



# Cow's urine as a yellow gold for bioelectricity generation in low cost clayware microbial fuel cell



Dipak A. Jadhav<sup>a</sup>, Sumat C. Jain<sup>b</sup>, Makarand M. Ghangrekar<sup>b,\*</sup>

<sup>a</sup> School of Water Resources, Indian Institute of Technology, Kharagpur, 721302, India

<sup>b</sup> Department of Civil Engineering, Indian Institute of Technology, Kharagpur, 721302, India

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## ABSTRACT

Treatment of cow's urine was first time explored in clayware microbial fuel cell (MFC) by varying dilution to have different chemical oxygen demand (COD) in the feed. Improvement in power output of MFC was attained with increase in feed concentration from 1.5 to 3 kg COD/m<sup>3</sup>; however further increase in influent COD up to 30 kg COD/m<sup>3</sup> decreased the power. Maximum power of 5.23 W/m<sup>3</sup> was attained in MFC fed with diluted urine of cow with COD concentration of 3 kg COD/m<sup>3</sup>, which was seven-fold higher than MFC fed with raw urine. Nitrate removal of 77 ± 4.1% and carbohydrate removal of 80 ± 3.9% were achieved in MFC fed with 3 kg COD/m<sup>3</sup>. Electrochemical analysis showed that electrogenic activity of anodic biofilm boosted at optimum feed concentration (3 kg COD/m<sup>3</sup>) of cow's urine in anodic chamber. Using two MFCs, fed with diluted cow's urine, maximum voltage of 1.36 ± 0.05 V in series connection and maximum current of 48 A/m<sup>3</sup> in parallel connection were achieved. Thus, cow's urine can serve as sustainable yellow gold to harvest bioelectricity using low cost clayware MFC, and to curb the water pollution likely caused from cattle sheds.

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## 1. Introduction

Urine of cow is a good digestive, laxative, neutralizing agent against toxins with very high therapeutic index and it is good biofertilizer [1]. Also, cow's urine is a source of vitamins, minerals, ions such as Na, N, Mg, Fe, Si, Cl, Mg, P, K, S, citric, succinic acid, lactose, calcium salts, enzymes, carbolic acid, etc. [2]. Due to high energy content value, it can be considered as a yellow gold. However, the biggest problem associated with use of cow's urine for agricultural purpose is the reuse of anthropogenic and animal waste nutrients on arable land and social view for food consumption from such land. Amongst the different types of waste received to wastewater treatment plant, about 75% of the nitrogen present in domestic wastewater is originated from urine, which accounts only 1% of the total volume [3]. Another associated problem is the nitrogen loss through ammonia evaporation during spreading and storage, and it contains pathogens like *Salmonella typhimerium* and *Pseudomonas aeruginosa* [4]. Therefore, there is a need to focus on efficient treatment of such urine, generated in cattle sheds, to avoid possible harmful effects of urine such as hygienic risks,

environmental pollution, and unpleasant smell.

Due to high concentration of nutrients, though cow's urine can be considered as a valuable resource for N, P and energy recovery, it is a pollutant if discharged untreated into the environment [5]. Most of the nitrogen in fresh cow's urine is available in the form of urea. Urine contains about 2% urea by weight, and each molecule of urea consists of four atoms of hydrogen, which are loosely bound to the molecule than the hydrogen atom in water. Splitting of these bonds would require less energy and generate electrons as well as protons more efficiently during chemical oxidation reactions. To harvest energy from these bonds in the form of direct electricity, bioelectrochemical technology such as microbial fuel cell (MFC) can offer a sustainable and effective solution simultaneously offering treatment to urine [6]. MFC works by employing live microbes, those feed on organic matter and nutrients present in urine for energy generation for their own metabolism, growth, and cell maintenance. Performance of MFC is governed by several factors such as operational conditions, substrate type, substrate concentration, type and source of microbial inoculums etc. [7,8]. Substrate concentration significantly affects power generation of the MFCs by controlling biological activity in anodic chamber [9].

Direct utilization of human urine for electricity generation in MFC has been reported [6] and the work was extended to charge

\* Corresponding author.

E-mail address: [ghangrekar@civil.iitkgp.ernet.in](mailto:ghangrekar@civil.iitkgp.ernet.in) (M.M. Ghangrekar).

## Nomenclature

MFC	Microbial fuel cell
CPE	Constant phase element
COD	Chemical oxygen demand
USA	United State of America
DO	Dissolved oxygen
OCV	Open circuit voltage
OV	Operating voltage
SHE	Standard hydrogen electrode
Ag/AgCl	Silver/Silver Chloride reference electrode
CV	Cyclic voltammetry
C	Biocapacitance

ECSA	Electrochemical accessible surface area
EIS	Electrochemical impedance spectroscopy
NH <sub>4</sub> <sup>+</sup> -N	Ammonium nitrogen
AC	Alternating current
NO <sub>3</sub> <sup>-</sup> -N	Nitrate nitrogen
TAN	Total ammonium nitrogen
<i>i</i> <sub>0</sub>	Exchange current density
<i>R</i> <sub>ct</sub>	Charge transfer resistance
<i>β</i>	Charge transfer coefficient
<i>b</i>	Tafel slope
<i>R</i> <sub>p</sub>	Polarization resistance
<i>R</i> <sub>s</sub>	Solution resistance
<i>W</i>	Warburg's diffusion element

mobile phone battery with stacked MFCs arrangement [10]. To utilize the energetic value of urine, researchers have used human urine [6], elephant's urine [11], cow's urine [4,12,13] as a substrate in MFC for bioelectricity generation. Maximum voltage generation of 1.1 V was reported in dual chamber MFC using cow dung and urine as fuel [13].

Power generation from cow's urine was studied only by couple of researchers by using salt-bridge MFC in which internal resistance was too high and attaining maximum urine treatment efficiency was not exploited [4,12,13]. Also, the fundamental electrochemical mechanisms have not been clearly understood for treatment of cow's urine in MFC. The aforementioned studies have not evaluated the effect of concentration of urine to enhance performance of the MFC. To overcome these shortfalls of earlier studies, the main objective of present study was to investigate the effect of different concentrations of cow's urine in the feed, measured as chemical oxygen demand (COD), on the performance of low cost clayware MFC with the help of electrochemical analyses. In order to scale-up the MFC technology, stacking of small scale MFC units is one of the option for harvesting the useful electricity while treating such waste. Thus, implementation of MFC implies (i) a plurality of units and (ii) grouping of the units into series and parallel electrical connections. To study the grouping effect of MFC units, effect of electrical connections of electrodes such as individual, series and parallel connections on the performance of MFC was also evaluated.

## 2. Material and methods

### 2.1. Urine collection

The urine of cow was collected from well maintained cow-shed located near to Kharagpur, India. Urine was collected from a single cow having age of about four years with average weight and fed with a uniform diet. The urine of cow was used fresh or within a week from collection having a pH of 5.8–6.3. Urine was stored at 4 °C and allowed 2–3 h to re-equilibrate to room temperature before it was fed in MFC.

### 2.2. MFC design and operation

The study was carried out in a dual chambered MFC with outer cathodic chamber volume of 2.5 L, made from plastic bucket and inner clayware pot as anodic chamber with working volume of 0.4 L (Fig. 1). The wall material of clayware pot itself served as a separator between anodic chamber and cathodic chamber. The anode and cathode were made up of carbon felt (Panex 35<sup>®</sup>, Zoltek Corporation, St. Louis, USA) with projected surface area of 394 cm<sup>2</sup> and 755 cm<sup>2</sup>, respectively (Fig. S1).



Fig. 1. Photograph of working dual chambered MFCs treating urine as a substrate in anodic chamber.

MFC was inoculated with mixed anaerobic sludge collected from septic tank bottom. The inoculum sludge was given heat pre-treatment at 100 °C for 15 min to suppress methanogens [14] and further cooled to room temperature before inoculation. The pre-treated sludge of 70 mL volume was added as inoculum in anodic chamber along with cow's urine, with different dilutions, as a substrate. To evaluate the effect of substrate concentration, MFC was fed with diluted cow's urine with COD concentrations of 1.5, 3, 3.75, 5, and 7.5 kg COD/m<sup>3</sup>, and using raw urine of 30 kg COD/m<sup>3</sup> feed concentration in sequence under different batch cycles. The required COD concentration in the feed was attained by diluting the raw urine with tap water except at the feed concentration of 30 kg COD/m<sup>3</sup>, where raw urine was used as feed. MFC was operated for 8 fed batch cycles of 5 days each under each feed COD concentration. Aerated tap water was used as catholyte and aeration was provided continuously with an aquarium pump (SOBO Aquarium air pump, China) to supply air at a constant rate of 3.5 mL/min.

Connections between the two electrodes were made with concealed copper wire through an external resistance of 100 Ω. For evaluating the effect of series and parallel connections of electrodes in stacked arrangement, the MFC mentioned above was fed with urine concentration of 3 kg COD/m<sup>3</sup> and another MFC with similar design was fabricated and fed with urine concentration of 5 kg COD/m<sup>3</sup>. Initially these MFCs were electrically connected together in series and operated for 30 days and then connected in parallel for subsequent operation of 30 days. The performance of MFC was evaluated in terms of power generation and COD removal

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