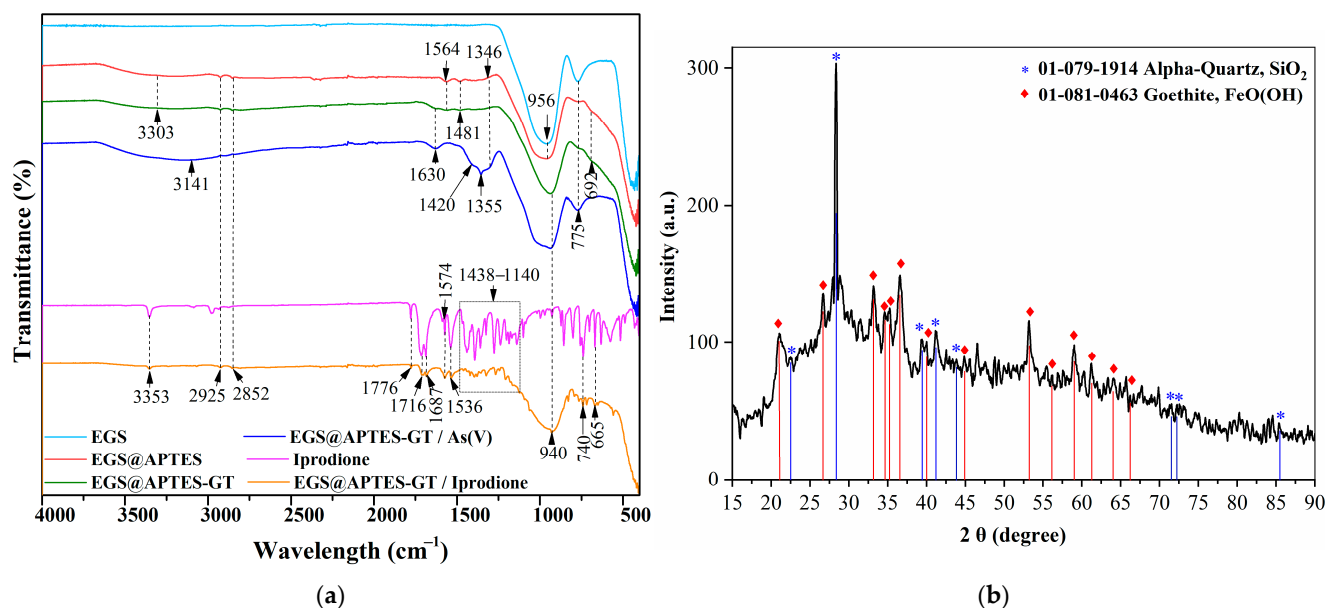


Figure 5. FTIR spectra of EGS, EGS@APTES, and EGS@APTES-GT before and after As(V) and Iprodione adsorption (a), and XRD pattern of EGS@APTES-GT (b).

The FTIR spectra of EGS (Figure 5a) show the characteristic vibration of the Si–O–Si and Si–O bands around 940 cm⁻¹ and 775 bands, respectively [42,43]. The new broad peak at 3200 cm⁻¹ in the spectrum of EGS modified with APTES and goethite presents the stretching vibrations of the N–H and O–H groups, respectively [45]. In addition, the new bands observed at 2925–2852/1481–1346 and 1564/692 cm⁻¹ were assigned to the C–H stretching/bending vibrations of the methyl and methylene groups and the N–H bending/deformations of amino groups in EGS@APTES, respectively. The intensity of these peaks decreases with the concomitant appearance of a new peak at 1630 cm⁻¹, assigned to the bending vibration of the O–H groups in Fe–OH in EGS@APTES-GT.

The increased intensity of the band at 775 cm⁻¹ in EGS@APTES-GT / As(V) (Figure 5a) is due to arsenate oxyanion complexation with OH groups at the adsorbent surface by forming an As–O–Fe bond [44]. Further, differences in the peak intensity, peak shifting, and appearance of the peak in the 1420–1355 cm⁻¹ region indicate different arsenate bonding interactions with surface functionalities. In the FTIR spectrum of EGS@APTES-GT / Iprodione, the appearance of new peaks confirms Iprodione effective removal. The bands in the 1776–1574 cm⁻¹ region is attributed to different carbonyl groups' (Figure 5a) stretching vibrations from the adsorbed Iprodione structure. The symmetric stretching vibrations of the C=C group in the aromatic ring skeleton appear at 1536 cm⁻¹, while one located at 1438 cm⁻¹ was attributed to the pseudo-symmetric N–C=O stretching in the imidazolodine-2,4-dione moiety. The deformation vibrations of the isopropyl group are observed at 1363 cm⁻¹ [36]. Due to the complexity of the Iprodione structure, the presence of 3,5-dichlorophenyl, 2,4-dioxoimidazolidine, carboxamide, and isopropyl functionalities (Figure S1) contributes to the attainment of a different interaction with EGS@APTES-GT surface functionalities. The presence of the dipolar/polarizable structure of 3,5-dichlorophenyl and 2,4-dioxoimidazolidine, proton-accepting sites in 2,4-dioxoimidazolidine and carboxamide moieties, and proton-donating sites in amide groups and non-polar isopropyl groups contributes to wealth adsorbate/adsorbent interfacial interactions. It is assumed that the electrostatic attraction of the negatively charged species and the positive adsorbent surface plays a dominant role in the adsorption process [48].

A diffractogram of the prepared hybrid adsorbent is presented in Figure 5b. The analysis results of EGS@APTES-GT confirm the presence of goethite and the α-FeOOH

phase with peaks at the diffraction angles of 21.1° , 26.3° , 33.2° , 45° , 53.1° , and 59° as the most apparent, in accordance with JCPDS PDF No. 01-081-0463 [49]. EGS are mainly based on silica crystalline phases, such as quartz.

3.2. Batch Adsorption Performance of EGS@APTES-GT

3.2.1. Influence of Solution pH on Adsorbent Efficiency

The most influential factors on the adsorption performance are pH-dependent ionic speciation and adsorbent surface ionization. The results of pH_{PZC} determination for EGS@APTES-GT (8.04) suggest that the effective removal of oxyanions could be achieved at $\text{pH} < \text{pH}_{\text{PZC}}$. Otherwise, the hydrogen bonding/donating capability of Iprodione is not significant and of a low susceptibility to the pH influence. On the contrary, the adsorption effectiveness strongly depends on EGS@APTES-GT surface ionization by creating ionized sites able to be established by either dipolar/polarizable and hydrogen bonding/donating interactions with different moieties present in the Iprodione structure. Due to this, the preliminary was performed with respect to the initial pH of the solution (a pH in the range 5–9). According to the results obtained, an optimal pH of 7 was selected for both As(V) and Iprodione removal. The pH-dependent ions speciation of As(V) was performed using MINTEQA 3.0 software (Figure S6). The selection of an optimal pH provides circumstances for the achievement of a good adsorption capacity, but also for an understanding of the adsorption efficiency under a range of pH values without the prior adjustment of the inlet pH. It could be indicative of the applicability of EGS@APTES-GT for real water applications with a wide range of pHs. It will be a subject of further investigation.

3.2.2. Adsorbents Isotherms

Adsorption isotherms are models that describe the distribution of the adsorbate species among the solid and liquid phases, and are an important methodology useful for understanding the adsorption mechanism. In this study, Langmuir, Freundlich, and Temkin isotherm models were used to describe the relationship between the adsorbed amount of arsenate and Iprodione on the hybrid EGS@APTES-GT adsorbent (SM S3.2.2). For that purpose, the anionic pollutant As(V) and Iprodione as the neutral pollutant [50] were used in this batch adsorption study. The values of the adsorption capacity (q_{max}), model parameters, and the coefficients of determination (R^2) for each used isotherm model obtained by a non-linear fitting methodology are presented in Table 1 and Figure S7.

The values of the coefficient of determination for the Langmuir fitting model were 0.98 and 0.96 for arsenate and Iprodione adsorption, respectively. These results indicate the monolayer coverage of the pollutant on the surface of EGS@APTES-GT [37]. The adsorption capacity of the EGS@APTES-GT increased as the operational temperature increased. The calculated q_{max} values at 318 K were 56.11 and 114.0 mg g^{-1} for arsenate and Iprodione, respectively. The essential feature of the Langmuir isotherm can be expressed by means of R_L [51] and in this study, the values of R_L calculated from Equation (S7) are shown in Table 1. The values of R_L at all temperatures and for all used pollutants indicate that the adsorption processes are favorable [52].

The correlation coefficients are the best in the case of Freundlich isotherm modeling. The adsorptive results, obtained according to non-linear Freundlich model fitting, is presented in Figure S7 and Table 1. An adsorption system is generally considered as favorable for $1/n$ values in the range from 0.1 to 0.5 and moderately favorable for the range from 0.5 to 1.0 [53]. Considering the high fitting validity from Table 1, it indicates that EGS@APTES-GT is a good adsorbent for arsenate and Iprodione removal by forming multilayer adsorbate coverage. In general, the results from Table 1 suggest a complex adsorption mechanism

achieved by the interplay of both physisorption, the main operative of Iprodione removal, and chemisorption, dominant in the complexation of arsenate species.

Table 1. Adsorption isotherm parameters ($C_{i[As(V)]} = 4.83 \text{ mg dm}^{-3}$, $C_{i[Iprodione]} = 9.81 \text{ mg dm}^{-3}$, pH 7, $t = 120 \text{ min}$, $m/V = 0.1\text{--}1.0 \text{ g L}^{-1}$).

Models and Parameters		Temperature (K)		
		298	308	318
As(V) adsorption				
Langmuir model	$q_{\max}, (\text{mg g}^{-1})$	51.01 ± 5.26	53.58 ± 5.59	56.11 ± 5.92
	$K_L, (\text{dm}^3 \text{ mg}^{-1})$	1.097 ± 0.21	1.121 ± 0.22	1.155 ± 0.22
	R_L	0.159 ± 0.01	0.156 ± 0.02	0.152 ± 0.02
	R^2	0.980	0.980	0.981
Freundlich model	$K_F, (\text{mg g}^{-1}) (\text{dm}^3 \text{ mg}^{-1})^{1/n}$	25.17 ± 0.13	26.92 ± 0.14	28.89 ± 0.16
	$1/n$	0.593 ± 0.02	0.602 ± 0.02	0.610 ± 0.02
	R^2	0.999	0.999	0.999
Temkin model	$A_T, (\text{dm}^3 \text{ g}^{-1})$	23.01 ± 6.90	24.13 ± 7.30	25.47 ± 7.76
	$B, (\text{mg g}^{-1})$	7.855 ± 1.17	8.116 ± 1.23	8.377 ± 1.29
	R^2	0.900	0.896	0.894
Iprodione adsorption				
Langmuir model	$q_{\max}, (\text{mg g}^{-1})$	94.28 ± 7.04	103.7 ± 8.39	114.0 ± 9.70
	$K_L, (\text{dm}^3 \text{ mg}^{-1})$	2.087 ± 0.43	2.012 ± 0.43	1.963 ± 0.43
	R_L	0.047 ± 0.03	0.048 ± 0.03	0.049 ± 0.03
	R^2	0.957	0.955	0.956
Freundlich model	$K_F, (\text{mg g}^{-1}) (\text{dm}^3 \text{ mg}^{-1})^{1/n}$	54.19 ± 1.26	59.23 ± 1.15	65.09 ± 1.09
	$1/n$	0.367 ± 0.13	0.386 ± 0.10	0.407 ± 0.08
	R^2	0.988	0.992	0.994
Temkin model	$A_T, (\text{dm}^3 \text{ g}^{-1})$	40.75 ± 10.6	42.98 ± 13.2	43.44 ± 14.1
	$B, (\text{mg g}^{-1})$	16.04 ± 1.43	17.13 ± 1.85	18.56 ± 2.20
	R^2	0.962	0.945	0.935

The parameter A_T (L g^{-1}) from the Temkin isotherm model represents the bond constant perceived in the maximal binding energy. Values of B from Table 1 are related to the variation of the adsorption energy and are positive. These values indicate that the adsorption reactions are endothermic [54].

Due to the high porosity originating by expanded glass aggregates, organic molecules as fungicides, regardless of their size, diffuse easily through the material so the higher adsorbent efficiency in comparison to inorganic pollutants [55] can be elucidated.

The adsorption capacities of EGS@APTES-GT for arsenate and Iprodione were compared to those from the literature (Table 2). Listed experimental conditions are based on concentrations and the pH range, temperature, and adsorbent mass-to-volume ratio. Table 2 summarizes these data and the adsorption capacities of other adsorption materials pointed out that EGS@APTES-GT, a highly porous and functionalized adsorbent material, has good adsorption properties. There are no reports of the Iprodione adsorption with adsorbent materials based on recycled glass modified with goethite.

Table 2. Comparison within other adsorbents.

Adsorbent		Pollutant	Conditions	q_e (mg g ⁻¹)	Isotherm Models	Ref.
FeOOH immobilized on the biodegradable root powder (waste biomass)		As(V)	$C_i = 10$ ppm, $T = 30^\circ\text{C}$, $\text{pH} = 9.0$, $m/V = 1$ g L ⁻¹	9.21	Langmuir	[56]
Goethite-impregnated fly ash (FAG)		As(V)	$C_i = 5.0$ ppm, $T = 45^\circ\text{C}$, $\text{pH} = 6.0 \pm 0.1$, $m/V = 0.2\text{--}2.0$ g L ⁻¹	31.7	Langmuir	[37]
Magnetite-impregnated fly ash (FAM)		As(V)	$C_i = 5.0$ ppm, $T = 45^\circ\text{C}$, $\text{pH} = 6.0$, $m/V = 0.2\text{--}2.0$ g L ⁻¹	19.1	Langmuir	[51]
(a) Magnetite (b) NC-MA/L-MG (c) MC-O/NC-L-MG		As(V)	$C_i = 20.0$ ppm, $T = 45^\circ\text{C}$, $\text{pH} = 6.0 \pm 0.1$, $m/V = \text{not given}$	(a) 91.2 (b) 85.3 (c) 18.5	Freundlich	[56]
(a) Iron-based adsorbent from mine waste (MIRESORB) (b) Granular ferric hydroxide (GFH)		As(V)	$C_i = 50$ ppm, $T = ./.^\circ\text{C}$, $\text{pH} = 6.6$, $m/V = 0.01\text{--}10$ g L ⁻¹	(a) 50.38 (b) 29.07	Langmuir Freundlich	[57]
(a) Recycled goethite (BT9) (b) Recycled goethite + MnO ₂ (MnBT9)		As(V)	$C_i = 10$ ppm, $T = \text{room}$, $\text{pH} = 3.5$, $m/V = 1$ g L ⁻¹	(a) 28.25 (b) 25.71	Langmuir Freundlich	[58]
Cell-MG hybrid membrane		Azoxystrobin	$C_i = 6.1$ ppm, $T = 25^\circ\text{C}$, $\text{pH} = 6.0$, $m/V = 0.11\text{--}1.11$ g L ⁻¹	35.3	Langmuir	[42]
		Iprodione	$C_i = 5.1$ ppm, $T = 25^\circ\text{C}$, $\text{pH} = 6.0$, $m/V = 0.11\text{--}1.11$ g L ⁻¹	30.2		
(a) Magnetic sugarcane bagasse (MBo) (b) Magnetic peanut shell (MPSo)		Iprodione	$C_i = 30$ ppm, $T = 25^\circ\text{C}$, $m/V = 2.0$ g L ⁻¹	(a) 25.5 (b) 2.16	Langmuir Freundlich Sips	[53]
Expanded Glass Spheres modified with APTES and goethite (EGS@APTES-GT)		As(V)	$C_i = 4.83$ ppm, $T = 25^\circ\text{C}$, $\text{pH} = 7.0 \pm 0.1$, $m/V = 0.1\text{--}1.0$ g L ⁻¹	51.0	Freundlich Langmuir Temkin	This work
		Iprodione	$C_i = 9.81$ ppm, $T = 25^\circ\text{C}$, $\text{pH} = 7.0 \pm 0.1$, $m/V = 0.1\text{--}1.0$ g L ⁻¹	94.3	Freundlich Langmuir Temkin	This work

3.2.3. Thermodynamic Study

In environmental engineering practice, energy and entropy parameters must be considered to define process spontaneity and feasibility. Values of thermodynamic parameters are the crucial indicators for the evaluation of the practical application of the considered adsorbent. The values of Gibb's free energy ($\Delta G^\ominus$), the standard enthalpy change ($\Delta H^\ominus$), and the standard entropy change ($\Delta S^\ominus$) for the pollutant's adsorption onto EGS@APTES-GT at three temperatures (298, 308, and 318 K) were determined using equations (S18)–(S20) (given in SM S2.5). Hence, from the slope and intercept of plot $\ln K_L$ vs. $1/T$, the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ were obtained and, together with the calculated $\Delta G^\ominus$ value, are given in Table 3.

Table 3. Thermodynamic parameters calculated for EGS@APTES-GT hybrid adsorbent.

Adsorbate	$\Delta G^\ominus$ (kJ mol ^{−1})			$\Delta H^\ominus$ (kJ mol ^{−1})	$\Delta S^\ominus$ (J mol ^{−1} K ^{−1})	R ²
	298 K	308 K	318 K			
Arsenate	−40.99	−43.15	−45.16	21.3	208.9	0.996
Iprodione	−43.53	−45.03	−46.54	1.34	150.5	0.991

The negative values of $\Delta G^\ominus$ indicate the spontaneity of the adsorption process, while a positive $\Delta H^\ominus$ confirms the favorable adsorption onto EGS@APTES-GT with the increase in the operative process temperature. The disruption of water hydration spheres and the transport of pollutant species through the bulk solution, within the pores, and through the surface boundary layer is a slightly more intensive process for Iprodione removal at higher temperatures. This effect is of higher significance for the EGS@APTES-GT/As(V) system. The positive value of $\Delta H^\ominus$ shows the endothermic nature of the process and the positive value of $\Delta S^\ominus$ indicates an increase in randomness at the solid–liquid interface. The results of this adsorption study indicate that chemisorption and physisorption dominate in arsenate and Iprodione removal, respectively. These conclusions were corroborated by an analysis of the FTIR spectra of EGS@APTES-GT before and after adsorption (Figure 5).

3.2.4. Adsorption Kinetics

In order to evaluate the kinetic performance of EGS@APTES-GT and investigate the adsorption mass transfer mechanisms, various models were used [59,60]. Table 4 shows the parameters obtained after fitting a time-dependent concentration change using three kinetic models: pseudo-second-order (PSO), the Elovich kinetic model, and the intra-particle diffusion model proposed by Weber and Morris (WM). The used kinetic models are explained in detail in SM S2.5.

Table 4. Kinetic data obtained using PSO, Elovich, and intra-particle diffusion model for arsenate ($C_i = 4.83$ mg dm^{−3}) and Iprodione ($C_i = 9.81$ mg dm^{−3}) adsorption using hybrid adsorbent EGS@APTES-GT at 298 K, pH 7.0 ± 0.1, and adsorbent mass/volume ratio 0.1 g L^{−1}.

Model	Parameter	As(V)	Iprodione
Pseudo-second-order	k_2 (g mg ^{−1} min ^{−1})	$4.18 \times 10^{-4} \pm 2.1 \times 10^{-5}$	$7.25 \times 10^{-4} \pm 3.1 \times 10^{-5}$
	q_e (mg g ^{−1})	41.83 ± 0.47	81.52 ± 0.57
	R ²	0.997	0.996
Elovich	α (mg g ^{−1} h ^{−1})	2.13 ± 0.51	244.9 ± 235.1
	β (mg g ^{−1})	0.130 ± 0.01	0.119 ± 0.02
	R ²	0.966	0.921
Weber–Morris Step 1 (Film/Intra-particle diffusion) Step 2 (Equilibrium)	k_{id1} (mg g ^{−1} min ^{−0.5})	2.54 ± 0.14	3.318 ± 0.38
	C_1 (mg g ^{−1})	1.10 ± 1.18	35.87 ± 3.26
	R ₁ ²	0.994	0.975
	k_{id2} (mg g ^{−1} min ^{−0.5})	0.511 ± 0.05	0.439 ± 0.08
	C_2 (mg g ^{−1})	25.30 ± 1.05	68.90 ± 1.69
	R ₂ ²	0.990	0.966

The adsorption process was the best fitted using the PSO model (Table 4), assuming the existence of chemisorption adsorption mechanisms for As(V) [37,61,62] and physisorption for Iprodione [42]. The correlation coefficients R², obtained by W-M, were higher in the case of arsenate, similar to the one obtained using the PSO model. According to the maximum

equilibrium adsorption capacities, the hybrid adsorbent selectivity sequence can be given as Iprodione > arsenate.

The two linear correlation lines, obtained using the intra-particle diffusion model, predict two dominating successive adsorption processes (Figure 6). The first step represents fast kinetics and the second part is followed by a very slow attainment of the equilibrium. A larger intercept found for the fungicide adsorption indicates higher resistance, which amounts to slower ionic transport due to intra-particle diffusion. The first linear step explains the external mass transfer from the bulk solution to the most available adsorbent surface, while the second step discloses processes of species diffusion through the porous structure of the adsorbent into the interior, approaching available surface-active sites, followed by the attainment of specific adsorbate/adsorbent interactions. This step highly depends on the adsorbent porosity, pore network density, total pores volume, pore size distribution, etc., so, in the second step of the process, the adsorption process continues at a low rate until the saturation of the available adsorptive sites is occupied [37,52,61].

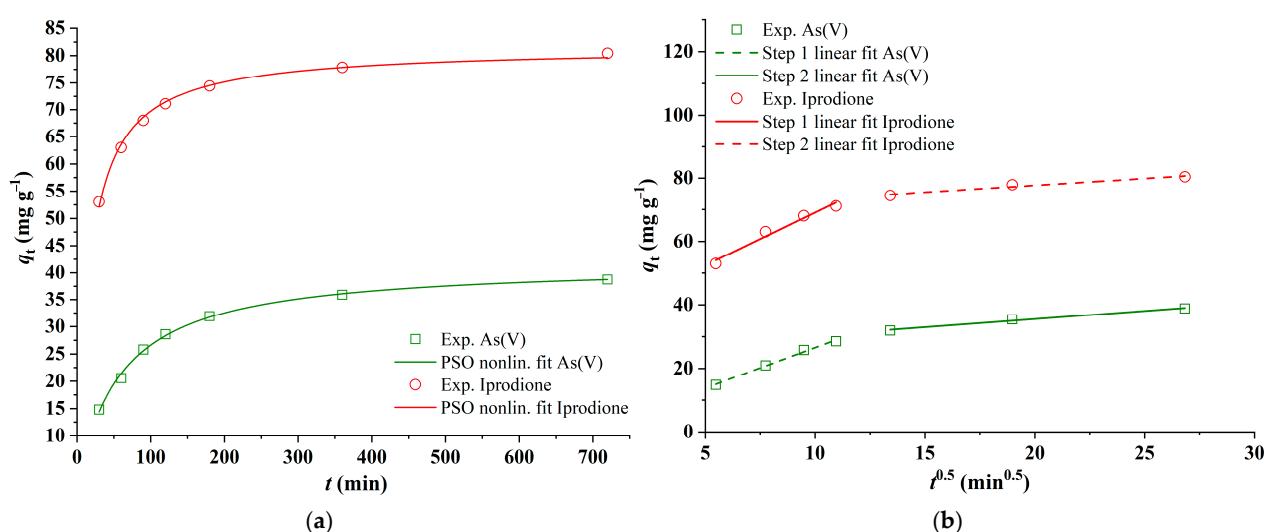


Figure 6. Pseudo-second-order model (a) and intra-particle diffusion model plots divided into two distinctive sections (b) for the adsorption of arsenate and Iprodione by the EGS@APTES-GT.

3.3. Fixed-Bed Column Adsorption Performance of EGS@APTES-GT

The testing of the potential applicability of the EGS@APTES-GT was performed in a column study with respect to the effectiveness of arsenate and Iprodione removal. In order to design and optimize the fixed-bed column adsorption process, different mathematical models were used to predict the breakthrough curve for the studied system. In this study, Yoon–Nelson (Y-N), Bohart–Adams (B-A), and Thomas models were used (SM S2.6) to predict the dynamic behavior of arsenate and Iprodione adsorption onto the EGS@APTES-GT hybrid adsorbent in a fixed-bed system (Table 5).

The correlation coefficient values for each model are found to be high, suggesting that the experimental data and model predicted data are in agreement with each other (Table 5). The value N_0 and constant k_{BA} , obtained from the Bohart–Adams model, are decreased with the increasing flow rate, which may be attributed to the insufficient time for an effective interaction between the adsorbate and adsorbent. The breakthrough curves of arsenate and Iprodione adsorption onto EGS@APTES-GT at three different flow rates (0.5, 1.0, and 1.5 mL min⁻¹) and at fixed-bed height of 5 cm are shown in Figure S8.

Table 5. Bohart–Adams, Yoon–Nelson, and Thomas models’ parameters for adsorption of As(V) and Iprodione onto EGS@APTES-GT hybrid material in a fixed-bed column.

Column Models/Parameters		Flow Rate (cm ³ min ^{−1})		
		0.5	1.0	1.5
As(V)				
B–A	K _{BA} (dm ³ mg ^{−1} min ^{−1})	0.082 ± 0.002	0.155 ± 0.003	0.224 ± 0.007
	N ₀ (mg dm ^{−3})	41.62 ± 0.236	36.86 ± 0.248	32.24 ± 0.313
	R ²	0.998	0.998	0.996
Y–N	K _{YN} (min ^{−1})	0.788 ± 0.017	0.748 ± 0.017	0.755 ± 0.022
	θ (min)	5.558 ± 0.031	4.923 ± 0.033	4.305 ± 0.042
	R ²	0.998	0.998	0.996
Thomas	K _{TH} (dm ³ mg ^{−1} min ^{−1})	0.163 ± 0.004	0.155 ± 0.003	0.156 ± 0.004
	q ₀ (mg g ^{−1})	41.62 ± 0.236	36.86 ± 0.248	32.24 ± 0.312
	R ²	0.998	0.998	0.996
Iprodione				
B–A	K _{BA} (dm ³ mg ^{−1} min ^{−1})	0.060 ± 0.001	0.123 ± 0.001	0.201 ± 0.002
	N ₀ (mg dm ^{−3})	89.81 ± 0.293	80.06 ± 0.172	70.51 ± 0.148
	R ²	0.998	0.999	0.999
Y–N	K _{YN} (min ^{−1})	0.594 ± 0.012	0.603 ± 0.007	0.657 ± 0.007
	θ (min)	11.80 ± 0.038	10.52 ± 0.023	9.266 ± 0.020
	R ²	0.998	0.999	0.999
Thomas	K _{TH} (dm ³ mg ^{−1} min ^{−1})	0.121 ± 0.002	0.123 ± 0.001	0.134 ± 0.001
	q ₀ (mg g ^{−1})	89.73 ± 0.292	80.00 ± 0.172	70.45 ± 0.148
	R ²	0.998	0.999	0.999

3.4. Desorption Studies

An important feature of the adsorbent is its ability to regenerate, which in a way represents its longevity. The efficiency of the adsorbent material can abate during usage (i.e., the precipitation of different species and pore clogging, the destruction or blocking of active sites, etc.), which determines the number of adsorptions–desorption cycles and has great influence on both economic and environmental indicators. Thus, the regeneration process of the used adsorbent can be repeated several times; however, the regenerated adsorbent has decreased the adsorption capacity in comparison to the unused one.

If not properly solved, the disposal of the exhausted adsorbents could generate environmental problems realized as the continual accumulation of highly polluted adsorbents, which could be a source of pollutant leaching. Using a proper technique for adsorbent regeneration and exhausted adsorbent disposal helps in improving the adsorption and economic efficiency by establishing a closed cycle through pollutant removal, decreases the overall cost both in the regeneration and the adsorbent production process, reduces the amount of hazardous generated waste, and solves the problem of waste disposal.

The optimization of the desorption procedure through the assessment of an effective desorbing agent combination along with the minimal degradation of the adsorbent properties, i.e., the adsorbent capacity, was performed (SM S3.4.1). In the processes of arsenic and Iprodione desorption, it was found that alkaline regenerants or inorganic salts have provided optimal results. Acidic regenerant agents have a degradative influence on the dissolution of iron and the deterioration of the adsorbent surface, causing an adsorption

efficiency decrease (higher for app. 15% in comparison to the results given in Figure 7, as an example, 32% of q_e was decreased for As(V) removal after the fifth cycle) and, thus, a decrease in the adsorbent usage period is obvious.

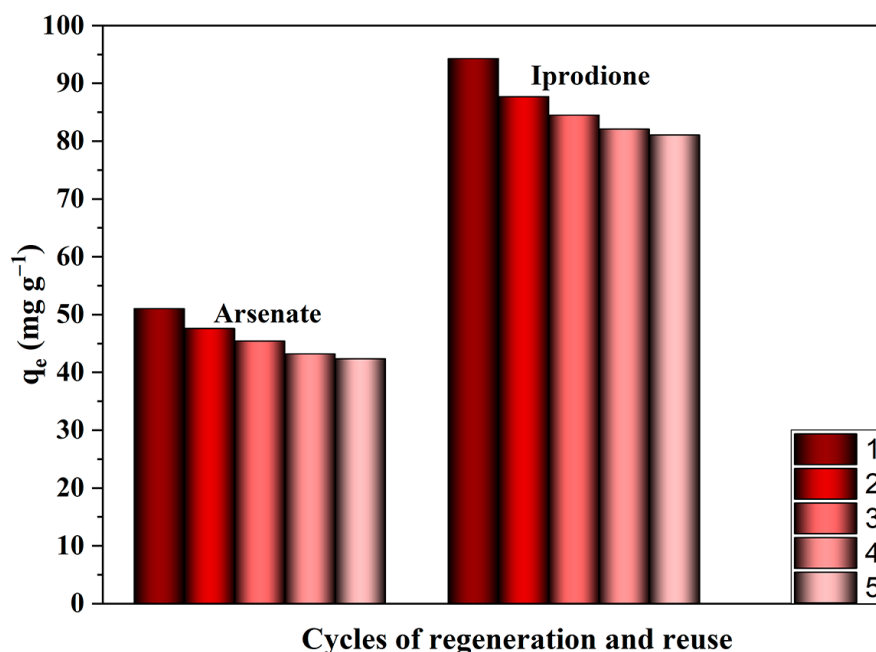


Figure 7. Adsorption–desorption regeneration cycles for the repeated adsorption of As(V) and Iprodione onto EGS@APTES-GT.

The best desorption system was found to be sodium hydrogen carbonate (NaHCO_3 , 4%) or sodium chloride (NaCl , 4%) for Iprodione, while a NaOH (2%)/ NaCl (2%) mixture for arsenate desorption. Fungicide desorption increases with both a pH and ionic strength increase (0.001 , 0.01 , and $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$), which indicates a physisorption mechanism.

For the adsorption capacity of EGS@APTES-GT, before and after the regeneration step, q_i and $q_{(i+1)}$ were further used for the calculation of the regeneration efficiency (RE, %) in the following operational conditions: an adsorbent mass of 10 mg and 10 mL of a pollutant solution, all at a concentration of 5 mg dm^{-3} and pH 7. The regeneration efficiency was calculated according to Equation (1):

$$RE = \frac{q_{(i+1)}}{q_i} \times 100 \quad (1)$$

The obtained results (Figure 7) for As(V) and Iprodione showed a small decrease in the adsorption efficiency of 17% and 14%, respectively, after the fifth reuse cycle, which ensures good EGS@APTES-GT adsorbent efficiency in an industrial-scale application and meets the requirement for a real application at optimal operational conditions. Oxyanions are heavily de-bonded from the iron oxide surface due to the creation of chemically bonded complexes either on the external or internal surface, i.e., outer- and inner-surface complexes [21,34,35], which can also be stated for the hybrid EGS@APTES-GT adsorbent. On the other hand, weak electrostatic bonding within the organic structure Iprodione could be easily be desorbed by either a strong base (NaOH) or ionic species (NaCl), a more effective process using a stronger base/nucleophile can be achieved, and the decision can depend on the desorption effectiveness, techno-economical parameters, and environmental impact.

3.5. Developed Technologies for Exhausted Adsorbent and Desorption Solution Disposal

Desorption processes inevitably generate polluted effluent water and an exhausted EGS@APTES-GT adsorbent, named *exEGS*. Consequently, the substantial focus of a subsequent investigation in this study was to design a technology to turn effluent water and generated *exEGS* treatment into a harmless or useful material of appropriate characteristics suitable for application as a building material. The arsenate in effluent water was chemically stabilized (Section 3.5.1), while Iprodione was subjected to photocatalytic degradation (Section 3.5.2). Additionally, generated *exEGS* was used as a reinforcement in UPe-based composites. Obtained composites were characterized using the FTIR technique (FTIR Analysis of UPe-Based Composites), and mechanical testing was performed in relation to the tensile properties, microhardness, and dynamic-mechanical analysis (Dynamic-Mechanical Testing of Composites Materials). Overall, the development of sustainable building materials based on the use of renewable resources or waste materials can contribute to the minimization of the negative environmental impact.

3.5.1. Arsenate Stabilization and Leaching Study

After the stabilization of the desorbed As(V) species in effluent water, the FeCl_2 and FeCl_3 blended solution or iron ion-containing washing solution showed that the arsenate concentration decreased by 95.14% and 96.86%, respectively. Inorganic pollution elements appeared to be effectively stabilized, with the leachate concentrations well below the regulatory limit values as obtained by the TCLP test (method given in SM S2.7.5). The obtained values are lower than the maximum permissible concentration of 10 ppb prescribed by the Environmental Protection Agency (EPA) [63].

3.5.2. Photocatalytic Degradation of Iprodione

The kinetics of the photocatalysis of desorbed Iprodione was studied at a constant catalyst dose under neutral conditions, and the obtained results are presented in Figure 8.

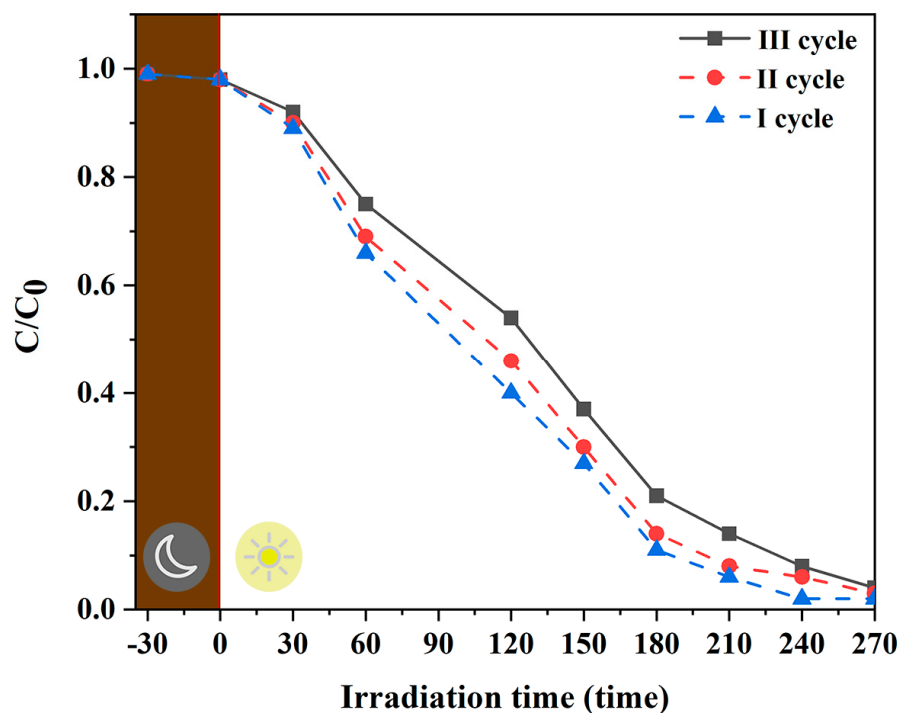


Figure 8. Reaction kinetics for degradation of Iprodione over ZnO photocatalyst.

At lower concentrations of the organic pollutant, a pseudo-first-order equation can be used to estimate the kinetic parameters of the photocatalytic reactions [64,65]. The obtained photocatalysis rate parameters of Iprodione degradation, using ZnO at 25 °C, $C_0 = 5 \text{ mg L}^{-1}$, and $t = 150 \text{ min}$, are $K (\text{min}^{-1}) = 0.02267$ and $t_{1/2} (\text{min}) = 30.6$. The determination of the chemical oxygen demand (COD) after 270 min of applied treatment gave $176 \text{ mg O}_2 \text{ L}^{-1}$, which is lower than the one prescribed by national legislation. The limit value of wastewater emissions from plants for textile processing and production is $200 \text{ mg O}_2 \text{ L}^{-1}$ [66]. This method was found to be applicative for effluent wastewater treatment containing Iprodione.

3.5.3. Stabilization of Exhausted EGS@APTES-GT Material in UPe-Based Composites

In the literature, studies on the development of adsorbents mostly focus on the development of the high removal capacity and on the regeneration of adsorbents without discussing the final disposal or stabilization of the effluent water or exhausted materials [33]. In order to solve the problem of the generated exhausted adsorbent in this study, the disposal of the spent adsorbent *ex*EGS, obtained after five cycles of adsorption–desorption processes, was solved by its use as a reinforcement in UPe-based composites.

FTIR Analysis of UPe-Based Composites

Figure 9 shows the FTIR spectra of the cured neat UPe matrix (a) and composites based on UPe reinforced with grinded *ex*EGS (UPe/*ex*EGS) at 2.5 wt.% (b), 5.0 wt.% (c), 7.5 wt.% (d), and 10 wt.% (e) additions.

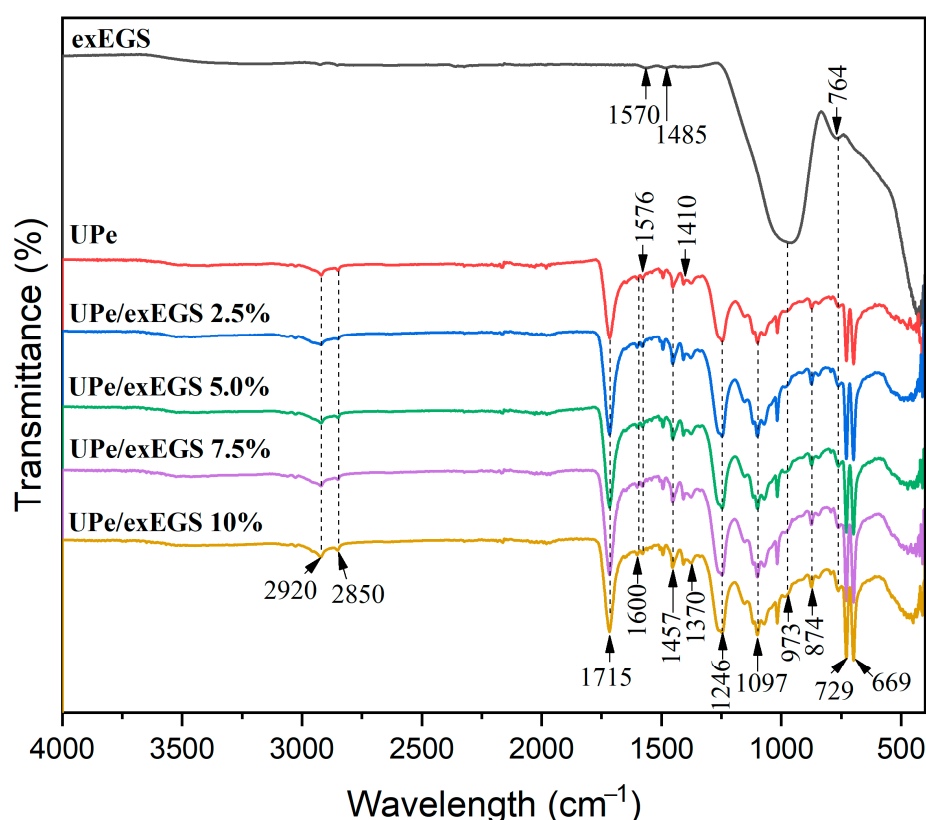


Figure 9. FTIR spectra of cured UPe resin and UPe-based composites reinforced with *ex*EGS at 2.5 wt.%, 5.0 wt.%, 7.5 wt.%, and 10 wt.% additions.

The bands observed at 2920 and 2850 cm^{-1} for UPe and its derived composites were attributed to asymmetric and symmetric C–H stretching vibrations, and ones in the 1457–1370 cm^{-1} region were assigned to the C–H bending vibrations of aliphatic moieties. The C=O stretching vibration of the ester carbonyl group was observed at 1715 cm^{-1} .

The two peaks' small intensities at 1600 and 1576 cm^{-1} were attributed to unsaturated C=C bonds in the phenyl ring of the terephthoyl unit and polystyrene in UPE resin. The bands related to the C–O and C–O–C stretching vibration appeared in the 1246 and 1100–1017 cm^{-1} regions, respectively [67]. Also, two strong bands, found in the regions from 874 to 698 cm^{-1} , were assigned to the C–H out-of-plane deformation vibration of the phenyl ring in the terephthoyl units and polystyrene structure. The intensity of most bands in UPe and its corresponding composites are of a similar intensity (Figure 9) with one exception: the appearance of a new band at 973 cm^{-1} assigned to the Si–O stretching vibration in exEGS. Generally, the spectra exhibit similarities between the samples, and the band's intensity is slightly proportionally increasing with the percent of the increase in the exEGS filler.

The statistical results, obtained by the use of principal component analysis, or PCA, are applied to obtain results which are easier for analysis. On the normalized spectra, PCA analysis was applied (Figure S9). The PCA analysis of the FTIR data has a large number of highly correlated variables and only the first few PCs can describe the spectral variables relating to the chemical components/functional groups in the spectra of samples. These variables have large eigenvalues showing a steep slope, while the others PCs are the contribution of noise and the forming plate in the Scree plot due to their small eigenvalues (Figure S10) [68,69]. Accordingly, the clustering of the spectral range in the FTIR spectra were performed in two ranges to select a proper spectral range by removing highly correlated variables. In order to determine the principal component numbers (PCs), we created the scree plot (Figure S10a) and drew the spectra (Figure S10b) of each PC [68,69]. The results presented in Figure S10 indicate that PC1 and PC2 are the valuable components, while others from PC3 to PC6 show very small bands i.e., small eigenvalues. The obtained results in Figure S11a, b indicate that PC1 and PC2 cover 91.84% and 7.06% of the total variance, respectively, for the spectral range of 4000–400 cm^{-1} . The similar results are obtained by PCA analysis in the 1800–400 cm^{-1} spectral range, and this range of the loading plot (Figure S11c,d) shows that PC1 and PC2 cover 86.73% and 11.97%, respectively. The obtained result shows high data variance in the investigated spectral ranges with changes in the intensity of the peaks.

Dynamic–Mechanical Testing of Composite Materials

The composites' reinforcement with exEGS was studied in relation to the mechanical properties. For instance, fly ash, recycled nylon fibers, and lightweight expanded glass aggregates can be used to create sustainable textile-reinforced cementitious composites [70]. The economics of recycling such composites could be revolutionized by the regeneration of the recovered glass fiber performance [71]. Table 6 displays the mechanical and dynamic–mechanical property results of polyester-based composites with varying exEGS contents.

The values of Young's modulus and the tensile strength of the composites with an increasing filler percentage are displayed in Table 6. When compared to the unreinforced resin, the composite's tensile strength is improved. The maximum strength of 28.31 MPa was observed with 10 wt.% of filler loading. It was observed that when the amount of filler grew, the exEGS particle reinforced the unsaturated polyester composite's tensile modulus. With the addition of 10 wt.% exEGS particles, the Young's modulus increased by 30.1% compared to pure resin. In the literature, it was found that there is an improvement in the mechanical properties of composites with waste glass [72]. Glass mirror scraps and poly(vinyl)butyral (PVB) waste from flat glass-producing facilities were the focus of Gorohovski et al.'s [73] research as raw materials for composites. The findings demonstrated that, out of all the compositions examined, the composite with 10% by weight of the filler

had somewhat better mechanical performances. It is possible to attribute the increase in the dynamic stiffness to the physical impact of the filler glass waste.

Table 6. Results of mechanical and dynamic–mechanical properties of polyester-based composites with different exEGS contents.

Sample	Mechanical Properties			DMA Properties	
	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	T_g (°C)	$\tan \delta$ Peak
UPe	22.48	0.79	612.4	97.70	0.710
UPe/exEGS 2.5 wt.%	23.15	0.83	668.1	98.62	0.711
UPe/exEGS 5.0 wt.%	25.94	0.97	712.4	98.63	0.712
UPe/exEGS 7.5 wt.%	28.31	1.11	796.9	98.65	0.724
UPe/exEGS 10 wt.%	27.83	1.04	765.0	98.64	0.721

The dynamic–mechanical behavior of polyester composites is given in Figure 10 and Table 6. Figure 10a,b depict representative dynamic–mechanical analysis (DMA) experimental results in terms of the storage and loss modulus versus temperature. According to the results, the composites reinforced with exEGS particles have discreetly higher modulus values across the entire temperature range.

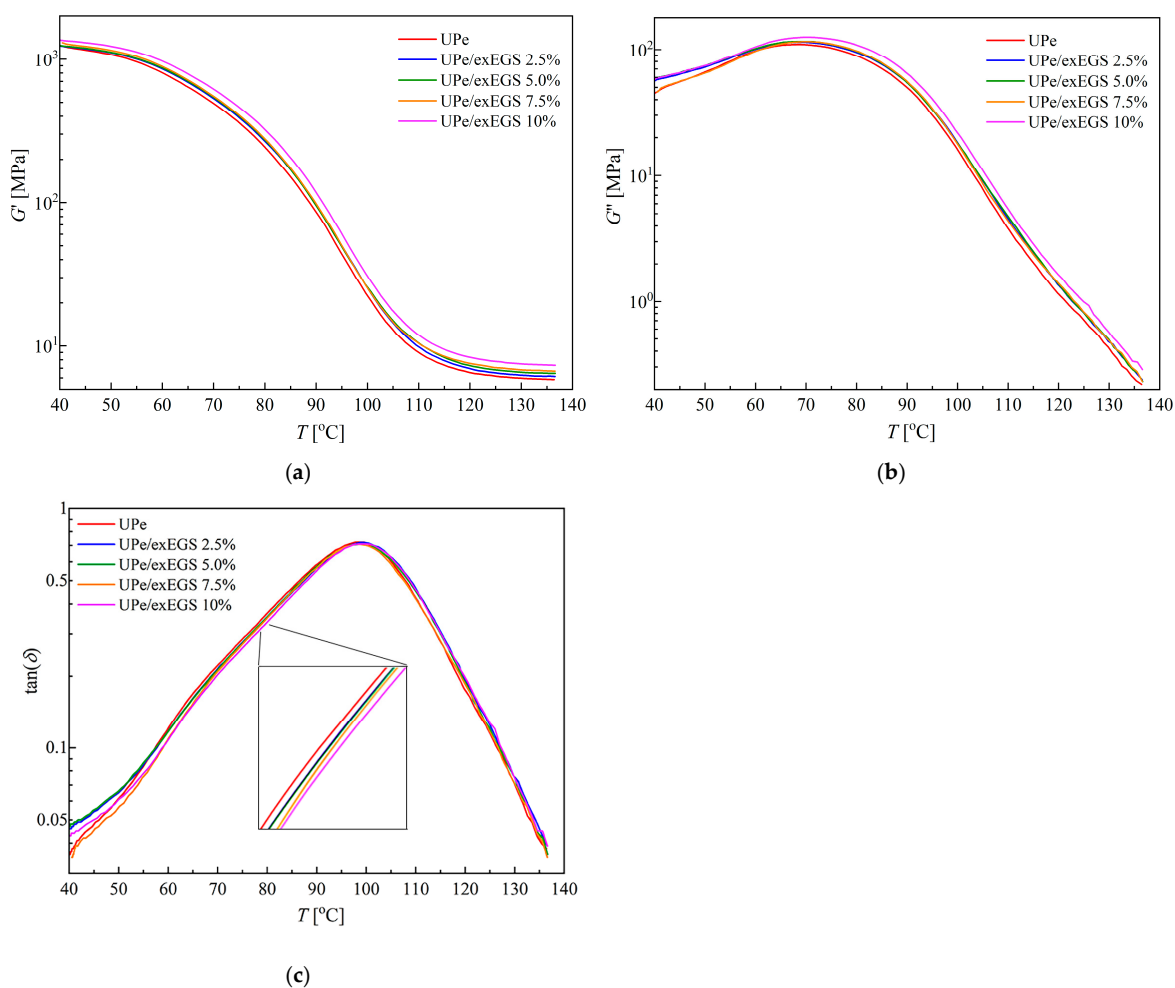


Figure 10. The variation of storage modulus (a), loss modulus (b), and loss factor (c) of UPe and UPe/exEGS composite materials.

A DMA analysis was used to examine the thermomechanical characteristics of cured neat UPe resin and various composite systems with *ex*EGS, meaning the viscoelastic characteristics of the cross-linked matrix and the resulting composites at temperatures ranging from 40 to 150 °C. Figure 10a depicts how the sample's storage modulus (G') changes with the temperature. The difference in the G' composition can be caused by a number of causes. These consist of elements like fiber–matrix interfacial interactions, filler dispersion, the reinforcement type, and the matrix type [74,75]. For all samples, G' decreases as the temperature rises, which is in line with higher temperatures causing more displacements of polymer segments [76]. The temperature at which the maximum damping factor value ($\tan \delta$) is attained is known as the glass transition temperature (T_g).

The damping factor graphs of composite materials with varying proportions of *ex*EGS (2.5 wt.%, 5.0 wt.%, 7.5 wt.%, and 10 wt.%) are displayed in Figure 10c and the relevant parameters such as the T_g and $\tan \delta$ peak high values are presented in Table 6. The composite materials lose less energy when there is good contact. Better interfacial adhesion inside the filler and resin matrix is indicated by a lower peak height [77]. The $\tan \delta$ height values for cured neat UPe resin and the resulting composites are comparable but with discrete differences.

Figure 11 shows the average microhardness values of composite samples with different *ex*EGS amounts. It was observed that with an increase in the proportion of particles (*ex*EGS), there is an increase in the microhardness of the composite compared to the pure matrix. For composites with 7.5 wt.% of *ex*EGS particles, the microhardness increased by 33.7%. After, a slow decrease was found. Bassyouni et al. [78] reported a similar pattern while studying polyurethane (PU)-milled light bulb glass composites. Achukwu et al. discovered that the microhardness rises with the percentage of reinforcement [79]. Moreover, the literature data, presented in Table S3, related to the mechanical properties of the composites based on different UPRs, are not of a wide distribution, and mainly, the values of the tensile strength are in the range found for the UPe/*ex*EGS 2.5–10 wt.% composites (Table 6). Thus, produced UPe/*ex*EGS 2.5–10 wt.% composites showed comparable or better mechanical properties to the published results (Table S3), which indicate the high potential applicability of the presented technology.

In general, the presented circular concept offers many advantages, as in the following: (i) a method of modification is relatively simple with a procedure based on non-toxic chemicals with the possibility of the recycling of the diluent, (ii) washing solutions contain mainly non-hazardous iron salts, (iii) materials showed good adsorption–desorption properties and all issue related to environmental concerns were solved, and (iv) the treated exhausted adsorbent used as the reinforcement in UPR provides composites with comparable or better mechanical properties than the literature findings. The environmental friendliness of the produced composites was confirmed by non-leaching characteristics according to TCLP. The main drawbacks relate to using commercial Poraver® GmbH, which excludes the possibility for the effective design of the textural properties of the adsorbent. Despite this, the developed technology offers a good alternative to Lewatit FO36 in relation to the financial and technological aspects, and the most beneficial relates to the environmental aspect regarding the developed disposal technology. Overall, the presented sustainable technologies are a scalable alternative which can offer significant a contribution to environmental protection.

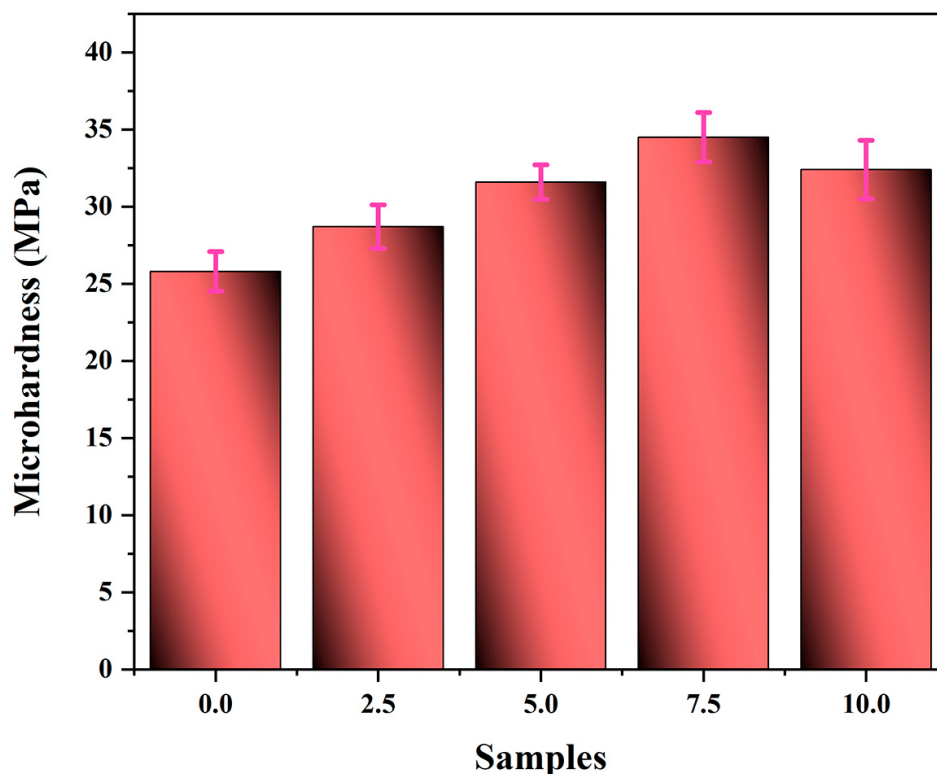


Figure 11. Microhardness of UPe/exEGS composite materials.

4. Conclusions

The sustainable development agenda related to the preservation of the planet is an enormously developing area and wealth of results have been achieved. Nevertheless, there are still many challenges, such as the increasing use of bio-based raw materials, a decrease in energy consumption, technological simplicity, end-of-life material recycling, and increased environmental friendliness that should be addressed. In line with this, herein, the achievement of some goals through sustainable technologies' development for wastewater purification and the valorization of generated waste materials into useful products is presented. This was achieved by the production of an effective EGS@APTES-GT hybrid adsorbent for arsenate and Iprodione removal, applied in both batch and dynamic modes in first step. In the next step, the desorption of saturated EGS@APTES-GT, after five adsorption–desorption cycles, provides an effluent solution which was successfully treated by applying the photocatalytic degradation of wastewater containing Iprodione and one with As(V) by chemical stabilization. The closed looped of adsorbent use was attained by exhausted adsorbent EGS@APTES-GT acid washing and grinding in order to obtain a material applicable as the reinforcement in UPe-based composites, i.e., UPe/exEGS. The testing of the mechanical properties of the UPe/exEGS composites showed a higher elastic modulus than pure resin. In comparison to pure resin, composites containing 7.5 wt.% of exEGS had an increased modulus of 30.1%, tensile strength of 25.9%, and microhardness of 44.9%.

At the same time, it is necessary to continue work on the development of low-cost, high-efficiency, and pollution-free technologies, promoting its widespread application in industrial production, and those that will fit into sustainable development goals.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app15063093/s1>, Figure S1: 2D (a) and 3D (b) structure of Iprodione; Figure S2: pH drift test for EGS@APTES-GT; Figure S3: EDS spectrum showing el-

emental composition of EGS@APTES-GT external surface in the selected point; Figure S4: EDS spectrum showing elemental composition of EGS@APTES-GT on the cross-section surface in the selected points; Figure S5: EGS@APTES-GT sphere's outer-surface EDS mapping with elemental concentration distribution; Figure S6: Speciation of As(V) obtained using MINTEQA 3.0 software ($C_i = 4.83 \text{ mg dm}^{-3}$ for As(V), $T = 25^\circ \text{C}$); Figure S7: Langmuir, Freundlich, and Temkin nonlinear isotherm models for arsenate (a) and Iprodione (b) adsorption on EGS@APTES-GT hybrid adsorbent; Figure S8: Breakthrough curves for arsenate (a) and Iprodione (b) removal by EGS@APTES-GT-packed column for different flow rates; Figure S9: FTIR-normalized spectra of UPe-based composites reinforced with ex EGS at 2.5 wt.%, 5.0 wt.%, 7.5 wt.%, and 10 wt.% addition; Figure S10. (a) The scree plot and (b) of the FTIR spectra UPe/exEGS composite; Figure S11. Loading plots and their related PCs' drawn spectra (a,b) of $400\text{--}400 \text{ cm}^{-1}$ and (c,d) $1800\text{--}400 \text{ cm}^{-1}$; Table S1: Quality certificate for DION FR 7721-00; Table S2: Column parameters. Table S3. Comparison of mechanical properties of UPR-based composite. References [80–111] are cited in the supplementary materials.

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Abbreviations

The following abbreviations are used in this manuscript:

EGS	Expanded Glass Spheres
GT	Goethite
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
FTIR	Fourier-transform Infrared Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
UPe	Unsaturated Polyester Resin
APTES	(3-aminopropyl) triethoxysilane
T _g	Glass Transition Temperature
DMA	Dynamic-Mechanical Analysis

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