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Ultrasonication pretreatment of real-field pulping wastewater from bagasse-based paper mill

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In this study an attempt has been made to evaluate the feasibility of utilizing ultrasonication as pretreatment process to treat pulping wastewater. Bio-electrochemical treatment and microalgal treatment have been used as secondary treatment process. Ultrasonication was performed in bath type sonicator at 60 kHz for various time intervals of 15, 30, 45 and 60 min. There were no significant changes in *p*H, TDS and COD of pulping wastewater after ultrasonication. The bio-electrochemical treatment of pretreated wastewater did not show significant improvement in treatment efficiency and color removal. Rather the MFC operating with pretreated wastewater showed poor electrochemical performance. Microalgae consortia collected from lily pond in the institute could decolorize the ultrasonically pretreated wastewater, but color of raw wastewater could not be decolorized by micro algal consortia. Ultrasonication could have modified the compounds in pulping wastewater, making them more accessible to microalgal metabolism.

Keywords: Bio-electrochemical, Decolorize, Microalgae, Pulping wastewater, Ultrasonication

Paper and pulp industry plays a prominent role in shaping India's economy. Indian paper mills provide livelihood to nearly 1.5 million people and direct employment to 5,00,000 people[1]. Global warming, environmental pollution and depletion of natural resources have prompted the nations across the globe to bring about prominent and stringent changes in their environmental policies. In India, Central Pollution Control Board, a statutory body was formed under the Water Act 1974 and was further entrusted with power under Air Act 1981 to control, monitor and prevent pollution in India [2]. CPCB classifies paper and pulp industry to red category due to generation of hazardous waste. It has laid down various limits and protocols to ensure these mills do not damage the existing natural resources. Paper mills are bound to treat the waste generated to prescribed standards before releasing into the natural environment. The wastewater composition, quantity and quality widely depend on the raw material used for paper manufacturing and the process employed in various paper making process[3].

Current treatment process employs a combination of chemical, physical and biological treatments. While physicochemical treatment process provides satisfactory waste mineralization, it tends to generate more hazardous secondary pollutants. Whereas, biological treatment such as aerobic and anaerobic bacteria treatment don't yield satisfactory results and increased the color of wastewater. Though fungal based treatment provided higher color removal and better wastewater treatment, it was not practically feasible to maintain operating conditions for fungal growth on large-scale basis. Microalgae based pulping wastewater was promising as microalgae was capable of metabolizing the compounds in wastewater and showed higher colour removal[4,5,6].

The need for cost-effective treatment process and the rising importance of energy efficient industrial practices has kindled the interest among research community to develop novel technology capable of satisfactory waste mineralization and energy neutral waste management practices. Microbial fuel cells (MFC) are electrochemical reactors working on basis of exo-electrogenesis for bioelectricity production[7]. These MFCs can treat wastewater with simultaneous production of electricity[8]. MFC consist of an anode and a cathode connected via an external circuit, where oxidation and reduction reactions occur respectively[9]. The wastewater which is provided as substrate on the anode side, will be oxidized by exoelectrogens that produce electrons, protons and CO_2[10]. The protons will be transferred to the cathode side via a proton exchange membrane(PEM), whereas the electrons will be transferred to the cathode via the external circuit[11]. At the cathode, in the presence of an oxidant, reduction reaction occurs to form pure water[12]. Thus, these MFC systems can reduce the Chemical Oxygen Demand (COD) of wastewater and simultaneously produce electrical energy[13]. Currently, many variations of MFCs have evolved such as Microbial Electrolysis Cell (MEC)[14], Microbial Carbon Capture Cell (MCC)[15], Microbial Desalination Cell (MDC)[16], Photosynthetic Microbial Fuel Cells (PMFC)[17] etc. based on their applications.

In our previous work on bio-electrochemical treatment of pulping wastewater from bagasse-based paper mill we could observe only 64% of COD removal and no change in colour of wastewater[18]. The complex nature of compounds present in the wastewater was held responsible for the low treatment efficiency by biological treatment processes. A combination of physicochemical and biological process was found to be efficient in most cases. Existing research on utilizing various combinations of physicochemical and bio-electrochemical treatment includes bio-electrochemical treatment followed by chemical coagulation[19] and electro coagulation followed by bio-electrochemical treatment process[20]. In both cases the treatment efficiency could be significantly improved.

Ultrasonication is a mechanical process of irradiating liquid suspension with ultrasonic waves. The extreme agitation at microscopic scale is capable of producing acoustic cavitation, that solubilizes complex pollutants in wastewater[21,22]. In this study we aim at utilizing ultrasonication as pretreatment process for breaking down complex pollutants present in the pulping wastewater followed by bio-electrochemical treatment in first case and microalgal treatment in second case.

Experimental Section

Pulping wastewater

Pulping wastewater was collected from the paper pulp and bleach plants of a bagasse-based paper mill located in Kavery river belt, Karur, Tamil Nadu. The collected wastewater was stored at 4°C until further use to prevent the growth of microbes. The COD of raw pulping wastewater was 3200-3400 mg/L.

Microbial fuel cell fabrication

Dual chambered microbial fuel cells were fabricated using plexi glass material with anode/cathode volume of 250 mL. Nafion 117 was used as proton exchange membrane and was placed between anode and cathode chamber. Graphite plates were used as electrodes and the total surface area of electrodes was 38 cm^2. Nafion 117 was pre-treated to activate the sulphonyl groups in order to improve proton conductivity[23]. Ferricyanide in phosphate buffer at *p*H 7 was used as catholyte[24]. No external inoculum was added. The biofilm formed on anode surface in MFC previously treating raw pulping wastewater was used as such. Every cycle/batch was terminated when OCV dropped below 200 mV. The electrical connections were made with copper wire and stainless-steel clips[25].

Ultrasonication

Ultrasonication of pulping wastewater was performed in bath type sonicator UCP-02, M/s Jeio Tech Co. Ltd, Korea. All the experiments were carried out at 60 kHz. Ultrasonication was performed for three different time intervals of 15, 30 and 60 min. The temperature of the system was not controlled and the temperature varied from 7 to 40°C.

Microalgae based treatment of wastewater

The *p*H of wastewater was in the range of 4.7-5.2. Microalgal consortia collected from lily pond of the institute, was used as inoculum. The *p*H of pond water was nearly 8. Hence at 8:2 ratio of pond water and wastewater, the *p*H of the mixture was 7.6. The experiments were performed in glass bottles and were placed near the window and no artificial illumination was used.

Results and Discussion

Ultrasonication pre-treatment of paper industry wastewater

Ultrasonication was used as a pre-treatment process to solubilize the complex organic compounds present in wastewater and to improve the total treatment efficiency. For all time intervals of 15, 30, 60 and 120 min of ultrasonication the TCOD (Total Chemical Oxygen Demand) of pulping wastewater was not affected while there was slight decrease in SCOD (Soluble Chemical Oxygen Demand). However, there was mild difference or no change in *p*H, conductivity and TDS. Previous studies on ultrasonication of paper and pulp industry wastewater has enumerated that sulphates and carbonates present in mild concentrations extensively contributed to scavenging the hydroxyl radicals from solubilizing organic compounds present in wastewater leading to no change in COD[22].

Bio-electrochemical treatment of ultrasonicated wastewater

To study the effect of ultrasonication pre-treatment on bioelectricity production and wastewater treatment ultrasonicated wastewater was used as anolyte in the microbial fuel cell previously treating raw wastewater. The biofilm was not disturbed and anolyte was completely replaced with ultrasonic pretreated paper industry wastewater. The lag time to reach peak OCV was 4 days for raw wastewater, but in case of pretreated wastewater the lag time was higher and trend of OCV with time followed a different pattern in case of 15 min and 30 min of ultrasonication. The lag time to reach peak OCV was 14 days and 20 days in case of 15, 30 min ultrasonication pretreated wastewater respectively (Fig 1).

The COD removal was 68% and 70% while 15 and 30 min ultrasonicated wastewater was used as anolyte, whereas in case of raw wastewater the COD removal was 64%. Ultrasonication pretreatment of wastewater did not majorly affect the treatment efficiency and the color of wastewater. Power curves and polarization curves provide us with information regarding the electrochemical performance of microbial fuel cell. Though, higher power density could be produced the power curves and polarization curves, they were distorted at high current density when lower external resistance was connected (Figs 2 and 3). The deterioration in fuel cell performance could be due to hostile or unfavorable conditions to the anodic biofilm, which is called as overshoot phenomenon[26]. The ultrasonication pretreatment of wastewater could have resulted in generation of toxic compounds limiting or suppressing exo-electrogenic growth in MFC[27].

Microalgal treatment of ultrasonicated wastewater

Microalgal consortia collected from lotus pond in the institute was used as inoculum. On the first day wastewater mixture was in brown colour in both cases of pretreated and raw wastewater. On the second day the mixture with pretreated wastewater was mild green and mixture with raw wastewater was brown. After nearly 19 days the pretreated wastewater was

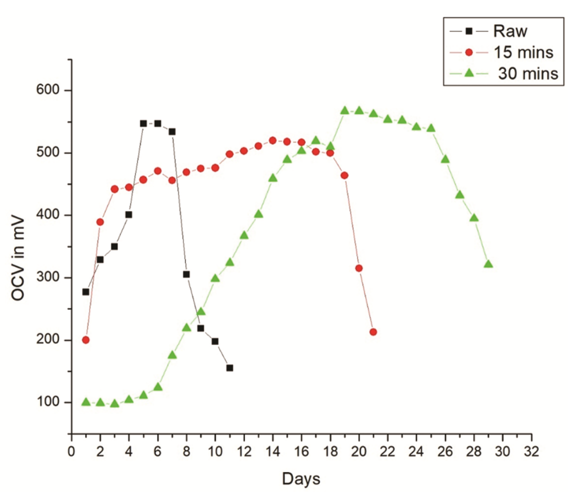

Fig. 1 — OCV trend of bio-electrochemical systems treating raw and pretreated wastewater.

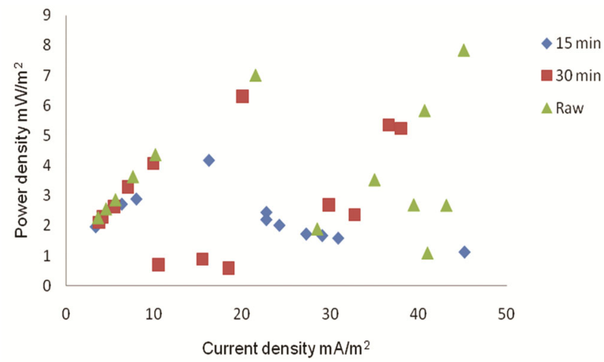

Fig. 2 — Power curves of bio-electrochemical systems treating raw and pretreated wastewater.

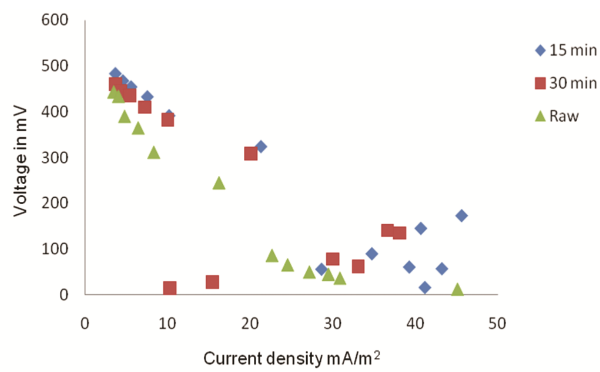

Fig. 3 — Polarisation curves of bio-electrochemical systems treating raw and pretreated wastewater

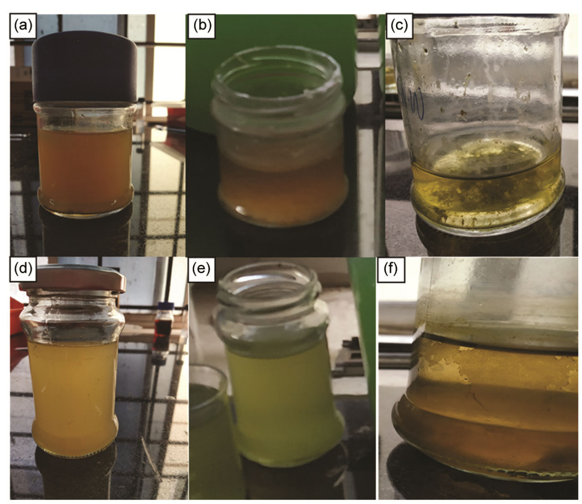

Fig. 4 — (a) Pretreated wastewater on day of inoculation of microalgae; (b) pretreated wastewater on second day; (c) pretreated wastewater decolourized in 19 days; (d) Raw wastewater on day of inoculation of microalgae; (e) Raw wastewater on seconday and (f) Raw wastewater after 19 days.

decolourised whereas the untreated/raw wastewater was brown in colour (Fig 4). The pretreatment process could have modified the compounds present in wastewater making them more accesible to microalgae or the compound could supress bacterial growth promoting microalgal growth[28].

In our future studies we aim at analysing the compounds present in raw wastewater and after pretreatment. Later, feasibility of pilot scale microalgal treatment of paper industry wastewater is to be evaluated.

Conclusion

Ultrasonication of pulping wastewater from bagasse based paper mill was not advantageous in terms of treatment efficiency. The COD, TDS and colour of wastewater was unchanged even after 120 min of ultrasonication in bath type sonicator. Later, utilisation of ultrasonic pretreated wastewater as substrate in MFC resulted in poor elctrochemical performance. However, ultrasonication followed by microalgal treatment could result in wastewater decolourisation. The Ultrasonication process could have modified the compounds present in wastewater, making it a better substrate for microalgal growth.

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