Employing Gel Polymer Electrolytes for Dye Sensitized Photoelectrochemical Devices

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Abstract

Dye sensitized photoelectrochemical (DSPEC) devices have attracted a considerable interest in the scientific community mainly due to their low cost in converting solar energy into electricity. Though the conventional crystalline silicon cells show higher efficiencies than DSPEC devices, there is a high potential for improving efficiency. A DSPEC device is a result of combination of several materials such as a photo anode, a counter electrode and an electrolyte. As far as electrolytes in DSPECs are concerned, liquid electrolytes have been widely employed. Due to their inherent drawbacks, attention has been diverted towards gel polymer electrolytes (GPEs) at present. GPEs are believed to be lying in between solid electrolytes and liquid electrolytes. They possess conductivities similar to liquid electrolytes and good mechanical properties similar to solid electrolytes. GPEs have been extensively used in various applications including batteries, super capacitors and artificial muscles. In this study, different GPEs have been prepared, characterised and tested in DSPEC devices.

GPEs were prepared by mixing and heating a polymer, an iodide salt with solvents. As the solvents, ethylene carbonate (EC) and propylene carbonate (PC) were used. Initially, the composition of the GPE was fine tuned in terms of conductivity and mechanical properties by varying polymer concentration and salt concentration. For the preparation of photo anode, titanium dioxide was grounded with acetic acid, ethanol and Triton X till an uniform slurry was obtained. It was casted on fluorine doped tin oxide (FTO) glass plates using doctor blade method. After sintering at 450 $^{\circ}$ C for 45 minutes and cooling down to room temperature, dye adsorption was done for 24 hours. As the dyes, commercially available Ruthenium dye as well as natural dyes were used. Having a platinum electrode as the counter electrode, DSPEC devices were fabricated in the configuration FTO / TiO₂/Dye/GPE/Pt and their performance were evaluated by measuring variation of photo current and voltage.

Optimization of the compositions of GPEs is an important factor to obtain a mechanically stable device. Also, proper heat treatments should be provided to the starting materials to result a good

quality electrolyte. Iodide ion contribution on conductivity should be sufficiently high to have an efficient iodide/triiodide redox couple which favours the high performance of DSPECs. Iodide salts with larger cations are preferred for that because when the cation is bulky, mobility of iodide anion becomes dominant. In addition, combining two iodide salts, one having a small cation while the other having a large cation, a noticeable improvement of the performance can be seen. Small cations have a high charge density which supports photo generation of electrons at the dye and faster diffusion at dye-semiconductor interface. This evidences the fact that both the size and the charge density assist the overall performance of the DSPECs. Results of DSPECs based on natural dyes are encouraging but it is needed to solve the problem of lower efficiency as well as the stability. Use of natural dye reduces the cost of the devices. On the other hand, Sri Lanka is rich in natural materials that can be used to extract dye. Hence, it is very much needed to take steps to minimize drawbacks of natural dyes. Anyway, application of GPEs is proven to be very suitable for DSPECs.

Keywords: Dye sensitized photo electrochemical devices ; efficiency ; gel polymer electrolytes ; photo current

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Removal of Methylene Blue by Adsorption onto Activated Carbon Developed from Bristle Coir Fibre

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Abstract

The progressive increase of industrialization in Sri Lanka and other countries has resulted in continuous increase of pollution of both surface and ground waters. Methylene Blue (MB) is an acid dye that is utilized for dyeing fabric, clothing (in the batik industry), paper and leather. There is rapid increase in the amount and the dye that is thrown into the natural water bodies leading to hazardous water contamination. Traditional methods of purification have found to be not efficient in eliminating the hazardous waste found in the effluent. However, recent studies conducted using activated carbon, as an adsorbent, has proved to be successful. However, commercially available activated carbon is expensive and this study looks at the possibility of using naturally available low cost materials such as coir fibre as an activated carbon precursor.

Coconut trees are widely grown in Sri Lanka and coir, the natural vegetable fibre, is extracted from the outer husk of the coconut. Coir fibre has higher amount of lignin and its internal structure is excellent for the production of activated carbon.

The objective of this study is to prepare activated carbon from chemically treated bristle coir fibres and characterize it and to investigate the equilibrium and kinetics model of adsorption of MB dye by thus prepared activated carbon from the coir fibre.

Bristle coir fibres were collected from the coir mill from a coastal area in the North Western Province of Sri Lanka. Before subjecting the raw coir fibre to heat treatment, they were scoured (with alkaline-bio) thoroughly and washed ultrasonically (Rocker Soner 203 H / Taiwan) with distilled water to remove excess chemicals and dried at 105 ^oC in electrical muffle oven for 5 hours. Scoured coir fibers were grinded by using ball mill machine (Fritsch supreme line Pulverisette 7/German) at 400 rpm for 10 minutes to produce coir micro level particles. The particle size was determined by particle analyzer (Fritsch Analysette 22 Nano Tec plus / German). Bristle coir micro level particles were leached with 0.5 M KOH for one hour and coir pulp was separated by filtering. Activated carbon was prepared by one step pyrolysis by chemical treatment with 0.1 M of Potassium Hydroxide (KOH). Scoured coir fiber particles pulp was fed in to tube furnace (Carbolite's / German) at 380 °C for fifty minutes in a nitrogen atmosphere. In order to understand the proximate analysis of adsorbent, properties such as pH, bulk density, moisture content, ash content, volatile content, and iodine number were determined using ASTM standard test methods. Activated carbon was characterized and the morphological features on the surface were observed with the Scanning Electron Microscope (SEM) and Fourier Transform Infra-Red (FTIR) (Shimatzu IR affinity- 01) spectroscopy analysis. Ultimate analyses of active carbon were done by EDX (ZEISS EVO LS 15 SEM with Oxford EDX). Adsorption studies were carried out batch wise and adsorption measurements were obtained by UV- spectro -photo meter (Shimadzu1800, Japan) at 645 nm.



The Figure shows the micrograph of coir fibre activated carbon. From the figure it can be clearly seen that micro size pore have developed evenly in the activated carbon particles. This helps in enhancing the adsorption of Methylene blue dye. Further, dye adsorption capability depends on the number of functional groups on the surface of the activated carbon.

Figure 1 : SEM image of coir activated carbon

Presence of strong adsorption peaks in the FTIR spectra thus indicates higher number of functional groups on the surface of the activated carbon obtain from coir fibres.

Adsorption data were modeled using Langmuir - Freundlich equation. The equilibrium data was best described by Langmuir model. The kinetic data were also applied to the pseudo first-order and pseudo second-order and intra-particle diffusion models. The kinetic data followed the two kinetic models but pseudo second-order model best described the kinetics of the adsorption process. The adsorbent capacities of coir activated carbon was compared with that of the commercial coconut shell activated carbon and the results show that coir activated carbon can be effectively used for first time as a low-cost renewable adsorbent alternative to commercially available Activated carbon in effluent treatments for the removal of excess dye materials.

Keywords: Activated carbon; Adsorption; Coir; Effluent treatment; Methylene blue