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Fabrication of carbon and sulphur-doped nanocomposites with seaweed polymer carrageenan as an efficient catalyst for rapid degradation of dye pollutants using a solar concentrator†

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Here we demonstrate direct use of sulphate rich seaweed polysaccharides, carrageenans, namely kappa (κ-), iota (ι-) and lambda (λ-) as source of sulphur and carbon doping in TiO_2 photocatalysts. During TiO_2 synthesis in the presence of sulphate rich carrageenan leaves, mainly residual carbon and sulphur doping resulted in a highly active photocatalyst. Evaluation of the dye degradation pattern shows rapid degradation of reactive black-5, methylene blue & methyl orange using modified TiO_2 nanocomposites in different light sources. Robust dye degradation was achieved between 1 and 4 h under daylight whereas, the use of a solar concentrator reduced the degradation time of MB and RB-5 to <5 min and MO solution was turned colourless within 20 min. The present study elaborates the effect of seaweed carrageenans in inducing heteroatoms like sulphur and residual carbon for the photodegradation of industrially important dyes.

Introduction

At present biomass based materials are receiving great importance from both academic and industrial sectors due to their sustainability and green features. Among several biomaterial sources, marine chemicals and seaweeds possess versatile characteristics due to their inherent saline environmental origin and growth. Further, seaweed cultivation offers both social and economic benefits. Therefore, for commercial aspects seaweeds fulfill the prerequisite of being low cost and easy to use. Carrageenans are one such red seaweed polysaccharide family available in 3 different sulphated forms and have been used in number of applications from food ingredients to water treatment agents. Most importantly, the number of sulphate groups on kappa (κ-, one sulphate), iota (ι-, two sulphates) and lambda (λ-, three sulphates) forms of carrageenans can be utilized effectively for *in situ* or post-modification of industrially important products.[1]

On the other hand, many researchers have explored the unique properties of several photocatalysts *via* non-metal doping. There have been several reports in the literature describing the properties and activities of several catalysts being influenced by non-metal dopants like carbon (C-) and sulphur (S-).[2,3] It is more evident from the photocatalytic degradation of dyes using TiO_2.[4] Several combinations of metal and non-metal dopants have been successfully used for doping TiO_2 targeting photodegradation applications. In several cases, a textile dye degradation study has been the common objective because textile industries consume large quantities of water and colouring agents in their manufacturing processes.[5,6] Modern day textile industries are vibrant and serve as essential part of our day-to-day lives. Despite stringent environmental regulations, industries still lack comprehensive wastewater treatment methods. Annually >500 tons of non-degradable textile colour wastes are being disposed of in natural streams without adequate treatments.[7]

It is estimated nearly 60 to 70% of hydrolyzed dyes remain in wastewater at the end of the dying process. Therefore, textile wastewater generally characterized by high concentrations of redundant dyes. It is also important to note that modern dye or colour pigments are designed to sustain harsh washing conditions in the consumer products like textile fabrics.[8] Among several textile dyes, reactive dyes are being used largely for

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