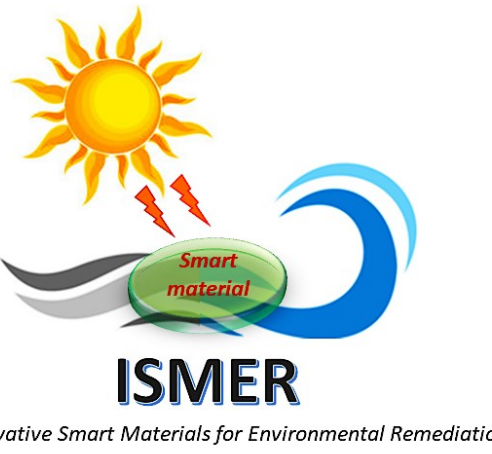# Floating smart-materials for water decontamination under solar light

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Introduction

Recently, groundwater pollution has driven the necessity to develop innovative and inexpensive smart-materials able to degrade toxic compounds, that lower drinking-water quality. In this regard, heterogeneous photocatalysis offers a green solution for water remediation. Titanium dioxide (TiO2) is the most used photocatalyst, however, to broaden its band-gap extending the photo-response to the visible region, it can be doped with conductive polymers, such as polyaniline (PANI) [1]. Moreover, a floating device can be adopted to overcome issues related to the use of slurry systems and maximize light utilization. Synthetic polymers, such as polyurethane (PU), have been commonly employed as floating materials for their light-weight, stability, and low cost. In the present work, visible light photoactive devices were prepared immobilizing PANI/TiO$_2$ composites on floating PU foams.
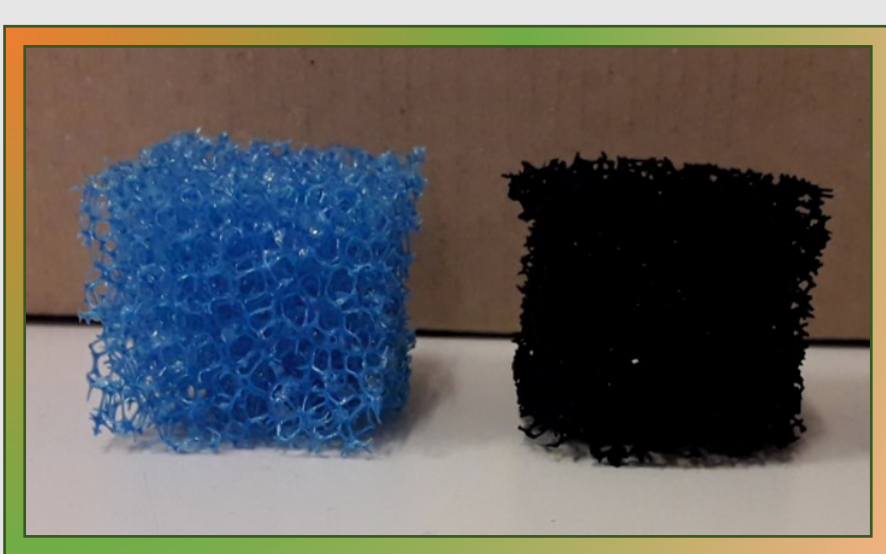
Methods

Fig.1: PU foam and PANI-coated PU foam

Two different types of PANI were produced. Traditional PANI (PANI1) was synthetized through a radical polymerization starting from aniline monomer, ammonium persulfate as oxidant and HCl as dopant [2]. An innovative PANI (PANI2) was synthetized using N-4(aminophenyl)aniline as reagent, hydrogen peroxide as oxidant in the presence of Fe^{3+} as catalyst and HCl as dopant [3]. PANI1 and PANI2 were deprotonated by an ammonia solution, then the powder was dispersed in dichloromethane and doped by 4-Dodecylbenzenesulfonic acid (DBSA) and Camphorsulfonic acid (CSA) [4]. Finally, TiO$_2$-P25 was dispersed in PANI-DBSA/CSA solution, where PU foam was added and impregnated (*Fig. 1*).

The materials were characterized by SEM-EDS and FT-IR. Photodegradation tests were performed using 0.25 g of coated-PU foam (0.07 g of catalyst) on a 10 ppm aqueous solution (100 mL) of rhodamine B (RHB). Before irradiation, each suspension was stirred for 30 min in the dark. Then, each mixture was followed by 180 min under light irradiation (*Fig. 2*); the light source, placed above the reactor, was a 300 W commercial solar lamp. Samples were analysed by UV-vis spectroscopy and HPLC chromatography, while the by-products characterization is under investigation by LC-MS. After the degradation test, coated-PU foams were rinsed with water and used for 2 recycles.
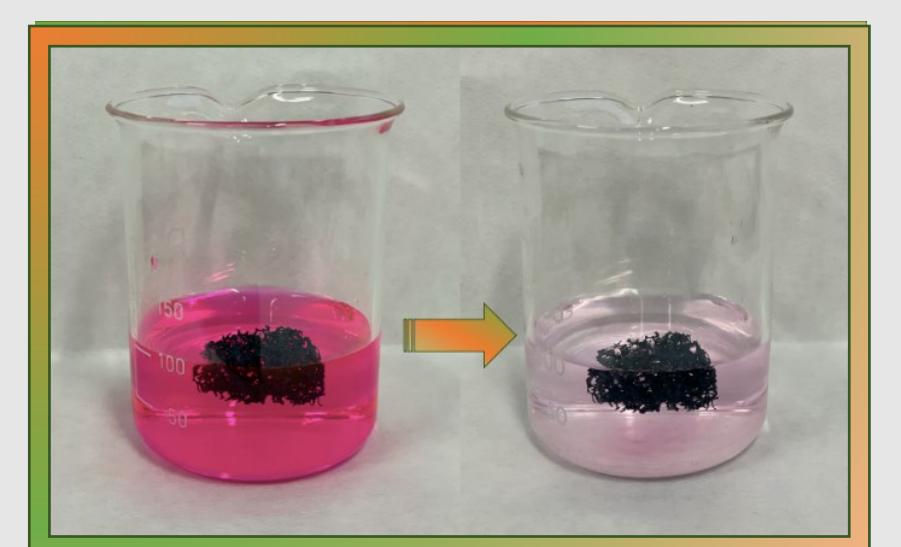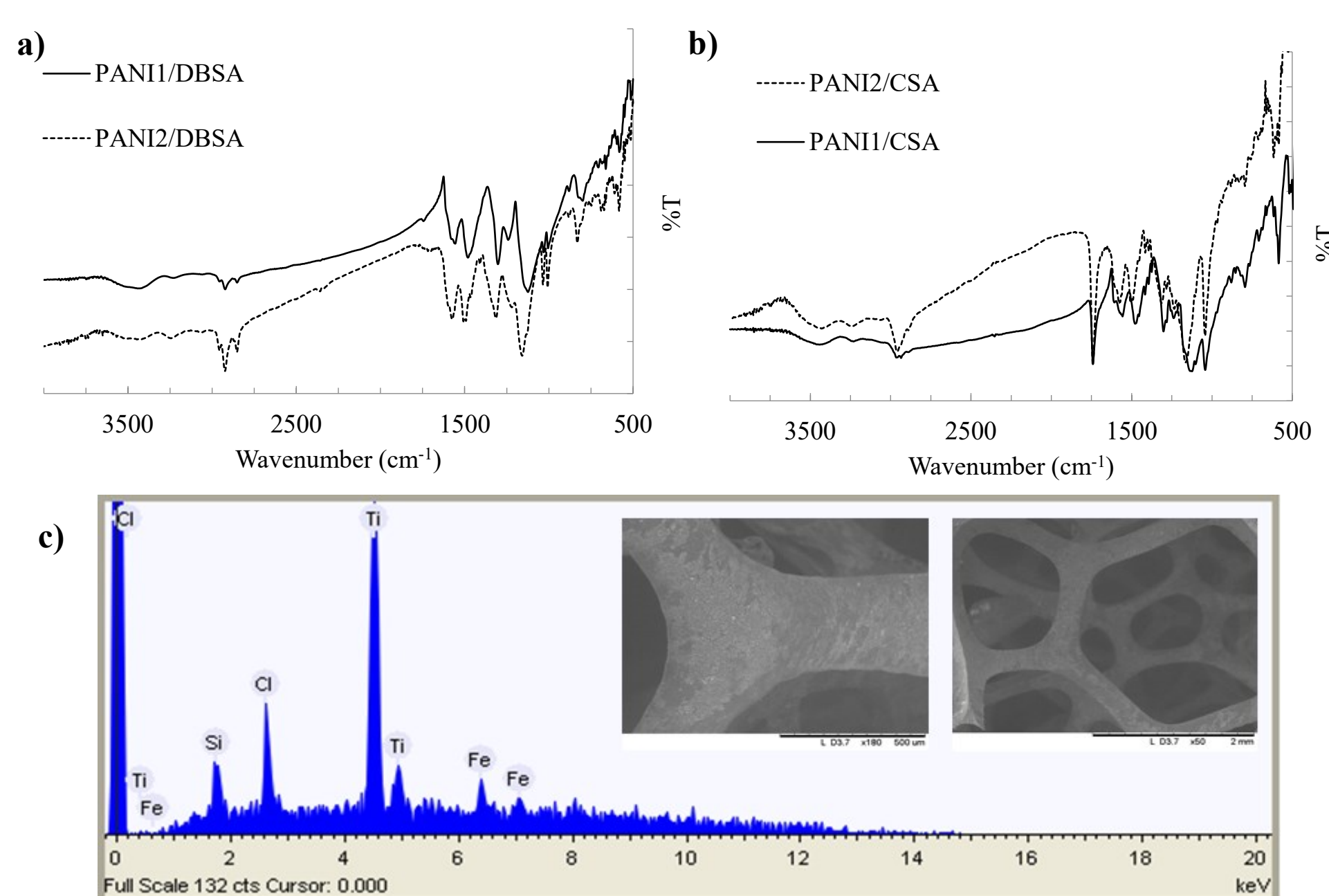

Fig.2: Photodegradation of RHB

Results

Fig.3: a)FT-IR spectra of PANI1-2/DBSA; b)FT-IR spectra of PANI1-2/CSA; c) SEM-EDS of PANI2/DBSA

FT-IR spectra confirm the structure of the polymer *(Fig. 3-a,b)*, whereas the presence of TiO$_2$ was proved by SEM-EDS (*Fig. 3-c*). PANI/DBSA and PANI/CSA behave differently during the photodegradation: while DBSA has shown mainly absorption properties, due to the length of the dopant alkyl chain which excludes the pollutant from the photoactive centers, instead the short length of CSA has led to about 10% of absorption in the first 30 min followed by photodegradation in the remaining 180 min (*Fig. 4*). Since PANI1 and PANI2 exhibited the same trend, it was decided to further investigate PANI2 because of its green synthetic pathway. All the materials underwent 2 reuses to assess their activity and stability. In the two recycles DBSA have displayed a decrease of the absorption efficiency caused by material saturation (*Fig. 5*). CSA has demonstrated the same absorption performance, however catalyst deactivation has induced a progressive decrease of photoactivity (*Fig. 6*).
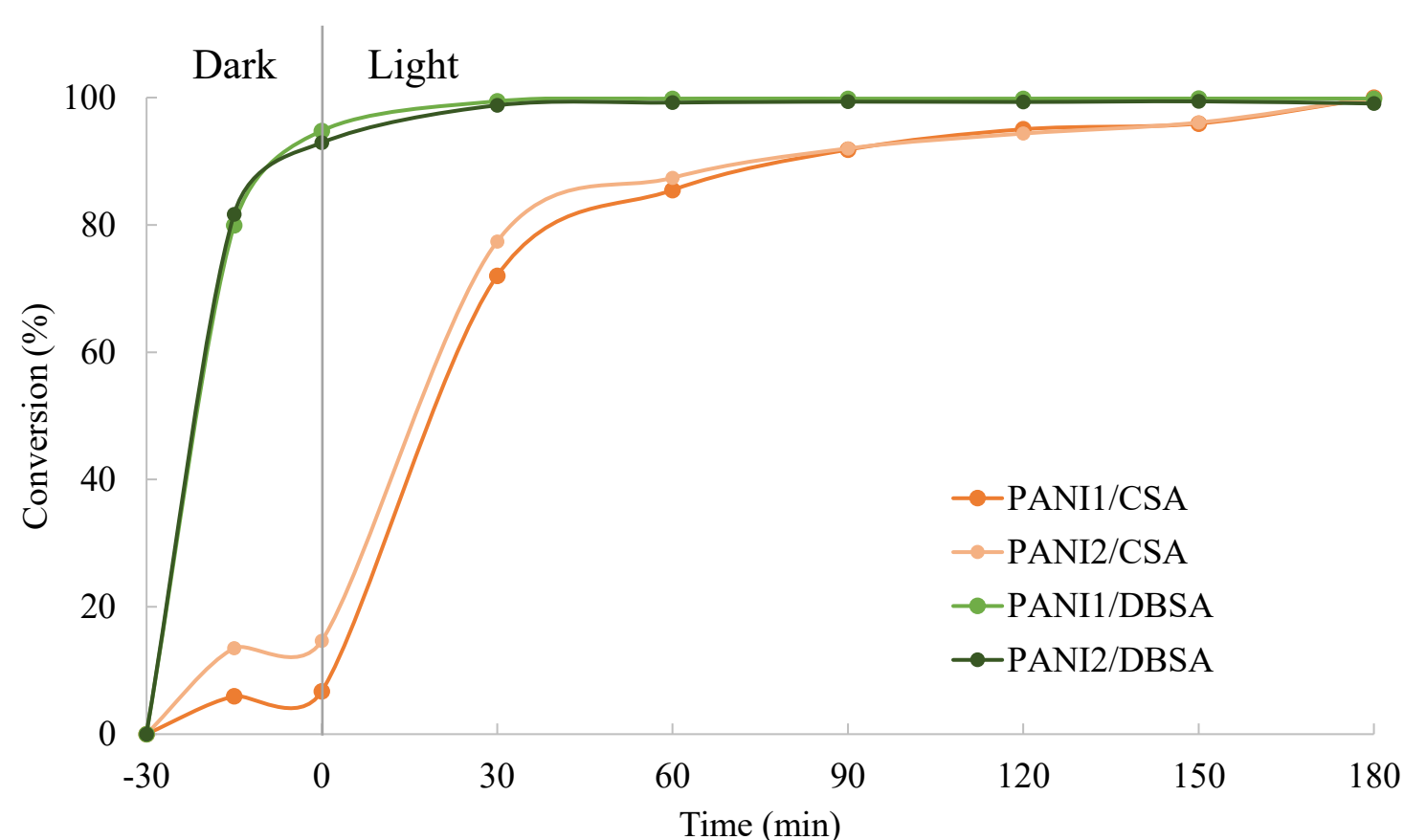

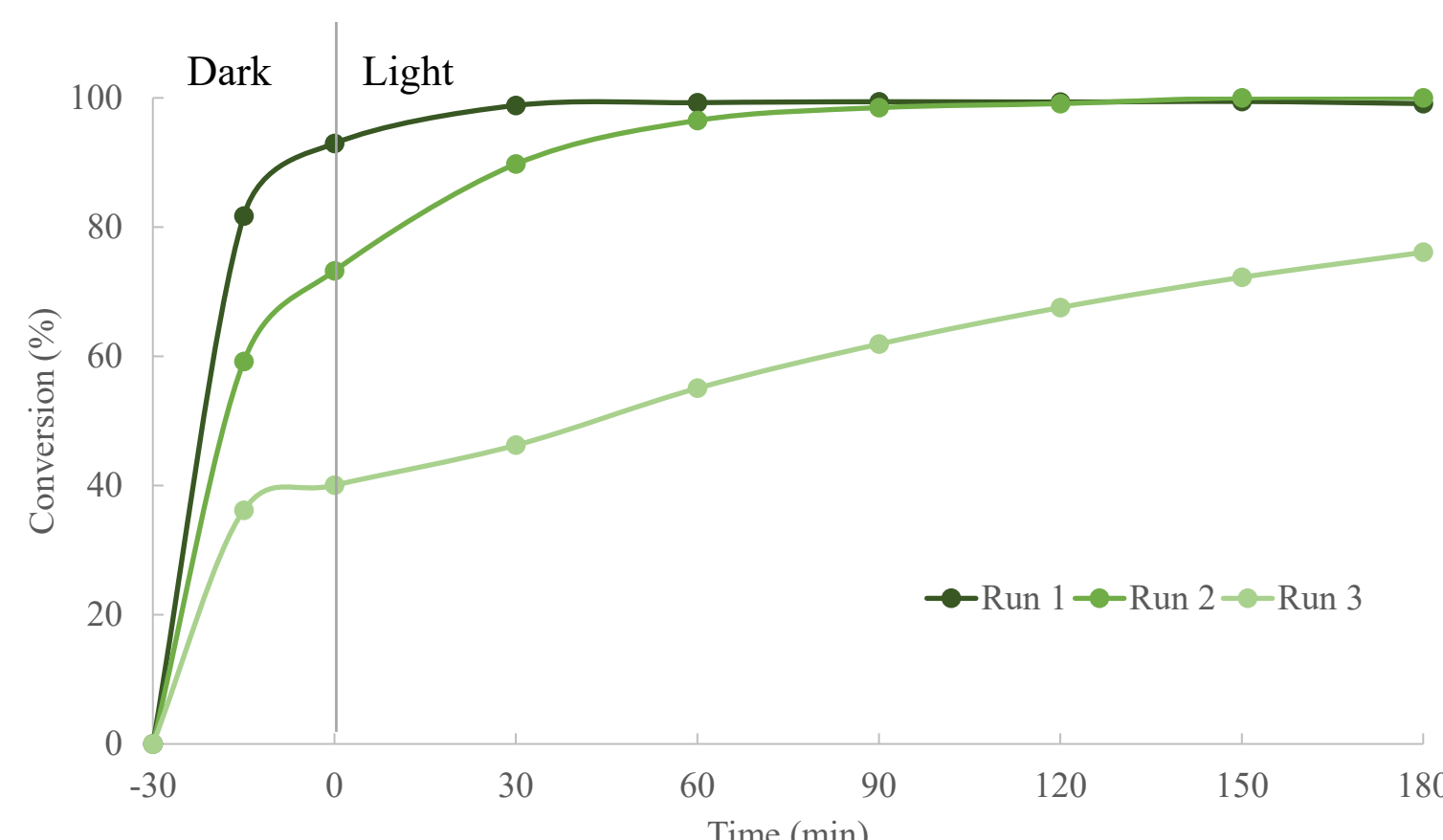*Fig.4: Photodegradation of RHB using PANI2/DBSA and CSA, and PANI1/DBSA and CSA*

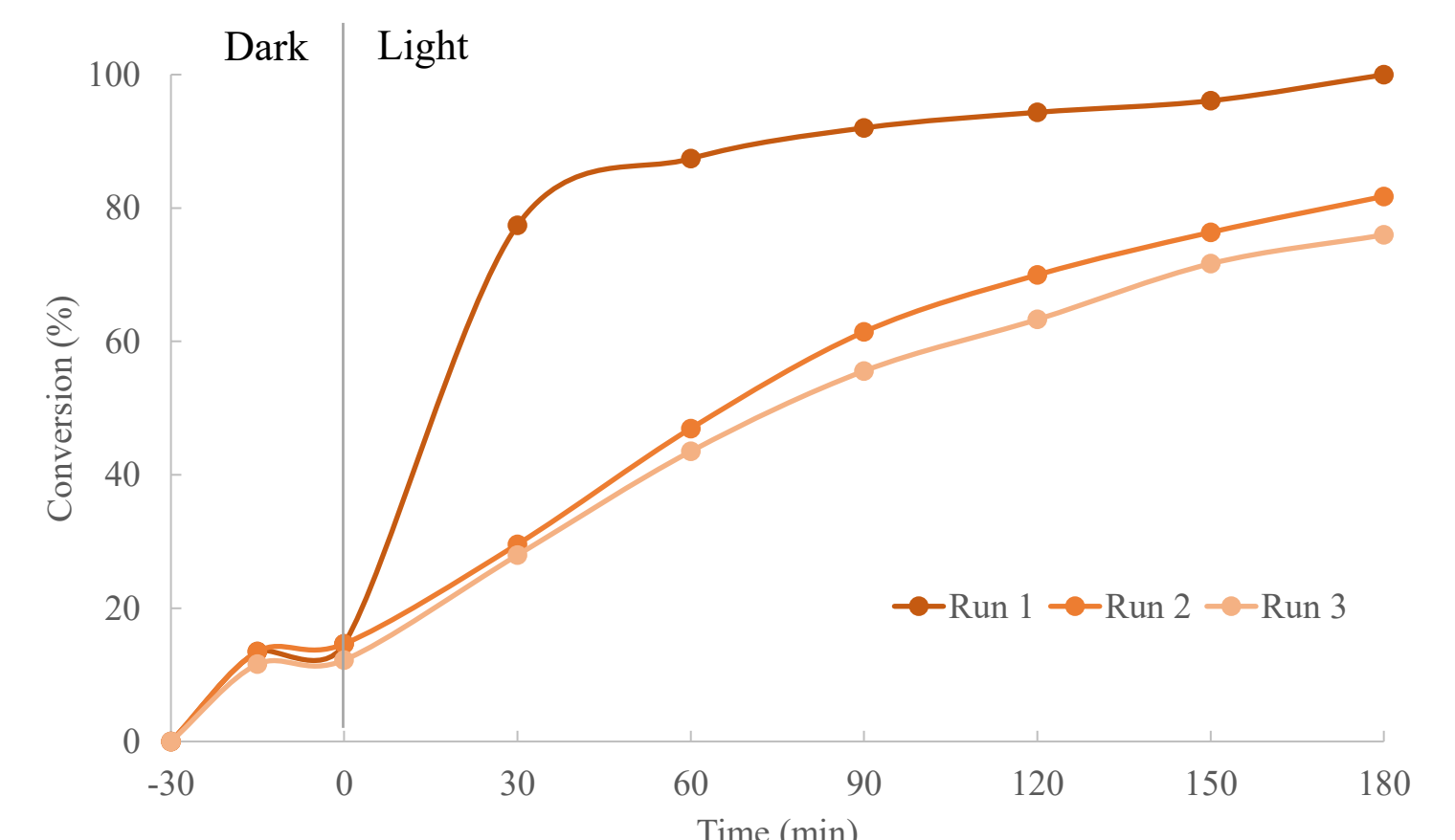*Fig.5: Recycle tests of PANI2/DBSA with RHB*

Fig.6: Recycle tests of PANI2/CSA with RHB

Conclusions

Floating coated-PU foams were successfully synthetized using PANI, DBSA-CSA and TiO$_2$. The impregnated foams were easily prepared through a traditional and green procedure, exhibiting a strong activity under solar light for the absorption and photodegradation of RHB. Furthermore, they remained stable and active even after 3 recycles without any regeneration process.

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[4] Y. Cao et al,. Synt. Met., **1995**, *69*, 187-190.