Treatment of Pharmaceutical Industrial Effluent By Microbial Fuel Cell (MFC)

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Abstract

Industrial wastewater presents a potential hazard to natural water system. This wastewater contains organic matter, which is toxic to the various life forms of the system. Industrial wastewater has complex mixture of chemicals whose behavior towards biological system can be different. Treatment of these wastes is therefore of paramount important. Wastewaters produced from pharma Industries pose several problems. Pharma industries are widely been used for the production of wide range of antibiotics, solvents and many by-products which are widely useful for both man-kind and in agriculture purpose. This study was designed a waste water treatment with an aim at minimizing and removing of COD, BOD, dissolved solids and toxic compounds, before it releases into a water body. In the present study efficiency of Microbial Fuel Cells (MFC) in removing contaminants was determined. It was found that MFC is much effective and cheaper method for treating waste water and for the removal of TDS, TSS, BOD, COD, Sulphates and Chlorides. Batch type anaerobic biological treatment plant was constructed and operated for pharma industry waste water treatment. The hydraulic retention time was 12 days. The treated water samples were collected for every 72 hours and tested for its pH, TSS, TDS, COD, BOD, Sulphates and Chlorides to evaluate the efficiency of the plant. The results obtained were quite appreciable as it reduced COD to 91.5% and a small amount of 335mV has also been produced.
Keywords: BOD, COD, Chlorides, Microbial Fuel Cell

I. INTRODUCTION

Effluent is defined by the United States Environmental Protection Agency as “wastewater - treated or untreated - that flows out of a treatment plant, sewer, or industrial outfall. Generally refers to wastes discharged into surface waters". The effluent is released from pharmaceutical industry during drug manufacturing. Pharmaceuticals encompass a broad class of chemicals, like over-the-counter and prescription drugs, veterinary drugs, diagnostic agents, nutraceuticals (e.g., vitamins).Some of the most representative pharmaceutical and personal care products found in receiving waters include antibiotics, lipid regulators, anti inflammatories, antiepileptic’s, tranquilizers, and cosmetic ingredients containing oil and grease. Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium, etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute [1]. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. The main pollutant releasing from the industrial waste water is oxygen function is measured in chemical oxygen demand (COD),biological oxygen demand(BOD) and while nutrient status of waste water is measured in terms of nitrogen and phosphorus. There are some other important quality parameters to measure that are pH, temperature, total dissolved solids (TDS) and total suspended solids (TSS) [2]. Thousands of tons of pharmaceuticals are used yearly with different purposes such as the prevention, diagnosis, cure and mitigation of diseases or just to improve the state of health not only in humans but also in animals [3]. Pollution by pharmaceuticals can occur in concentrations of parts per billion (ppb), or parts per trillion (ppt) (where 1 ppt equates to 1 mg/L) [4]. Where appropriate, a pharmaceutical manufacturing plant should prepare a hazard assessment and operability study and also prepare and implement an emergency plan that takes into account neighbouring land uses and the potential consequences of an emergency.

Microbial Fuel Cells have the potential to simultaneously treat wastewater for reuse and to generate electricity; thereby producing two increasingly scarce resources. While the Microbial Fuel Cell has generated interest in the wastewater treatment field, knowledge is still limited and many fundamental and technical problems remain to be solved [5]. Microbial fuel cell technology represents a new form of renewable energy by generating electricity from what would otherwise be considered waste, such as industrial wastes or waste water etc. A microbial fuel cell [Microbial Fuel Cell] is a biological reactor that turns chemical energy present in the bonds of organic compounds into electric energy, through the reactions of microorganism in aerobic conditions. The study was under taken with following objectives are Characterization of waste water, Microbial Fuel Cell treatment of pharma industry waste water and Effect of MFC to reduce the impurities for various parameters [6].

II. MATERIALS AND METHODS

A. Microbial Fuel cell using a Salt Bridge:

Dual chambered MFC was constructed using air-tight plastic bottles of 1 litre volume each (anode and cathode chamber). A side opening of 1 cm radius was made at a height of 12.5 cm from the bottom of the bottle (approximately at the centre) on each bottle and was connected with a PVC pipe(length=20cm; diameter=2cm). Agar of 2gms along with 2gms of sodium chloride (NaCl) salt was prepared by heating it in a water-bath of 100ml and the molten agar was allowed to cool down and poured into the PVC pipe and sealed at one end using cello-tape. The agar was left undisturbed to solidify [7]. The PVC pipe containing the salt-agar mixture was fixed between the two bottles using epoxy material and behaved like the salt-bridge assisting in the proton transfer mechanism during the MFC operation. Carbon rods (height= 12cm; diameter = 0.75 cm) were used as electrodes. The distance between the two electrodes was maintained at distance of 15 cm in the MFC setup. Copper wires were used to connect the electrodes to the circuit. An external resistance (R) of 10Ω was connected and the readings were measured using a digital multimeter [8]. Constructed salt bridge MFC is shown in Fig.1.

Fig. 1: Microbial Fuel Cell for the treatment of Waste water

The collected sample was analyzed using standard methods in order to monitor the biodegradation process taking place inside the MFC. Many parameters are used to determine waste water performance. In this study the parameters analyzed were pH, TSS, TDS, BOD, COD, Chlorides and Sulphates and Dissolved oxygen to evaluate efficiency of the reactor. The waste water sample is collected for every 72 hours and its various parameters are evaluated. During the operation, voltage is also checked by using a multimeter.

III. RESULTS AND DISCUSSION

The values of various parameters like pH, colour, temperature, dissolved oxygen, COD, BOD, TSS, TDS, Chlorides and Sulphates before the treatment of sample effluent are as shown in Table 1.

Table – 1
Characteristics of pharmaceutical industry waste water:

S.NO	Parameter	Untreated Effluent
1.	Colour	Dark Brown
2.	Temperature	32^0C
3.	pH	7.98
4.	Dissolved Oxygen	1.8
5.	BOD	62
6.	COD	1940
7.	TSS	484
8.	TDS	2600
9.	Chlorides	1200
10.	Sulphates	2469

A. Effect of Microbial Fuel Cells:

Sample taken from the pharmaceutical industry waste water is treated by Microbial Fuel Cells. In the process, two bottles, one having the waste water sample and the other having the tap water is taken. Carbon electrodes are dipped into each bottle and a salt bridge is attached between two bottles through which flow of electrons takes place. Moreover, an aerator is also placed in the bottle having waste water. During the treatment samples were taken at constant intervals of 72 hours to determine its various parameters i.e. pH, Total Suspended Solids, Total Dissolved Solids, Chemical Oxygen Demand, Biological Oxygen Demand, Sulphates, chlorides.

MFC is known to be one of the cheapest methods for reducing COD values in waste water. In the present operation, the value of COD has reduced from 1940mg/lt to 330mg/lt. Besides reducing the toxicity MFC also produces Voltage. The voltage produced can be checked by connecting electrodes to the Multimeter.

Effect of MFC on various parameters is as follows:

1) Effect of pH:

pH of the waste water sample was determined using pH meter. The experiments were carried out in the pH range of 5 to 9. The variation of pH of the sample taken at regular intervals of 72 hours is presented in the Fig.2. Results show that pH of the waste water has decreased. The addition of vinegar, which serves as food to microorganisms, is responsible for the acidic nature of the waste water sample. pH has decreased from 7.98 to 6.5 which is in the permissible levels of BIS standards.

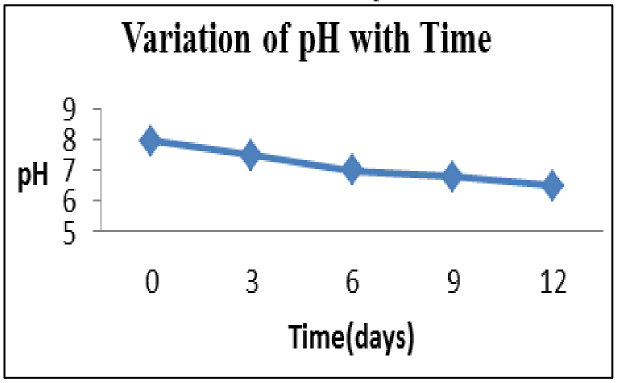

Fig. 2: Variation of pH with Time

2) Effect of Chemical oxygen demand (COD):

The Chemical Oxygen Demand test (COD) determines, the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test which is used to measure pollution of domestic and industrial waste. The waste is measured in terms of equality of oxygen required for oxidation of organic matter to produce CO_2 and water. It is a fact that all organic compounds with a few exceptions can be oxidizing agents under the acidic condition. COD test is useful in pinpointing toxic condition and presence of biological resistant substance. For COD determination samples were preserved using H_2SO_4 and processed for COD determination after the entire sampling operation was complete.

During operation, MFC was continuously monitored for waste (as COD) removal to enumerate the potential of fuel cell to act as wastewater treatment unit. COD of the waste water sample at different time intervals are presented in the Fig. 3. Results show that COD of the waste water has decreased from an initial of 1940mg/lt to 330mg/lt. The tap water showed its potential for COD removal indicating the function of microbes present in wastewaters in metabolizing the carbon source as electron donors[9]. Continuous COD removal was observed during 12 days of operation.

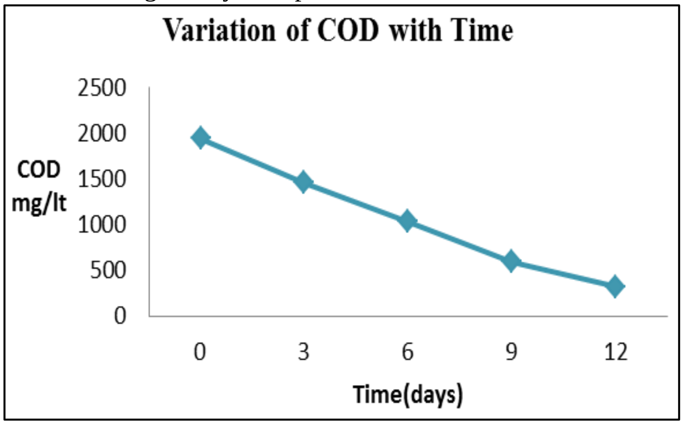

Fig. 3: Variation of COD with time:

IV. Effect of Biochemical oxygen demand (BOD)

Biological oxygen demand is the amount of oxygen required for microbial compounds in water. This demand occurs over some variable period of time depending on temperature, nutrient concentration and the enzymes available to indigenous microbial populations, the amount oxygen required to completely oxidize the organic compounds to Co_2 and water through generations of microbial growth, death, decay and cannibalism.

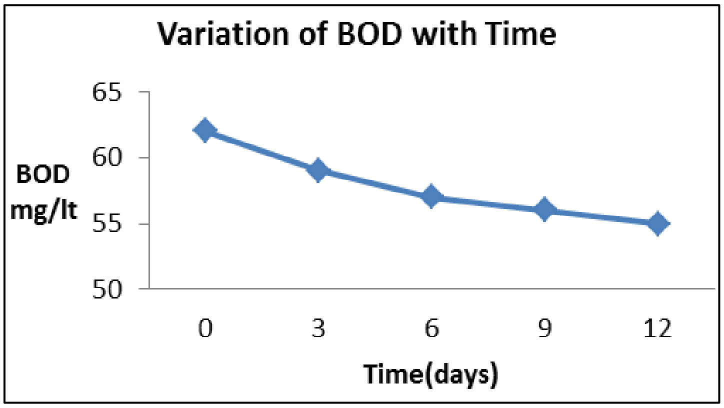

Fig. 4: Variation of BOD with Time

The effect of MFC on BOD of the waste water sample is illustrated in the Fig. 4 Results show that BOD has decreased from an initial value of 62mg/lt to a final of 55m/lt. The decrease in BOD is due to continuous aeration and the action of sludge.

V. EFFECT OF DISSOLVED OXYGEN

Dissolved oxygen analysis measures the amount of gaseous oxygen (O_2) dissolved in an aqueous solution. It refers to the level of free, non-compound oxygen present in water or other liquids. It is an important parameter in assessing water quality because of its influence on the organisms living within a body of water. In limnology (the study of lakes), dissolved oxygen is an essential factor second only to water itself. A dissolved oxygen level that is too high or too low can harm aquatic life and affect water quality.

The variation of Dissolved oxygen with time is presented in Fig.5. Results show that dissolved oxygen increased from 1.8mg/lt to 4.5mg/lt. The reason for increase in the Dissolved oxygen of waste water sample is due to decrease in the levels of BOD and COD in the waste water sample and aeration.

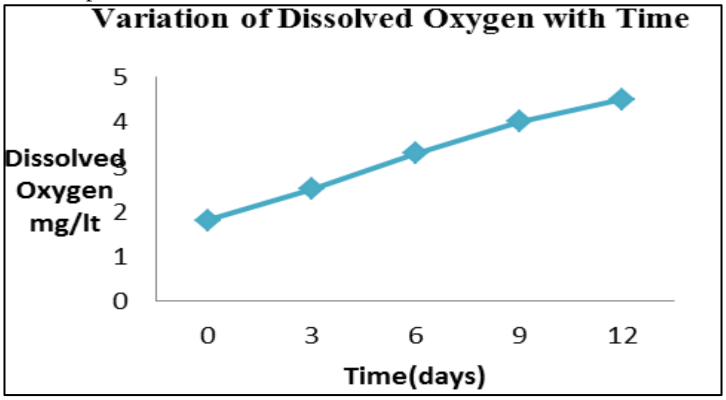

Fig. 5: Variation of Dissolved oxygen with time

VI. EFFECT OF TOTAL DISSOLVED SOLIDS

TDS is the total mass content of all inorganic and organic substances present in liquid in the form of solids, ions, molecules and suspended micro granules. Generally, the definition is that the solids must be small enough to survive filtration through the sieve the size of two micrometer. Though TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects) it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

MFC showed its potential for Total Dissolved Solids removal. The effect of MFC on total dissolved solids of the waste water sample at regular intervals is presented in the Fig.4.5. Experimental data indicated that dissolved solids were decreased continuously during the 12 day operation. The TDS of the waste water sample has decreased from 2600mg/lt to 2150mg/lt. B.G. Mahendra et al. has decreased the dissolved solids from 1000mg/lt to250 mg/lt using MFC. The removal of dissolved solids was possibly due to availability of biodegradable substrate in wastewater sample leading to competitive inhibition in microorganisms.

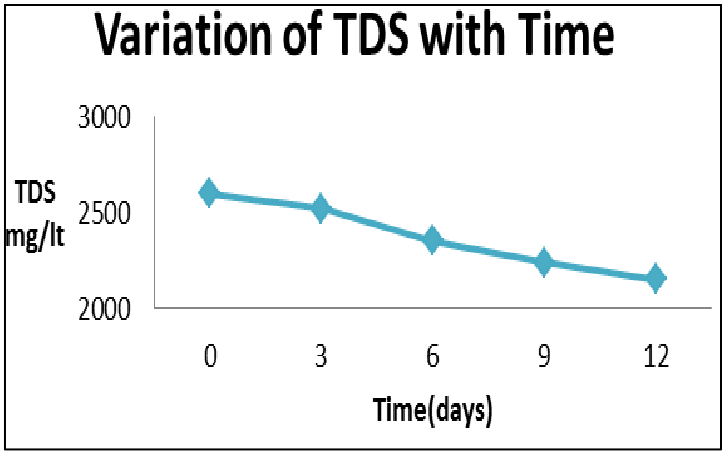

Fig. 6: Variation of TDS with Time

VII. EFFECT OF TOTAL SUSPENDED SOLIDS

Total suspended solids is a water quality measurement usually abbreviated TSS. It is listed as a conventional pollutant in the U.S. Clean Water Act. This parameter was at one time called non-filterable residue (NFR), a term that refers to the identical measurement: the dry-weight of particles trapped by a filter, typically of a specified pore size. However, the term "non-filterable" suffered from an odd (for science) condition of usage: in some circles (Oceanography, for example) "filterable" meant the material retained on a filter, so non-filterable would be the water and particulates that passed through the filter. In other disciplines (Chemistry and Microbiology for examples) and dictionary definitions, "filterable" means just the opposite: the material passed by a filter, usually called "Total dissolved solids" or TDS. Thus in chemistry the non-filterable solids are the retained material called the residue.

Effect of MFC on the removal of TSS of the waste water sample is demonstrated in Fig. 7. The Experimental data shows that the amount of TSS in the sample has decreased with the elapse of time. The decrease of the suspended solids in sample may be due to availability of biodegradable substrate in wastewater sample leading to competitive inhibition in microorganisms.

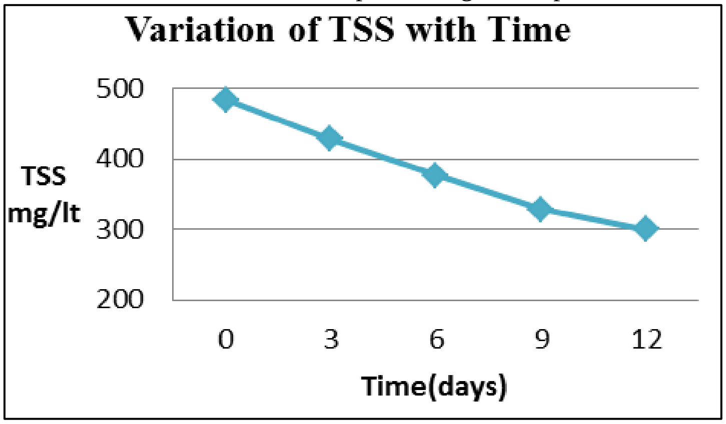

Fig. 7: Variation of TSS with Time

VIII. EFFECT OF CHLORIDES

Chlorides are generally present in natural water. The presence of chloride in the natural water can be attributed to dissolution of salts deposits discharged of effluent from chemical industries, oil well operations, sewage discharge of effluent from chemical industries, etc

The effect of MFC on chlorides of the waste water sample is presented in Fig. 8. The experimental data shows that chlorides content has decreased from 1200mg/lt to 450mg/lt. The removal of chlorides in the sample may be attributed to the availability of biodegradable substrate in wastewater sample leading to competitive inhibition in microorganisms.

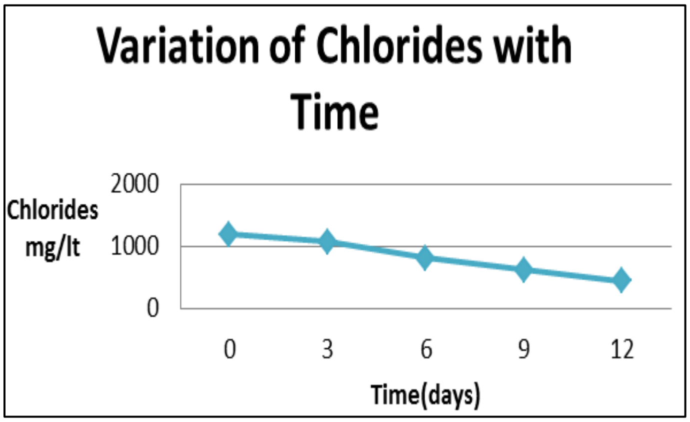

Fig. 8: Variation of Chlorides with Time

IX. Effect of Sulphates

Sulphate is one of the major cation occurring in natural water. Sulphate being a stable, highly oxidized, soluble form of sulphur and which is generally present in natural surface and ground waters. Sulphate itself has never been a limiting factor in aquatic systems. The normal levels of sulphate are more than adequate to meet plants need. When water is over loaded with organic waste to point that oxygen is removed then sulphate as an electron acceptor is often used for breakdown of organic matter to produce H_2S and produce rotten egg smell.

The effect of MFC on Sulphates is shown in Fig. 4.8. Results clearly show decrease in Sulphates from 2469mg/lt to 1100mg/lt. The removal of Sulphates in the sample may possibly due to the availability of biodegradable substrate in wastewater sample leading to competitive inhibition in microorganisms.

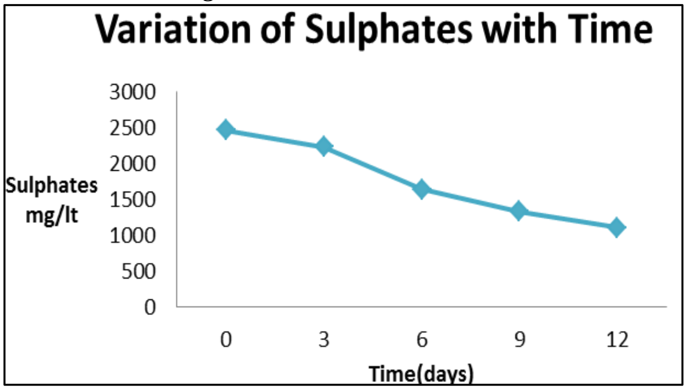

Fig. 9: Variation of Sulphates with Time

Table – 2
The Physico-chemical parameters of treated and untreated sugar industry effluent

S. No	*Parameter*	*Untreated Effluent*	*Treated Effluents*	*BIS standards (Bureau of Indian Standards.)*
1.	*Colour*	*Dark Brown*	*Light Brown*	*--*
2.	*Temperature*	*32^oC*	*30^oC*	*--*
3.	*pH*	*7.98*	*6.5*	*6.5-9.0*
4.	*COD (mg/lt)*	*6400*	*330*	*250*
5.	*BOD (mg/lt)*	*62*	*55*	*50*
6.	*Dissolved Oxygen (mg/lt)*	*1.8*	*4.5*	*4-6*
7.	*TDS (mg/lt)*	*2600*	*2150*	*2100*
8.	*TSS (mg/lt)*	*484*	*300*	*600*
9.	*Chlorides (mg/lt)*	*1200*	*450*	*600*
10.	*Sulphates (mg/lt)*	*2469*	*1100*	*1000*

X. CONCLUSION

It was observed that the basic principle guiding for the removal of toxicity and the production of electricity is the availability of bio-degradable compounds present in the waste water sample. The COD removal denotes the function of microbes, present in wastewaters in metabolizing the carbon source as electron donors. It was observed that MFC has succeeded in achieving the COD removal efficiency of 91.5% and also in generation of 330mV. The study demonstrated that microbial fuel cell technology was able to treat pharma industry wastewater successfully, and microorganisms present in the wastewater are for removal of COD, BOD and other parameters. MFC technology may provide a new method to offset wastewater treatment plant operating cost, making wastewater treatment more affordable for developing and developed nations.

REFERENCES

[1] M.P.D.Prasad, N.Aswini and V.Sridevi. (2014). Treatment of Pharmaceutical Waste Water by Exigency Methods: A Review, Indian Journal Of Applied Research (IJAR), Volume: 4 Issue: 10 October, ISSN - 2249-555x
[2] APHA-AWWA-WEF, Standard Methods for the examination of water and waste water,21st ed. American public Health Association, American Water Works Association and Water environmental federation, Washington ,DC,USA,(2005).
[3] Daughton C.G. and Ternes T.A. (1999), Pharmaceuticals and personal care products in the environment: agents of subtle change. Environmental Health Perspect, 107, 907–937.
[4] Heberer T., (2002). Tracking persistent pharmaceutical residues from municipal sewage to drinking water, Journal of Hydrology, 266 (2–3), 175–189
[5] Min, B., Cheng, S. and Logan B. E. (2005). Electricity generation using membrane and salt bridge microbial fuel cells, Water Research, Vol No.9, pp1675–86
[6] M.M. Ghangrekar and V.B. Shinde,(2006). Wastewater Treatment in Microbial Fuel Cell and Electricity Generation: A Sustainable Approach, Paper presented in the 12th international sustainable development research conference. April 6-8, , Hong Kong.
[7] Allen R.M., Bennetto H.P. (1993). Microbial fuel cells: electricity production from carbohydrates. Appl. Biochem. Biotechnol. 39-40; 27-40.
[8] Delaney G. M., Benntto H. P., Mason J. R., Roller H. D. Stirling J. L., Thurston C. F. (1984). Electron transfer coupling in microbial fuel cell: 2. Performance of fuel cells containing selected microorganism mediator substrate combinations. J. Chem. Technol. Biotechnol. 34B; 13-27.
[9] B.G. Mahendra and Shridhar Mahavarkar (2013), Treatment of wastewater and electricity generation using microbial fuel cell technology, International Journal of Research in Engineering and Technology, IC-RICE Conference, Vol. No: 3, Issue. No. 4 | Nov-2013