PHOTOCATALYTIC DEGRADATION OF BODIPY DYE WITH A SHUNGITE BASED PVA HYDROGEL UNDER UV-LIGHT IRRADIATION

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Abstract - The contamination of water with dyes is a critical problem for the environment and a great deal of research is invested to produce the novel adsorbent composites with high adsorption capacity and at the same time gaining a major goal to alleviate their non-biodegradable and toxic nature. Therefore, many researchers put their attention to developing sustainable, biodegradable and nontoxic adsorbent systems with the photocatalytic property. Herein, a nanocarbon based natural source called shungite (SHT)was combined with PVA hydrogel to illustrate the degradation of aluminescent Bodipy dye in an aqueous solution via UV-light irradiation. SHT-PVA hydrogels have been characterized by FTIR and studied their swelling properties and thermal behaviors by TGA.

Keywords - Shungite, Bodipy, Organic Dye, Removal, PVA, Hydrogel

I. INTRODUCTION

Hydrogels can swell up to several times of their original volume in aqueous solutions and interact with dyes or heavymetal ions via dispersion forces such as Van der Waals forces, *π-π* interactions and hydrogen bondsand results in the removal of metal ions and organic dyes from aqueous solutions via these molecular interactions [1].Hydrogels are generally divided into three classes, according to their starting material, called naturalhydrogels, synthetic hydrogels, and hybrid hydrogels formed by the combination of natural and synthetic based polymers. They can also be categorized according to their cross-linked types in the gel as physically and chemically cross-linked hydrogels. Among hydrogel systems, polyvinyl alcohol (PVA) hydrogels have tri-dimensional network with excellent biocompatibility, high elastic modulus and non-toxic properties [2]. In recent years, hydrogel systems have been combined with special sorbents in order to utilize as sorbent-basedhydrogel composite materials to remove dyes and heavy metals[3].

Due to the tremendous increase in industrialization, organic dyes pollution has been become an important problem for the environment and aquatic life, as well.When they are degraded, their breakdown products are generally toxic and carcinogenic because of the side toxic products are generated such as aromatic compounds, naphthalene, and benzidine[4]. Therefore, it is important to remove dyes and their side products via a hydrogel-based system from aqueous medium.

As a special type of sorbent material,"Shungite" is a natural mineralcomposed mostly of carbon nanoparticles (≤ 10 nm) and disordered carbon with different minerals such as pyrite, quartz, sericite and chlorite [5]. The shungite is referred to as natural metastable non-graphitized carbon with fullerene like globules, aggregate of stacks of graphene layers and natural carbon. The carbon content in shungite presents with a content from 25 to 98% results to different types of shungite and additionally cause to the differentiation in their appearance. The rest of the part of shungiteincludessilica, alumina, various micro and macro sulfur, chromium, zinc, nickel and lead at low percentages (≈ 2-5 %) [6]. The special structure depends onthe carbon matrix in the rock fullerene, molecular sphericalcompounds of 60-70 carbon atoms,which is obtained by mining minerals with special physical, chemical and therapeutic properties. Due to their excellent physical and chemical properties, shungite composites have been tailored as a sorbent, catalyst, polymer filler, or Li-ion ion battery electrodes [7].

In this study, a shungite based PVAhydrogel was synthesized via the freezing and thawing method and some physical and chemical properties of the synthesized hydrogels were investigated. As an application, it is the first time, we demonstrated the fluorescence quenching and photodegradation of a well-known Bodipy dye byshungite-PVA hydrogelunder UV-light exposure.

II. EXPERIMENTAL

2.1. Materials and Methods

Materials

The following reagents were used in the experiments:dust shungite with 80 % of carbon (Kazakhstan),Poly(vinyl alcohol) (PVA) (89.000), Sodium tetraborate decahydrate (borax) $Na_2B_4O_7 \cdot 10H_2O$, and deionized water. Bodipy dye (1,3,5,7 tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) was synthesized according [9].

2.2 Preparation ofPure PVA- Hydrogel.

10 % (w/v) PVA solution was prepared in 25 mL of dd. H_2O and heated to 70°C. When the PVA was dissolved, 5 % of borax (w/w) dissolved in 5 mL of 25 mL dd. H_2O was added and stirred for 15 mins. at 70°C. The resulting transparent solution was transferred to a petri dish and dried at 70°C for 45 mins. Three cycles of freezing and thawing methodshave been applied to the synthesized PVA hydrogel [8].

2.3Preparation of Shungite/PVA Hydrogel

10 % PVA(w/v) solution was prepared in 25 mL of dd. H_2O and heated to 70°C. Shungite (3.75 g) was introduced to the prepared PVA solution. Shungite and PVA ratio was adjusted to 60:40 % (w/w). The mixture was stirred for 10 mins, then borax (1.25 g)was dissolved in 5 ml dd. $H_2O$was added to the black-colored solution and furtherstirred for 15 mins.at 70°C. The resulting, black-colored solution was transferred to a petri dish. The sample was dried at 90°C for 45 mins.Afterward, a 4 mm thick hydrogel was formed as a result of 3 freezing-thawing cycles, with a 12 h freezing step at 4°C and 6 h thawing step at 25°C.

2.4 Interaction of 1,3,5,7 tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (Bodipy Derivative) with Shungite-PVA Hydrogel

A solution of the Bodipy derivative ($5x10^{-5}$M) was prepared in EtOH: H_2O (1:1). Shungite-PVA hydrogel was immersed into 20 mL of the Bodipy solution and placed in a shaker at a rate of 200 rpm. While it was shaken, it was irradiated with UV-light (6W) for 15 mins. at room temperature. After that, the shungite-PVA hydrogel was removed from the solution and compared their luminescence intensity under UV light. As a blank experiment, (a) Bodipy solution, (b) dust shungite in Bodipy solution, (c) PVA hydrogel in Bodipy solution were also irradiated with UV-light under the same conditions.

2.5 Characterizations of the Hydrogels

2.5.1 Fourier-Transform Infrared (FTIR) Spectroscopy:FTIR spectra were obtained using the single beam Fourier transform-infrared spectrometer (Schimadzu, Miracla 10 model). FTIR spectra of the samples were obtained in the range of 4000–400 cm^{-1} in transmission mode made discs with KBr.

2.5.2 Thermogravimetric Analysis (TGA): TA Instruments SDT 650 was used to perform a differential thermogravimetric (TG/DTA) analysis simultaneously. Heat was generated at a rate of 10 °C per minute in air up to 800 °C.

2.5.3 Swelling Studies

Dynamic swelling studies were made by gravimetric measurements. The hydrogel samples were placed in falcon tube and suspended in 20 mL of dd. H_2O at 25 °C. The hydrogel samples were removed at different time intervals (1h, 2h, 3h, 4h, 6h, 16h and 24h) and weighed on an analytical balance after excess solution was blotted free of the surface water using a filter paper.

In this experiment, the mean values of three duplicate measurements were presented. The results were calculated in the following Equation-1:

$$Q(\%) = \frac{m_1 - m_2}{m_2} \, x \, 100 \qquad \text{(Eq-1)}$$

where, Q is the swelling ratio in percentage (%), $m_1$is the swollen mass, and $m_2$is the dried mass [10].

III. RESULTS AND DISCUSSION

3.1 Synthesis of Shungite Based PVA Hydrogel

On the contrary, different synthetic nanocarbons such as carbon nanotubes, graphenesetc., nano-sized carbon included shungite are natural minerals and they have amphiphilic characteristics. They interact with both polar and nonpolar mediums by forming stable dispersions. Therefore, it was easily mixed with 10 % of PVA solution homogenously. Sodium tetraborate decahydrate (borax) was used as a crosslinker agent to produce both PVA hydrogels and shungite-PVA hydrogels. When borax dissolves in H_2O, it produces boric acid ($B(OH)_3$), $B(OH)_4^-$ and Na^+ species[11].

$$Na_2B_4O_7.10H_2O \rightarrow 2B(OH)_3 + 2B(OH)_4^- + 2Na^+ + 3H_2O$$

The crosslinking between borax and PVA results in two different complex structures (a) *a monodiol complex* generated by the reaction of the tetrahydroxy borate anion with the diol (-OH) groups in PVA (b) *bidiol complex* formed by the complexation between two hydroxyl groups in borate anion with another adjacent diol in PVA[12]**(Fig 1A)**. In addition, shungite also increases the toughness of the hydrogel due to its trace amount of metal ingredients.

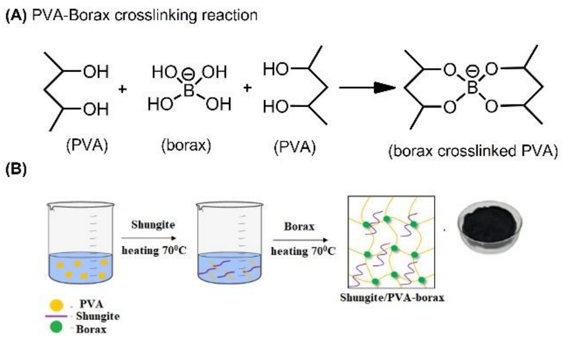

Fig. 1(A)Chemical structure of the prepared hydrogels, (B) Schematic illustration of the hydrogel's preparation

3.1. FTIR Spectroscopy

To prove the functional groups in hydrogels, FTIR spectra of the (A) Shungite-PVA hydrogel; (B) pure

Shungite; (C) PVA-borax hydrogel and (D) pure PVA are depicted in **Fig 2**. FTIR results show that a broad band showing up at 3301 cm^{-1}; 3594 $cm^{-1}$and 3288cm^{-1}in Fig 2A, 2C and 2D, respectively, is a prominent band that corresponds to stretching vibrations of the hydroxy group*ν*(OH) in PVA. For the samples A, C and D at 2905-2948 cm^{-1}attribute to C–H stretching in CH_2 groups. Also, the appearance of new peaks at 1541 and 968 cm^{-1} is attributed to O-B-O bending, B-OH stretching and B-O stretching, respectively in Fig 2C [13], which proves that crosslinking was generated successfully.

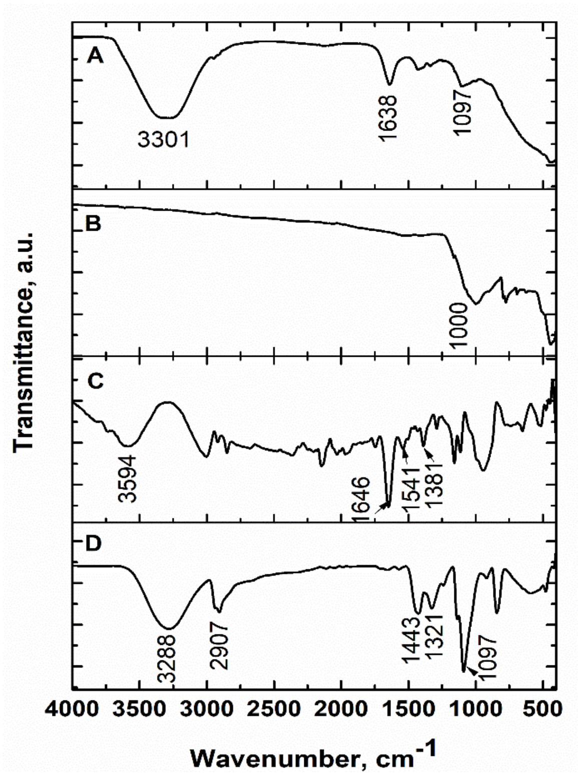

Fig.2 FTIR spectra of (A) Shungite-PVA hydrogel; (B) pure Shungite; (C) PVA-borax hydrogel and (D) pure PVA

3.2 Thermal Gravimetric Analysis (TGA) Studies

Fig. 3 shows the DTA-TG curves for hydrogels measured in a nitrogen atmosphere. Samples' weight decreases as temperature increases, indicating that the sample is continuously decomposing. TGA curves are shown in Fig.3 (A) for PVA-borax hydrogel and (B) for Shungite/PVA-borax hydrogels. For all hydrogels, the results showed three steps toward weight loss. The first weight loss began at 40°C and finished at 270°C for these samples due to the evaporation of water. The second weight loss from 250°C to 350 °C can be explained by the decomposition of a bond of PVA-borax crosslink or decomposition of a free polymer. Due to the degradation of the polymer, the third weight loss began at 300°Cand rapidly progressed to 500°C.

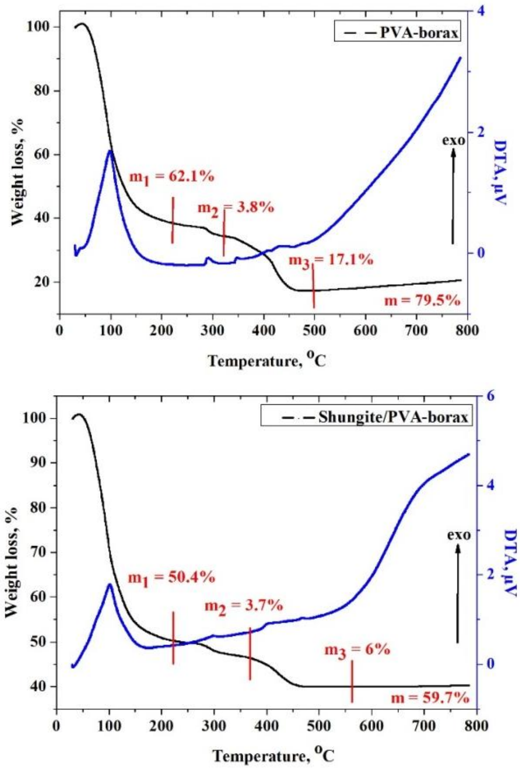

Fig.3 Thermograms of the samples: PVA-borax and Shungite/PVA-borax

Regarding thermal stability, the Shungite/PVA hydrogel performed better stability than the PVA-borax, which was possible due to the formation of an intermolecular bond between shungite and PVA.

3.3 Swelling Studies

The swelling kinetics depend on the chemical composition and the preparation method of the hydrogel. According to Eq-1, shungite-PVA hydrogels have been reached swelling equilibrium after 6 hours with 61% swelling (Fig 4). However, pure PVA hydrogels swelled up in 6 hours, with the degradation. The addition of shungite resulted in higher mechanical durability compared to pure PVA hydrogel.

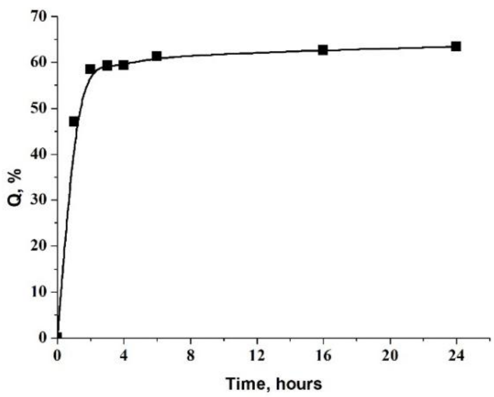

Fig.4 Swelling capacity versus time for shungite/PVA-borax hydrogel

3.4 Fluorescence Quenching and Photocatalytic Degradation of Bodipy Dyeby Shungite-PVA Hydrogels

As an application, shungite-PVA hydrogels interacted with luminescence Bodipy solution under UV-light. Due to the adsorption sites on the shungite-PVA hydrogels, firstly most of the dissolved Bodipy dyes were uptaken by the hydrogels. After irradiation by UV-light, photocatalytic degradation has been occurred due to the photocatalyst effectof shungiteand resulted in diminishing the luminescence intensity in Bodipy dye. In the blank experiments, there was no change in the luminescence intensity compared to pure Bodipy solution.

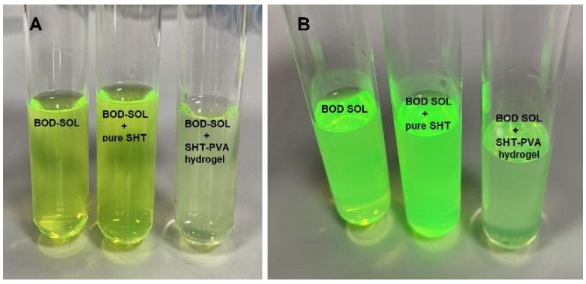

Fig.5 Comparison of the luminescence intensities of Bodipy solution, pure dust shungite in Bodipy solution and Shungite-PVA hydrogel (A) under daylight, (B) under UV light.

IV. CONCLUSIONS

As conclusion, shungite-PVA hydrogels have been synthesized with moderate swelling capacity, high thermal stability and high mechanical durability. The preliminary studies show that Bodipy dyes as a model dye can easily and quickly degradein the presence of shungite-PVA hydrogel due to their high dye uptake capacity and photocatalytic properties. This study will lead to new applications of shungite based hydrogels concerning the removal of dyes from aqueous solutions.

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E-HEALTH LITERACY IN PEOPLE WITH RHEUMATOID ARTHRITIS

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Abstract - Health e-literacy presupposes abilities to research, find, estimate, evaluate, integrate and apply the gains obtained from the electronic environment in order to solve health problems. Objective: To assess the level of e-health literacy in people with rheumatoid arthritis (RA). Observational study with 139 participants with rheumatoid arthritis, with a mean age of 63.05 years, 79.86% of whom were women. The scales “Cross-cultural adaptation and validation to Portuguese of the European Health Literacy Survey – HLS-EU-PT” (Saboga-Nunes, L., Sorensen, K. (2013)) and “eHEALS: The eHealth Literacy Scale” were applied. ”(Norman, & Skinner, 2006). It was found that in 30.2% of the participants, e-health literacy is inadequate, in 44.6% it is reasonable and in 25.2% it is high. Age, area of residence, educational qualifications and professional activity influence the level of e-health literacy. As the level of health literacy increases, so do the levels of e-health literacy. Promoting the development of health literacy facilitates the implementation of e-nursing interventions that promote continuity of care for people with RA, so personal factors need to be considered.

Keywords - e-literacy; Telenursing; Health; Rheumatoid Arthritis;

I. INTRODUCTION

The e-Health conceptualization reflects "the use of information and communication technologies in support of health and health-related areas"(1).
Lapão (2019) advocates that “new technologies are an important opportunity for new digital services, which allow users to play a more active role in health management”. (2) The e-nursing interventions included here aim to provide, in a systematic way, educational support and health interventions, in order to increase the capacity and confidence of users in the management of their problems. This allows you to improve your understanding of your health condition, assess progress and problems arising from your pathology, set goals that allow behavior change and improve problem-solving skills. In this way, people are oriented to develop self-management skills and to modify self-care behaviors, dealing with chronic situations. (3)
A 2017 study postulates that the nursing of the future will be developed by increasingly qualified professionals, focused on advanced practice, whose knowledge will support their leadership in the reorganization of the practice of care, in partnership with other professionals and with greater proximity to users. of health services. (4)
The Directorate-General for Health (2019) of Portugal states that this is a path with great potential in the areas of disease prevention, protection and health promotion, and it is essential to ensure interdisciplinary cooperation adapted to people's needs, in order to prevent the increase in health inequalities. It is, however, essential to recognize that not the entire population is familiar with the digital world. Although many people use digital media to manage their health, there are also groups of elderly, vulnerable or disadvantaged socio-economic backgrounds who do not use these media because they have limited access to them or have low levels of e-health literacy. (5)
People with rheumatoid arthritis (RA) make many decisions about their disease every day, so a computer-adapted online self-management program could support decision making. However, its development requires the active participation of users (6).
Rheumatoid arthritis is a chronic disease with an evident decline in functional capacity, quality of life, and an increased risk of comorbidities (7).
Taking into account the information exposed and showing in the scientific literature a gap in knowledge regarding the association between sociodemographic characteristics (sex, age, education level, area of residence and professional activity) and levels of health literacy with e-health literacy levels of people with rheumatoid arthritis, the objective of this study is to explore the existence of this relationship.

II. METHODS

The descriptive-analytical-correlational study was conducted according to a cross-sectional approach with 139 participants, 79.86% female aged between 26 and 85 years, an average age of 63.05 years, assisted at the Rheumatology Consultation at Centro HospitalarTondela -Viseu, Portugal, from February to May 2020.
The data collection instrument included, in a first part, questions of a sociodemographic nature and later the scales “Cross-cultural adaptation and validation to Portuguese of the European Health Literacy Survey – HLS-EU-PT (8)(9) and “eHEALS: The eHealth Literacy Scale”(10) . The scales, respectively, allowed the measurement of health literacy and the