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Optimization of tannin rigid foam as adsorbents for wastewater treatment☆

J. Sánchez-Martín[a,*], J. Beltrán-Heredia[a,1], A. Delgado-Regaña[a], M.A. Rodríguez-González[b,*], F. Rubio-Alonso[c,*]

[a] Department of Chemical Engineering and Physical Chemistry, Faculty of Science, University of Extremadura, Avda. de Elvas, s/n, 06071 Badajoz, Spain
[b] Area of Mineralogy and Cristalography, Faculty of Science, University of Extremadura, Avda. de Elvas, s/n, 06071, Badajoz, Spain
[c] Instituto de Cerámica y Vidrio, CSIC, Kelsen, 5, 28049 Madrid, Spain

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ABSTRACT

Tannin rigid foams are presented as novel adsorbents for wastewater remediation. Although these materials are known since long time ago, this is one of the newest applications in environmental technology. The efficiency of the different combinations of reagents in the foam synthesis were studied by using Response Surface Methodology, and the optimum category was subsequently tested on dye, surfactant and pharmaceutical removal. The results are promising for the three types of pollutant. Structural differences based on FTIR, Raman spectroscopy and other superficial characterization techniques confirmed the intrinsic adsorption benefits of this optimum category if compared with other tannin rigid foams. Optimum tannin rigid foam was obtained with 0.03 g of furfuryl alcohol, 0.11 g of formaldehyde, 0.25 g of diethyl ether and 0.20 g of p-toluensulfonic acid per g of Weibull Black tannin extract. With this combination of reagents, up to 250 mg g^{-1} of Methylene Blue removal was reached and a significant elimination of several dyes and surfactants was feasible.

1. Introduction

Materials science is nowadays a knowledge field that needs even more multidisciplinarity. Modern world presents new necessities and many of them are related with the need for novel multipurpose materials. Because of that, the interaction between different sciences (such as environmental technology, chemistry, materials science and applied physics) is almost mandatory if scientists want to give a complete response to difficult and complex problems society is facing right now (Nordberg and Gianotti, 2011).

This multidisciplinarity also encourage scientific community to search for specific new utilities of known novel materials, that is, to find as many applications as possible to the high number of new materials that are being developed every day (Bradley, 2011). This is the reason one can find an overwhelming list of researching articles that might be easily linked to this scope (Cerrutti et al., 2012; Rao, 2001; Zhu et al., 1998). However, in order to get the best from these novel materials, it is needed to explore their properties not only for one established usage, but for others and especifically for those that may worry the scientific community. Water quality and wastewater disposal is undoubtedly one of them.

Tannin rigid foams (TRF) are well known materials and their importance is growing nowadays. Since the first papers where these novel wood-based adhesives were introduced to scientific community (Pizzi, 1980) to the last approaches to mechanical properties of such materials (Celzard et al., 2010), TRF have attracted the interest of a large number of researchers. Basically, they are derived from tannin feedstocks such as Quebracho (*Schinopsis balansae*), Black Wattle (*Acacia mearnsii*) or Pine (*Pinus pinaster*). The polymerization process include the mixing of the reagents, the expansion stage (foam forming) and the aging.

The chemical fundamentals for the synthesis of TRF lay in the tannin gelification, which is a reasonably known process and can be found in some of our previous papers (Beltrán-Heredia et al., 2011a,b). The main difference with this gelification is the fact that tannin immovilization is performed in combination with the expansion of a blowing solvent agent. This occurs within a time range of 10–30 s after mixing the gelating components and constitutes a very delicate process. Little deviations either in the addition of the solvent or in the crosslinking product (mainly formaldehyde) may drive to a non effective foam because of lack of hardness or volume (Tondi et al., 2009). Several details of the gelation and foaming process can be found in the Supplementary material.

☆ Supporting Material available.

* Corresponding authors.
E-mail addresses: jsanmar@unex.es (J. Sánchez-Martín), jbelther@unex.es (J. Beltrán-Heredia), angela.del.reg@gmail.com (A. Delgado-Regaña), marodgon@unex.es (M.A. Rodríguez-González), frubio@icv.csic.es (F. Rubio-Alonso).
[1] Tel. +34 924289300x89033.

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The growing disposal of wastewater into the environment recently make the water contamination one of the most important tasks to take care of. New challenges must be faced because the *environmental matter* is a global concern (Muga and Mihelcic, 2008). Apart from the classical water pollutants, such as pesticides (Palanisami et al., 2009), diverse organic loads (Hench et al., 2003) or industrial effluents (Maceda-Veiga et al., 2012), novel and impactant contaminants are considered as *emerging pollutants*: dyes and colorants (Lacour et al., 2001), surfactants (Aboulhassan et al., 2006) or pharmaceuticals (Beltrán-Heredia et al., 2012). The adsorption of such contaminants can be a possible solution in order to remove them from the environment.

Some of our previous works showed tannin-derived adsorbents were found to be consistent products for the removal of a large variety of pollutants such as dyes (Sánchez-Martín et al., 2010), detergents (Sánchez-Martín et al., 2009) or pharmaceuticals (Beltrán-Heredia et al., 2012). However, these materials cannot be used for any other purpose, as TRF are able. Moreover, TRF presented a large list of synthesis variables, such as the amount of reagents, the reaction time, the temperature, etc. Because of that, the optimization of this synthesis can be a chance for enlarging the list of advantages these materials present with their characterization as optimal adsorbents for dyes, detergents and pharmaceuticals.

This article explores the feasibility of TRF as wastewater remediation agents. This should be an added advantage for these novel materials, and will enhance the utility of such products. Attending to the most ubiquitous pollutants, tannin rigid foams were tested on dye, surfactant and pharmaceutical removal. This investigation consists of three different and concomitant parts: firstly, a Design of Experiments was carried out for optimizing the synthesis of the adsorbent. This experimental procedure was planned according to previous preliminary trials, which revealed the probable presence of an *optimum point* inside this range. These experiments are not shown, but they predicted a change in the general tendency of removal efficiency according to the well known one-facto-a-time process, hence the applicability of a complex method such as Design of Experiment. Secondly, the resulting optimal category of the rigid tannin foam was intrinsically studied confronting the removal efficiency of the samples with the physical and chemical characterization of such products. Lastly, the optimum adsorbent was tested on several different pollutants of each family.

2. Materials and methods

2.1. Reagents and model compounds

Several chemicals were used for the lab synthesis of TRF:

- Commercial tannin extract from *A. mearnsii* de Wild (namely *Weibull black*) was kindly supplied by TANAC Inc. (Brazil).
- Furfuryl alcohol ($C_4H_3OCH_2OH$) was purchased to Sigma–Aldrich (USA) in 98% purity grade.
- Formaldehyde (HCHO) was purchased to Panrean (USA) under aqueous solution (37% purity grade).
- p-Toluensulfonic acid ($CH_3C_6H_4SO_3H$) was purchased to Fluka (France) in analytical purity grade (98%).
- Diethyl ether ($C_4H_{10}O$) was purchased to Sigma–Aldrich (USA) in analytical purity grade (99.5%).

Methylene Blue ($C_{16}H_{18}N_3SCl$) was selected as model compound for pollutant simulation. It is a cationic dye widely used in coloration industries. The human long exposition to this dye can cause increased heart rate, vomiting, shock, cyanosis, jaundice and many other dangerous injuries (Tamez et al., 2008). It was purchased to PANREAC (Spain).

Apart from this dye, other pollutants were included in the evaluation of the optimum adsorbent:

- Detergents are long-chain anionic surfactants and this chemical family includes a large variety of products. Some of them are Polyoxyethylene (3.5) sodium lauryl ether sulfate (SLES, $C_{12}H_{25}(OCH_2CH_2)_{3.5}OSO_3Na$), sodium dodecylbenzene sulfonate (SDBS, $C_{18}H_{29}SO_3Na$), sodium laurylsulfate (SLS, $CH_3(CH_2)_{11}OSO_3Na$), sodium dodecyl diphenyl ether disulfonate (SDDED, $C_{35}H_{56}S_2O_7Na_2$), sodium dioctyl sulfosuccinate (SDSS, $C_{20}H_{37}SO_7Na$), polyoxyethylene sodium nonylphenol sulfate (SNS, $C_{17}H_{28}SO_5Na$), sodium triethanolamine lauryl sulfate (TEA-LS, $C_{18}H_{40}NSO_4Na$) and sodium lauryl sulfoacetate (SLSA, $C_{14}H_{27}SO_5Na$). All of them were purchased to CHEM SERVICE Inc. (USA).
- Cationic and anionic dyes such as Methylene Blue (cationic one) were also included in the test of the adsorbent ability. These were Amaranth, Tartrazine and Quinoline Yellow (these last ones with anionic electrical character). They are colorants similar to Methylene Blue which are normally used as food additives (Mpountoukas et al., 2010). They were purchased to Acros (USA).
- Many chemical species are included as pharmaceuticals. We have included a pure antibiotic compound (Trimethoprim), which is widely used in human and veterinary medicine worldwide acting as an inhibitor in the chemotherapy treatment due to its antifolate effect by interaction with dihydrofolate coenzymes (Bekci et al., 2006). Other refractory pollutants linked to pharmaceutical industries are parabens, which are considered as *emerging pollutants* (Yamamoto et al., 2011) not easy to handle. In this work we included methyl, ethyl, propyl and butylparaben. All of these chemical species were purchased to Sigma–Aldrich (USA).

Chemical structures of these compounds are shown in Supplementary material.

2.2. Buffered solutions

The trials with added pollutant were performed with pH-stable media. To this end, a pH-7 buffer solution was prepared of 1.2 g of NaH_2PO_4 and 0.88 g of Na_2HPO_4 in 1 L of distilled water. The pH was then adjusted to 7 with HCl 1 M or NaOH 1 M. All reagents were analytical grade from PANREAC (Spain).

2.3. Tannin rigid foam production

Furfuryl alcohol (65% aqueous solution), distilled water and formaldehyde were introduced in a reactor. Once the mixture is homogeneous, tannin extract (5 g) is added and mixed with the help of a glass stick. Diethyl ether and p-toluensulfonic acid are added subsequently and stirring is kept for 10–15 s. Finally, the stirring is stopped and the mixture and the catalyst (strong acid) are allow to act. Since the reactor is thermically isolated, the self-condensation of furfuryl alcohol and the condensation of the tannin extract with the alcohol and formaldehyde take place simultaneously and exothermically. The evaporation of the boiling solvent (at ca. 35 °C) at the same time causes the expansion of the foam. The product is obtained after 30 s. It is chopped into little pieces and cured for 24 h for eliminating the non-evaporated solvent. The pills were reduced into powder in order to maximize the contact surface with the help of a manual blender. Finally, the adsorbent was washed up for removing any rest of reagent and dry at 60 °C overnight. The conservation of these adsorbents is carried out in a shelled test tube.