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Composite Lightweight Materials with Upgraded Physicochemical Functionality and Improved Economic Feasibility †

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Abstract: In recent years, research has revolved around materials with superior functionality. Despite the encouraging results, their commercial use is limited due to high production costs. The major drawback of nanomaterials is their tendency to form aggregates that limit their activity. In order to overcome barriers, the synthesis of advanced, composite materials is proposed. These materials must exhibit high mechanical strength, adhesion between substrate and coating, and enhanced properties when compared to the substrate or the coating. In the present work, expanded perlite substrates were coated or impregnated with materials with a variety of physicochemical characteristics. The influence of the substrate's physical properties on the performance of the produced composite materials was studied.

Keywords: expanded perlite; microspheres; composites; titania; photocatalysis; paraffins; phase change materials; construction materials; chitosan; heavy elements removal

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1. Introduction

In recent years, research has revolved around materials with superior physicochemical properties, such as multifunctional and smart materials for energy applications, nanomaterials that are accelerated by physical stimuli to adsorb or prevent the adsorption of chemical substances, etc. Although the research results are encouraging, these materials are soft and have a tendency to agglomerate or form gels [1]. These obstacles have a direct impact on technical and economic efficiency and, consequently, the exploitation of their commercial products.

In order to overcome barriers, the synthesis of advanced composite materials is proposed, i.e., materials that consist of suitable substrates either coated with multifunctional materials or impregnated with them, so as to enhance the physicochemical properties of the counterparts and reduce the overall manufacturing cost [2]. Among the various parameters that must be considered when synthesizing these materials, the mechanical strength of the substrate, the adhesion rate between the substrate and coating, and the performance of the final complex materials are crucial. Moreover, the coating or impregnation technique must ensure the uniform distribution of the multifunctional material on the substrate without the formation of aggregates.

Over the last few years, the use of expanded perlite as a substrate has expanded to include advanced and innovative applications. It has been reported that besides the

traditional applications of perlite as a simple structural and insulating material, the use of composite materials of expanded perlite with (i) paraffin [3] as a PCM (Phase Change Material) for insulation and therefore energy saving; (ii) bacteria [4] for the self-healing of cracks in concrete; and (iii) airgel [5] (aerogel) for the preparation of high-performance insulating material is an efficient alternative to conventional materials. In addition to the above, the ability of expanded perlite to float in water, as a lightweight material, explains its utilization in photocatalytic applications [6], regarding organic and inorganic pollutants, and in the sorption of heavy metals, when appropriate chemical surface modification with organic [7,8] or inorganic [9] overlays is applied. In the aforementioned applications, the expanded perlite that is utilized refers to commercial products with specific physical characteristics and specifications. According to a literature review at the time this research was conducted, only one research group [10] was found that had studied the effect of the morphology of expanded perlite on the growth of graphite nanotubes (carbon nanotubes) on such a substrate. They found that growth was strongly affected by the specific surface area of perlite samples, and it was more efficient in the case of perlite particles with a coarse surface and increased specific surface.

The aim of this research was to investigate the impact of the substrate's morphology on the physicochemical behavior of the lightweight composite. Expanded perlite substrates of different particle size distributions with tailored properties were prepared. The different sizes included medium, fine, and ultra-fine fractions. The materials that were examined as coatings included photocatalytic nanomaterials, such as titanium dioxide (TiO_2), or organic biosorbents, such as chitosan and paraffins, as phase change materials. The final composites were examined based on their ability to absorb heavy elements as well as their photocatalytic activity. Finally, stable compositions of PCM/perlite composite materials were determined for their utilization into construction final products (mortars and plasters).

2. Materials and Methods

2.1. Perlite Substrates

Raw perlite was obtained from Sunrise Resources, Nevada, US. The provided sample was a typical amorphous aluminosilicate glass with minor secondary crystalline phases of feldspars.

Initially, the raw perlite was crushed in a jaw crusher and sieved to produce the various raw medium and fine grades. Medium grade revealed a particle size distribution (PSD) of 1.18–0.5 mm and the fine grade of 0.3–0.075 mm, respectively. As for the ultrafine grades, production was accomplished via milling by a pulverizer. Milling time was adjusted to achieve a raw particle size below 0.063 mm. The fineness of the produced material was characterized by air-jet sieving.

The expansion process was carried out through a vertical lab-scale perlite expansion furnace, operating with LPG, which could expand all the different grades (Figure 1). All the grades were expanded at different loose bulk densities (LBDs) and exhibited various physical characteristics in terms of open/closed porosity, mechanical strength, and water/oil absorption. This was achieved by modifying the LPG consumption and, thus, the expansion temperature until the desired density was obtained.

2.2. Perlite-Chitosan BioComposites: Fabrication—Batch Absorption Studies

High-molecular-weight chitosan, oxalic acid, hydrochloric acid, sodium hydroxide (NaOH), and heavy metal salts ($CuSO_4$, $NiSO_4*6H_2O$, $CoSO_4*7H_2O$) were provided by Sigma-Aldrich Chemical Corporation. The fabrication of the biocomposites was carried out based on the rapid neutralization method described in the literature [7,8,11,12]. The basic characteristics of these samples are summarized in Table 1.

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

Figure 1. Vertical lab perlite-expansion furnace operating with LPG. (**a**) Furnace. (**b**) Module for expanding ultrafine grades.

Table 1. Characteristics of perlite/chitosan biocomposites.

Grade/Substrate Codes	Raw Grade (Particle Size)	LBD (kg/m^3)	Biocomposite Codes
Ultrafine—Microspheres/UF-257	−0.063 mm	257	BCUF-257
Fine Grade/F-90	0.3/0.075 mm	90	BCF-90
Medium Grade/M-110	1.18/0.5 mm	110	BCM-110
Medium Grade/M-170	1.18/0.5 mm	170	BCM-170

A ternary metallic solution of 50 ppm Cu, 50 ppm Ni, and 50 ppm Co was prepared. The pH of the stock solution was adjusted to 5. Sorption experiments were performed by adding 0.5 g of biocomposites to 100 mL of the metallic solution while the samples were placed on a magnetic stirrer. Throughout all tests, the pH of the solution was maintained (pH = 5) using 0.1 N NaOH and 0.1 N HCl solutions. These conditions were selected based on results obtained from previous experiments regarding the optimum conditions for maximum metal uptake [11]. The metal concentration of the solution was measured every 30 min using Atomic Absorption Spectroscopy (AAS) until equilibrium was reached.

2.3. Photocatalytic Composites: Fabrication—Characterisation of Photocatalytic Properties

The synthesis of nano-titanium dioxide (TiO_2) was accomplished by employing a hyperbranched polymer, poly(ethylene)imine, through the method of wet chemical precipitation [12]. The resulting precipitant was retrieved via centrifugation, washed with ethanol, dried at 60 °C for 6 h, and finally calcined at 600 °C. For the synthesis of the core–shell material, the resultant nano-TiO_2 was dispersed in ethanol and an appropriate amount of HNO_3 was added. The samples were placed on a stirring plate in an ultrasound bath for 15 min. Finally, the expanded perlite was added to the samples with a ratio of titanium dioxide–expanded perlite of ½ *w*/*w* under mild stirring. The samples were collected via filtration (PE6@TiO_2). The characterization of these samples is summarized in Table 2.

The photocatalytic properties of the samples were assessed spectroscopically (UV-vis spectroscopy) under natural solar light according to a model reaction: the reduction of 4-nitrophenol to 4-aminophenol in an excess of sodium borohydride [13,14].

Table 2. Characteristics of perlite–titanium dioxide nanoparticles (PE@TiO_2).

Grade/Substrate Codes	Raw Grade (Particle Size)	LBD (kg/m^3)	Photo-Composite Codes
Ultrafine—Microspheres/UF-222	−0.063 mm	222	PE4@TiO_2
Ultrafine—Microspheres/UF-257	−0.053 mm	257	PE6@TiO_2

2.4. Perlite–PCM Composites: Fabrication—Mortar Preparation

The PCMs used were commercial paraffins, RT21HC and RT31 products, from the Rubitherm RT-line. Perlite substrates of fine (0.3/0.075 mm) and medium (1.18/0.5 mm) PSD, expanded at 50–90 kg/m^3 and 110–170 kg/m^3, respectively, were impregnated with the abovementioned paraffins. The loading of the fabricated composites reached 70% in paraffin. Leakage tests took place at room temperature and at 40 °C for 4 h. Then, 10 mL of the perlite–PCM composite was weighed and placed on pre-dried and weighed filter paper. After 4 h, the composite was removed and the filter paper was weighed again. The weight difference was attributed to the paraffin loss from the composite. The optimum compositions were determined.

3. Results and Discussion

3.1. Perlite Substrates

The physical properties of the expanded perlite samples are shown in Tables 3–5. As expected, the expansion process had a great impact on the physical properties of the produced substrates. As the expanded perlite grain became lighter, water and oil absorption increased. At the same time, the grain also becomes more friable.

Table 3. Physical properties of medium expanded perlite samples.

Substrate Code	LBD (kg/m^3)	Water Load (mLH_2O/gperl)	Oil Absorption (g oil/g Perlite)	Compression Resistance (Vol Reduction)	Skeletal Density (kg/m^3)
M-110	95.9	2.07	2.93	72.1%	822.3
M-130	123.0	2.09	2.16	62.2%	426.6
M-170	167.8	1.61	1.85	41.4%	508.9

Table 4. Physical properties of fine expanded perlite samples.

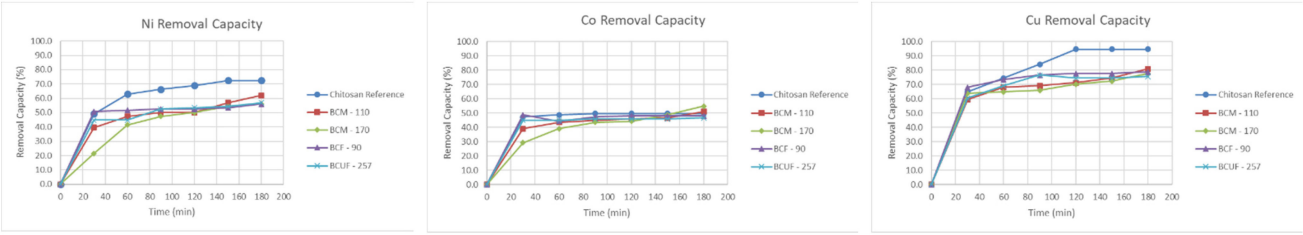
Substrate Code	LBD (kg/m^3)	Water Load (mLH_2O/gperl)	Oil Absorption (g oil/g Perlite)	Compression Resistance (Vol Reduction)	Skeletal Density (kg/m^3)
F-50	46.9	9.36	5.48	72.1%	822.3
F-70	67.4	6.45	4.45	62.2%	426.6
F-90	89.4	4.67	3.28	55.9%	439.2
F-120	119.8	3.66	2.40	45.6%	484.6
F-140	141.3	3.21	2.06	41.4%	508.9

Table 5. Physical properties of ultra-fine expanded perlite samples.

Substrate Code	Particle Size	LBD (kg/m^3)	Oil Absorption (g oil/g Perlite)	Compression Resistance (Vol Reduction)	Skeletal Density (kg/m^3)
UF-222	−0.063 mm	222.2	1.17	34.6%	1214.2
UF-257	−0.053 mm	256.5	0.94	30.9%	1237.4

3.2. Perlite–Chitosan Biocomposites—Batch Absorption Studies

Contact time is a key factor that affects the absorption process. The removal capacities of Ni(II), Co(II), and Cu(II) by chitosan–perlite biocomposites and a chitosan reference as a function of time are presented in Figure 2. It is evident that all composites achieved more than 75% of the reference equilibrium removal capacity when containing only 50% of the active material, supporting an increased economic feasibility. The morphology of the substrate also affects the removal capacity of the biocomposites. Fine and ultra-fine substrates had comparable behavior with the reference during the first 30 min of the experiments.



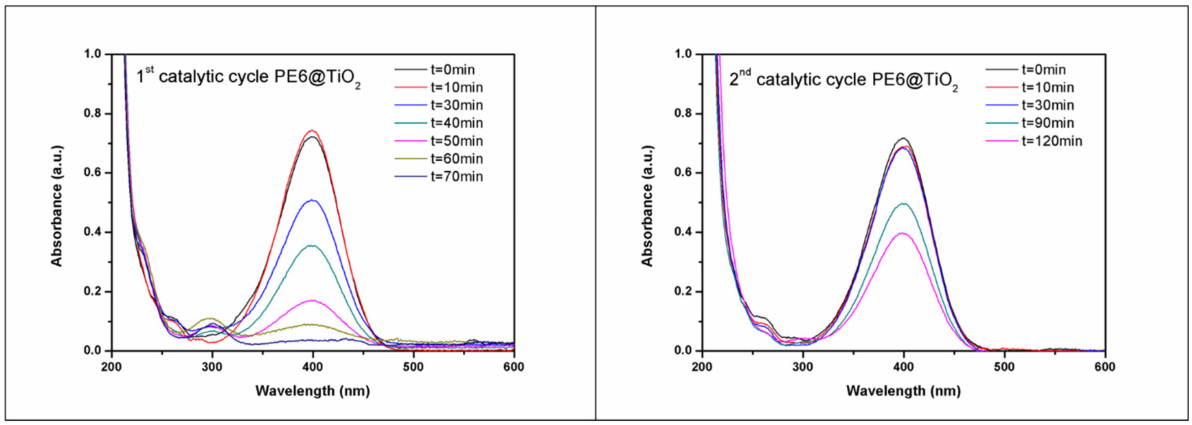
(**a**) (**b**) (**c**)

Figure 2. Batch absorption studies of different biocomposites for (**a**) Ni, (**b**) Co, and (**c**) Cu removal.

During the experiments, it was observed that the perlite–chitosan composites floated in the solution due to their lightweight structure. On the other hand, the pure chitosan beads remained sunk unless stirred. This is a great advantage regarding the removal of the adsorbents from the solution when the adsorption procedure is over.

3.3. Photocatalytic Composites

The optimum photocatalytic composites (PE6@TiO_2) enabled the adsorption of 4-nitrophenol on the porous substrate and the subsequent degradation of the pollutant, as displayed in Figure 3. PE6@TiO_2 enabled the complete adsorption/degradation of 4-nitrophenol within 70 min. It must be mentioned that the proposed photocatalyst is reusable and requires no further purification steps prior to its use; furthermore, it enables a 48% reduction in the concentration of the aqueous organic pollutant within 2 h during a second photocatalytic cycle.



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

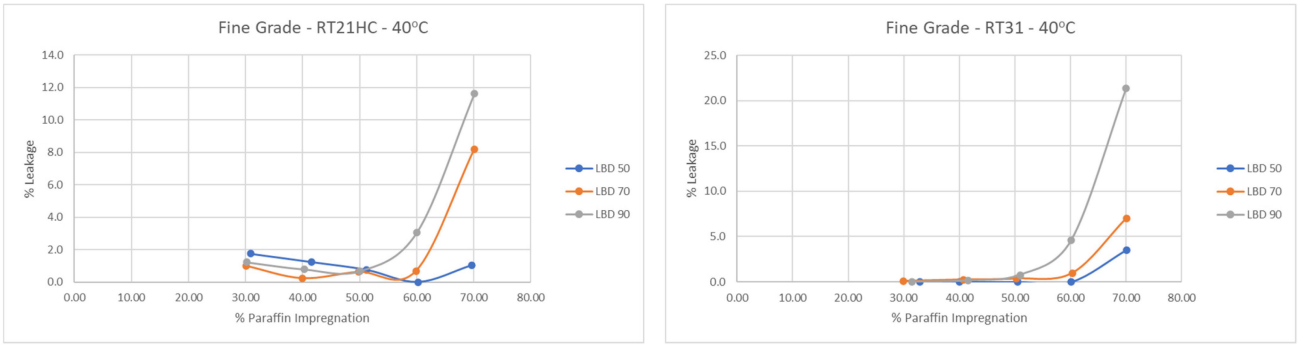
Figure 3. Spectra of 4-nitrophenol reduction to 4-aminophenol in the presence of the PE6@TiO_2 photocatalyst under sunlight exposure for one (**a**) and two (**b**) process cycles.

The prepared systems are compatible and, in some cases, exhibit improved behavior compared to other photocatalytic systems reported in the literature. As far as the degra-

dation of 4-nitrophenol is concerned, CuO nanoparticles achieved 95.3% reduction under the conditions of pH 6.0 and 90 min of degradation time [15]. After being loaded on appropriate substrates, pure TiO_2 systems showed an improvement in efficiency from 87% to 99% after 180 min of reaction [16].

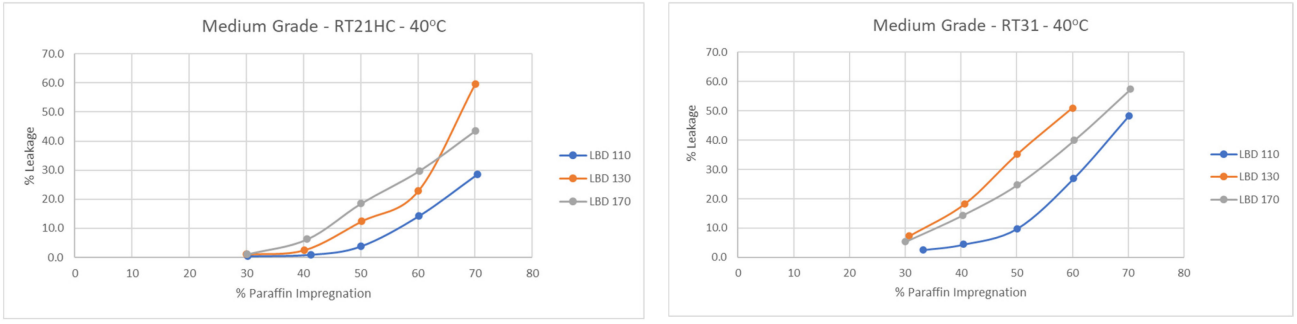
3.4. Perlite–PCM Composites

In order to determine the optimum composition of the perlite–PCM composites in order to obtain a stable structure, the samples were tested in terms of paraffin leakage on filter papers for 4 h at room temperature and 40 °C. The results at elevated temperate are shown in Figures 4 and 5. In the case of phase change composites, not only the size but also the physical characteristics of the perlite substrate have a great impact on the optimum composition of the prepared composites. The fine grades exhibit much lower leakage than the medium grades. In particular, the lighter composites can contain up to 60% of paraffins with minimum leakage (<2%). The innovative PCM composites developed by in.mat-Lab showed improved inflammability compared to the commercial micro-encapsulated PCMs. Their production process without the use of other chemicals emphasizes the economic and environmental benefits compared to competition.



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

Figure 4. Leakage tests of PCM composites prepared by impregnating fine-grade expanded perlite at different densities in paraffin (**a**) RT21HC and (**b**) RT31.



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

Figure 5. Leakage tests of PCM composites prepared by impregnating medium-grade expanded perlite at different densities in paraffin (**a**) RT21HC and (**b**) RT31.

4. Conclusions

During this research project, significant knowledge was acquired regarding the properties of complex lightweight perlite materials and the impact of the substrate, expanded perlite, on the properties of the final composite materials. Moreover, it was confirmed that the use of perlite as a substrate in these applications improved the technical performance and, consequently, the cost-effectiveness of the final products.

Regarding the environmental applications, the perlite composites achieved 75–100% efficiency compared to the reference chitosan despite the fact they contained only 50% of this biomaterial.

Regarding the photocatalytic properties of expanded perlite–titanium dioxide materials, the results verify the synthesis of an efficient photocatalyst. (PE6@TiO_2) enables the complete degradation of the aqueous pollutant, 4-aminophenol (100%), within 70 min, and the photocatalyst can be reused, without being purified, for a second photocatalytic cycle with almost 48% degradation efficiency.

As far as construction materials are concerned, insulating composites containing up to 70% phase change materials were synthesized and retained their properties at elevated emperatures.

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