



Design and development of electro-chemical water quality sensor

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Abstract

It is essential to find out the concentration of impurities present in the contaminated water quantitatively to distinguish the different water samples. The principle goal of this research work is to develop and demonstrate the efficiency and capability of an electrochemical water quality monitoring sensor using cyclic voltammetric technique implemented with PIC16f877 microcontroller. To develop this advanced electro-chemical impurities sensing technique, a detailed analysis need to be carried out on different water samples. The experiment has been conducted on different water samples using the newly developed sensor and it could able to distinguish the water samples based on their corresponding voltammograms. The VIT tap water has got the highest current response of 0.04Amps for a voltage sweep of +/-2Volts indicating higher contamination level when compared to all other water samples.

Keywords: Electro-chemical sensor, cyclic voltammetry, voltammogram, potentiostat, water contamination.

Introduction

Environmental pollution is one of the most important problems for human health (Cornaby, 1981). The presence of toxic metals, metalloids and their compounds is a major concern due to their toxicity to many forms of life (Friberg & Vonk, 1985). Pollution of water resources is a potential danger to human health and the environment (Hasany & Chaudhary, 1997). Safe and clean water is requirement for good public and environmental health.

A significant percentage of the world population is in need of safe water supplies for consumption. The WHO has estimated that over 2 million people die from a disease caused by contamination of drinking water and improper sanitation a year (Cornaby, 1981).

The main sources of water contamination are: (1) Human activities near water supply, (2) Lack of proper water treatment, and (3) Lack of regulation and enforcement in public health systems.

Traditionally, environment or industrial process samples are taken on site and removed to laboratory facilities where electrochemical, chromatographic, and spectroscopic methods are employed to detect, observe, and quantify any ions or ionic species within the sample. Examples of typical methods utilized include inductively coupled plasma mass spectrometry (ICP MS), differential pulse anodic stripping Voltammetry (DPASV), graphite furnace atomic absorption spectrometry (GF AAS), cold vapor atomic absorption spectrometry (CV AAS), and cold vapor atomic fluorescence spectrometry (CV AFS) (Piech & Kubiak, 2007; Giacomino *et al.*, 2011).

However, these test methods vary in sensitivity to the charged species of interest (dependent on method employed), take an undesirable amount of time to obtain results, test equipments are very expensive and space consuming, and the samples have a greater probability of contamination or loss due to the handling and transport prior to testing (Forsberg *et al.*, 1975; Wang, 2000).

Advantages of this new microcontroller based electrochemical water quality monitoring system that is capable of real time process monitoring or real time environmental monitoring include improved process control, minimization of environmental impact, and ability for continuous monitoring with options for early detection (Feeney & Kounaves, 2000; Wang, 2000) where, the greatest advantage is the rapid return on the test results, enabling quick action responses, inexpensive and easily available components etc.

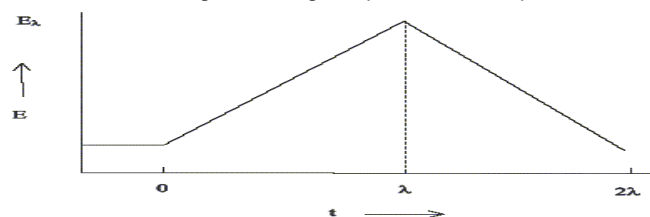
The objective of the work is to develop a low cost reliable water quality sensing system. Parameters and characterization of this sensing system are proven along with the operating theory and justification of design and usage.

Cyclic voltammetry

Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time like linear sweep voltammetry. Cyclic voltammetry takes the experiment a step further than linear sweep voltammetry which ends when it reaches a set potential. When cyclic voltammetry reaches a set potential, the working electrode's potential ramp is inverted.

This inversion can happen multiple times during a single experiment. Fig.1 shows a typical potential sweep applied in a CV experiment. The current at the working

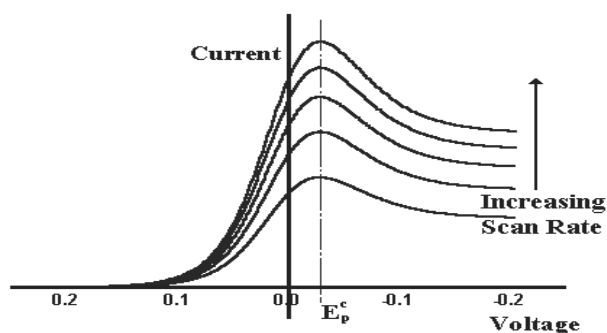
Fig. 1. Triangular potential sweep



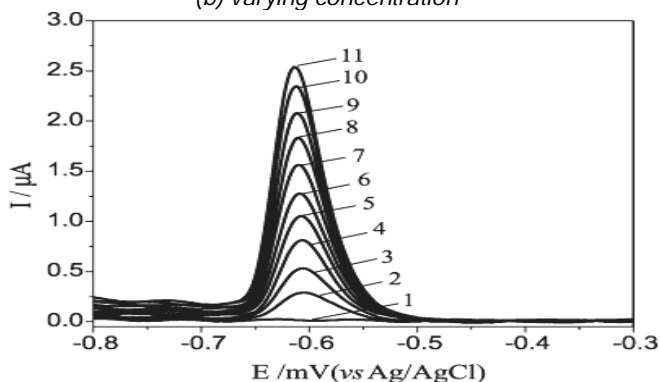
electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution (Kounaves, 2002). Cyclic voltammetry is extensively discussed below.

Voltammogram

Fig.2 (a) voltammogram of a redox process with varying scan rate



(b) varying concentration



A plot of current as a function of applied voltage is called voltammogram. It is the resultant plot after voltammetry and is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction. Fig.2 (a) and (b) shows voltammogram of a typical redox process with different scan rates (a) and concentration (b) of the species. The peak current of each scan shift upward with scan rate, peak occurring at the same voltage (E_p).

For a reversible couple, the peak current is given by the Randles-Sevcik equation (Wang, 2000).

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$

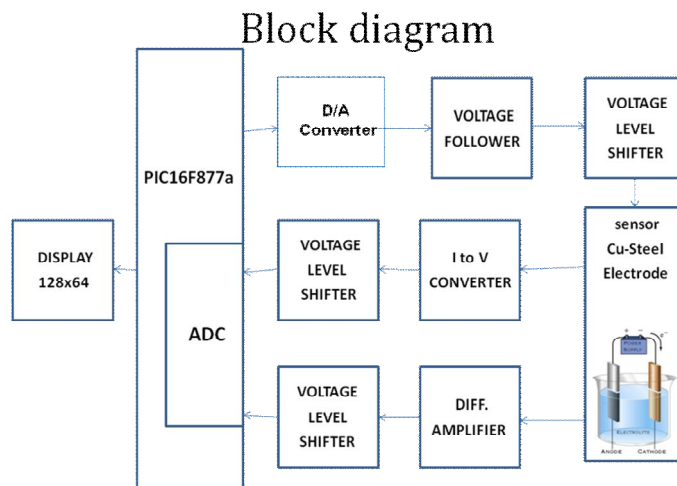
where n is the number of electrons, A is the electrode area (in cm^2), C is the concentration (in mol cm^{-3}), D is the diffusion coefficient (in $\text{cm}^2 \text{s}^{-1}$), and v is the scan rate (in Vs^{-1}). Accordingly, the current is directly proportional to concentration and increases with the square root of the scan rate.

The ratio of the reverse-to-forward peak currents, i_{pa}/i_{pc} , is unity for a simple reversible couple. The separation

between the peak potentials is $0.0592/n$, where n is the number of electrons.

Experimental

Fig. 3. Block diagram of the experimental setup.



Block diagram of the experimental setup

Fig.3 shows the block diagram of the water quality monitoring system. The microcontroller generates the digital equivalent of the driving voltage. The digital to analog converter (R-2R ladder circuit) converts it into analog voltage. This has to be converted into -2 to +2 range. In order to achieve this voltage range, level shifter and attenuator comprising of operational amplifiers (LM 324 n) is used.

The circuit makes use of an 8 bit R-2R ($1\text{K}\Omega$ and $2\text{K}\Omega$) ladder circuit, a level shifter and an attenuator. The Operational Amplifier used here is LM 324n. The output of the DAC is given to positive terminal of a level shifter through buffer. Buffer avoids any loading effect in the circuit. The op-amp U2B acts both as a level shifter and an attenuator. 2V output from a voltage divider circuit is given to the negative terminal of op-amp U2B. This means that it always subtracts 2V from the positive terminal voltage and this op- amp provides an attenuation of 0.8.

Electrode EMF signal conditioning circuitry

Since the microcontroller cannot read any negative voltage, the voltage across the electrode has to be level shifted first. We make use of a voltage adder together with a differentiator (U2A in Fig.4) here. The differentiator output is the difference in voltage of the two electrodes. It is given to a voltage adder circuit. Fig.4 is the simulated circuit assuming a voltage of 2V across the electrodes.

Output of the differentiator = $(V_2 - V_1)$ (since all equal resistors)

Output of the voltage adder circuit is

$$V_{out} = -(R_f / R_{in}) * (-2 + 2.5)$$

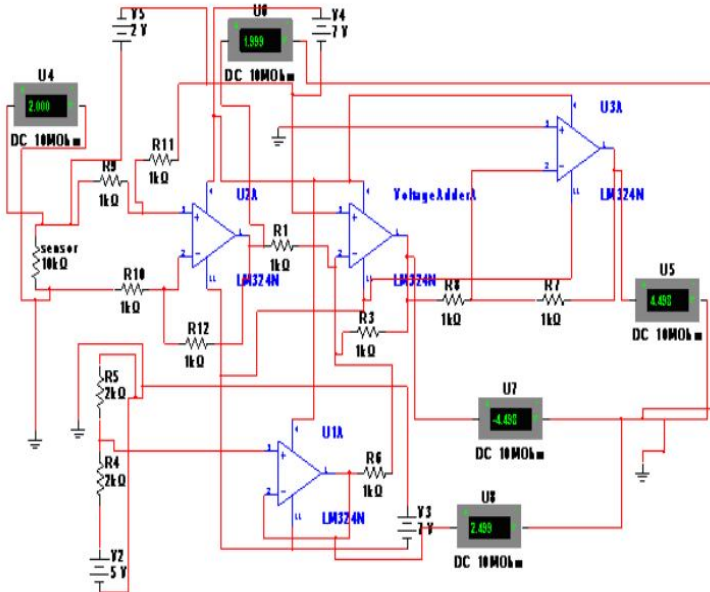
$$= -(1\text{k}/1\text{k}) * (-2 + 2.5)$$

$$V_{out} = -0.5$$

$$\text{Output of the inverter, } V_{out} = - (1/1\text{k}) (V_{in})$$

Simulated result = +0.5 V
 = +0.5 V

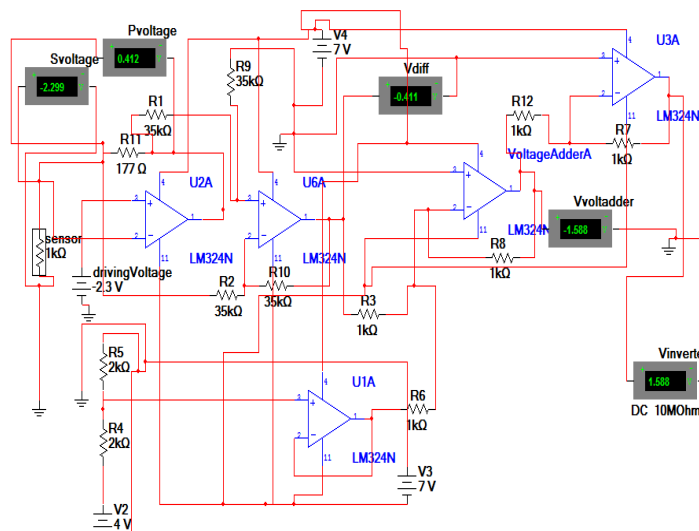
Fig. 4. Circuit for signal conditioning of voltage across electrodes (2V across electrodes).



Electrode current signal conditioning circuitry

As Microcontroller cannot read the current directly it has to be converted to voltage and then level shifted to 0V to 5V range and given to ADC. Fig.5 is the simulation of circuit for current signal conditioning. The sensor (electrodes) is connected to the negative terminal of the Opamp (U2A in Fig.5). Driving voltage is applied to the positive terminal. Through the virtual ground the driving voltage is applied to the electrodes. The resistor R11 is the current to voltage converter.

Fig. 5. Circuit for signal conditioning of current through the electrodes.



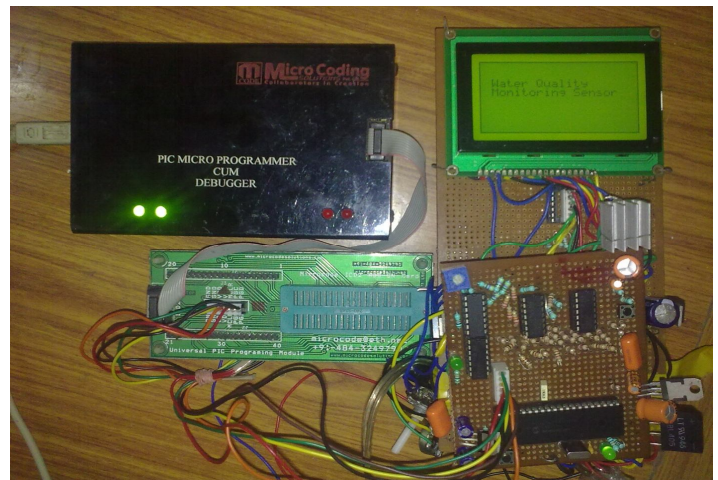
This resistance (R11) is actually a potentiometer. The voltage across this pot is proportional to the current through the electrodes. The output of the differentiator (U2A) is the voltage proportional to current. But this voltage is bipolar and cannot be given to the ADC of microcontroller. So it has to be made unipolar. This is done with the help of a voltage adder circuit. The voltage adder (U6A) adds the output voltage of the differentiator and a variable voltage from a voltage divider circuit. R5 and R4 are actually arms of a potentiometer.

Programming

Program used for this application requires multiple tasks to run simultaneously. This is an ideal contender for RTOS (Real Time Operating System) programming. Hi-Tech C compiler is used to make the RTOS programming easy in C language instead of assembly language.

A time sharing RTOS was programmed as a framework to run all tasks. Tasks to drive the LCD, read the user input, analog to digital conversion(ADC) , count the delay and generate the voltage (to DAC) are used. Another task called 'current status' controls which task has to be executed each time. Microchip MPLAB IDE v8.6 is the software used to program the PIC16f877a microcontroller along with a PIC microcontroller cum debugger kit (Fig.6).

Fig. 6. In Circuit Serial Programming (ICSP) using a PIC micro programmer cum debugger.



A technique known as In Circuit Serial Programming is used to program the micro controller as shown in Fig.6. This method allows us to use same circuit board for both programming and application.

Result

Voltammetry on Double Distilled Water

Voltammetry on double distilled water is important and had to be carried out first because it has the minimal amount of species present in it. Voltammetry is carried out with tin coated copper (working) and stainless steel (reference) electrodes separated by 2 cm and dipped in 8 cm length.

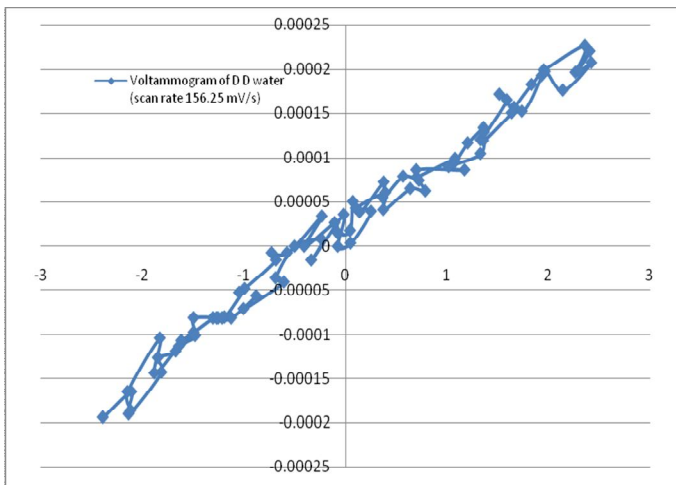
Voltammogram of Double Distilled Water
(Scan rate: 156.25 mV/s)

Fig.7 shows the voltammogram of double distilled water (D.D water) scanned at 156.25 mV / s. This scan rate is achieved by setting delay1 as 800 ms. There will be a voltage change of 5 volts (40 steps × 125 mV) for ramp up, from -2 to +2.

$$\text{Scan rate} = 5V / (40 \text{ steps} \times .8 \text{ sec}) = 156.25 \text{ mV/ sec.}$$

There are about five readings are taken when the electrodes are kept at 8 cm depth and 2 cm apart. The graph is plotted using the average values. From the Fig.7 it is clear that the D.D water tested does not contain any species, as it traces the path in forward and reverse scan, there is no visible peaks. The maximum current reached is around 0.2 mA.

Fig. 7. Voltammogram of D.D water.



Voltammogram of Double Distilled water mixed with Salt (1000:5)

First salt is mixed with D.D water in an approximate ratio of 1000:5. The solution is scanned at two different

Fig. 8. D.D water, D.D water with salt solution (1000:5) at different scan rates.

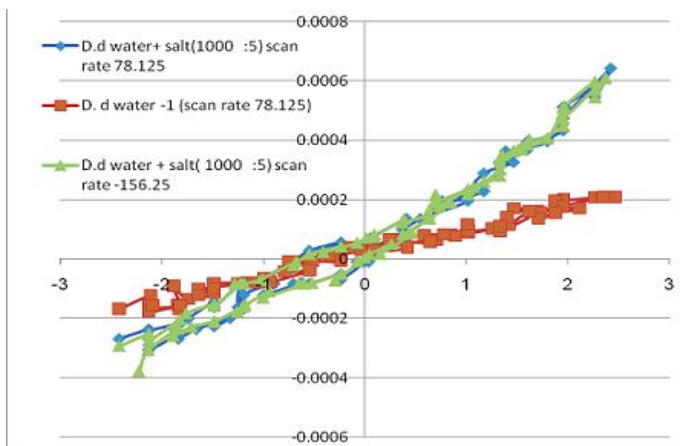
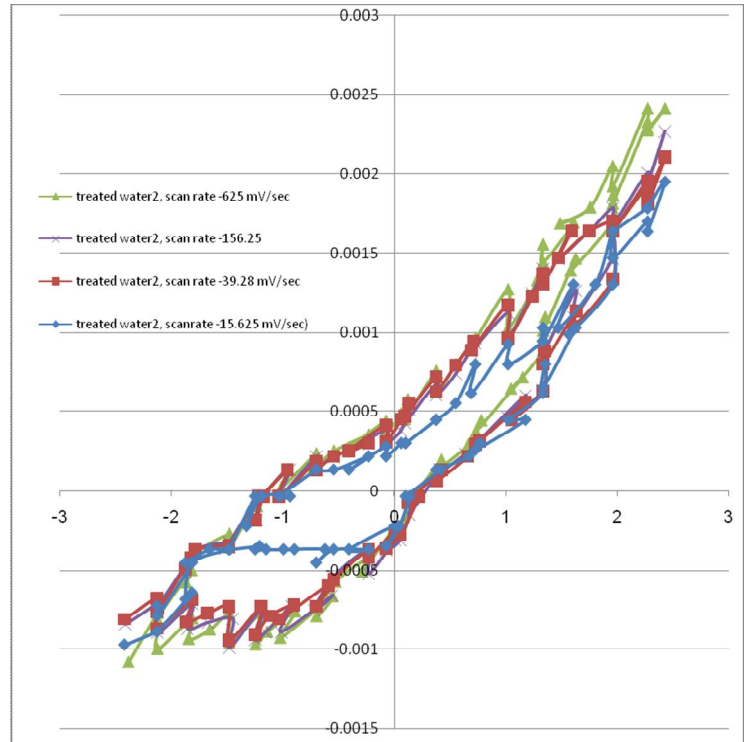


Fig. 9. Voltammogram of treated water at different scan rates.



rates 78.125 and 156 mV/s. Voltammogram of D.D water and salt is shown in Fig.8. From the plot it is clear that after adding the salt the conductivity of the solution increased and the path traced by forward scan and reverse scan are different. The area covered by plot gives us an indication about the amount of salt contained in the solution. The peak current and the area increases as we increase the amount of salt in the D.D water again agreeing to the above mentioned equation.

Fig.10. Voltammograms of treated water, D.D water and salt in D.D water solutions.

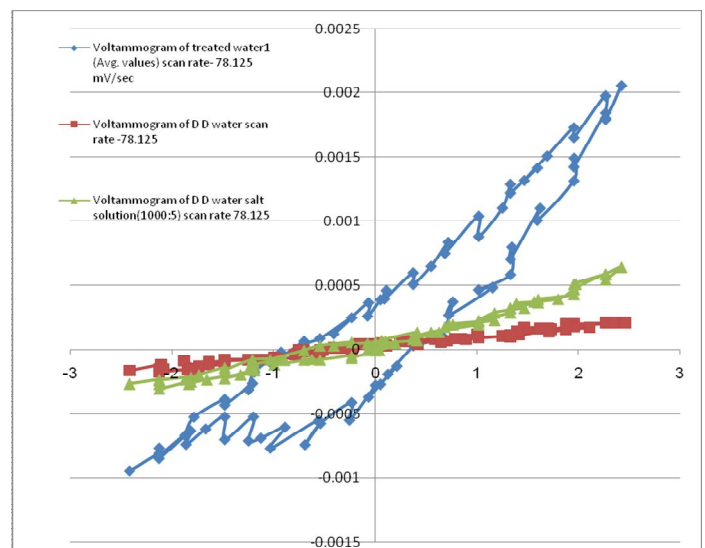


Fig. 11. Voltammogram of treated water obtained in the graphical display (JHD12864E) 128 x 64 pixel.

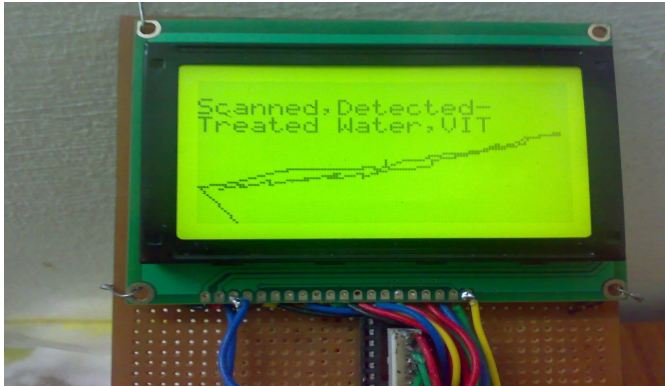


Fig. 12. Comparison of different bottled waters.

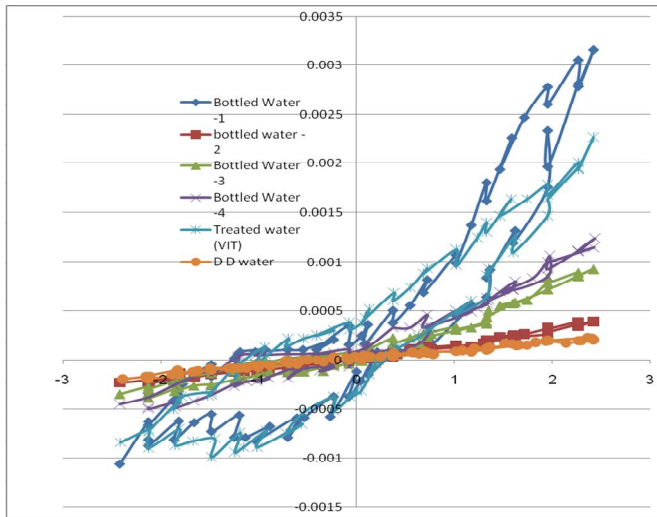


Fig. 13. Comparison of voltammogram of treated water (VIT) and Bottled Water -1(bottled natural mineral water).

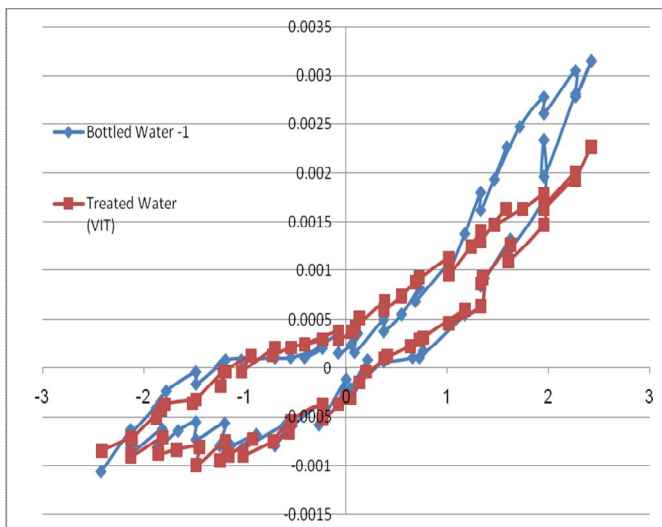


Fig. 14. Voltammograms of treated water with electrodes kept in different depths and gap.

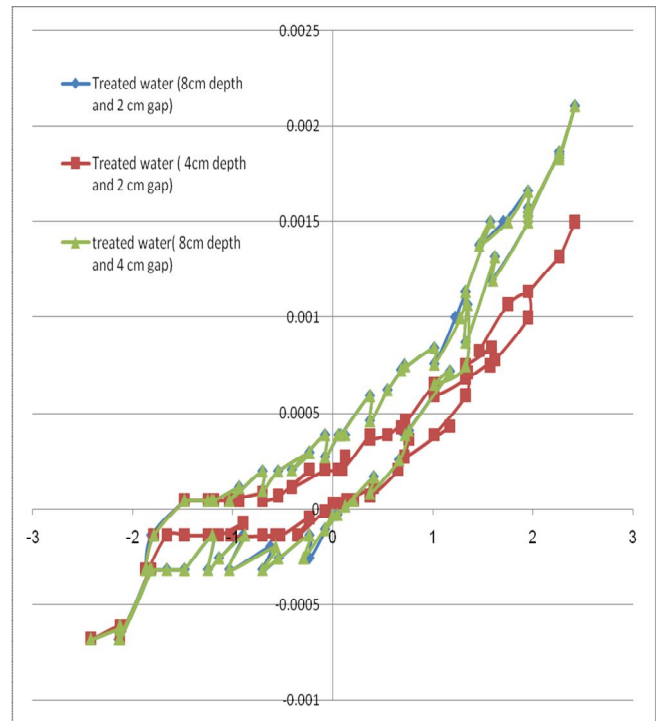


Fig. 15. Voltammogram of tap water and treated water.

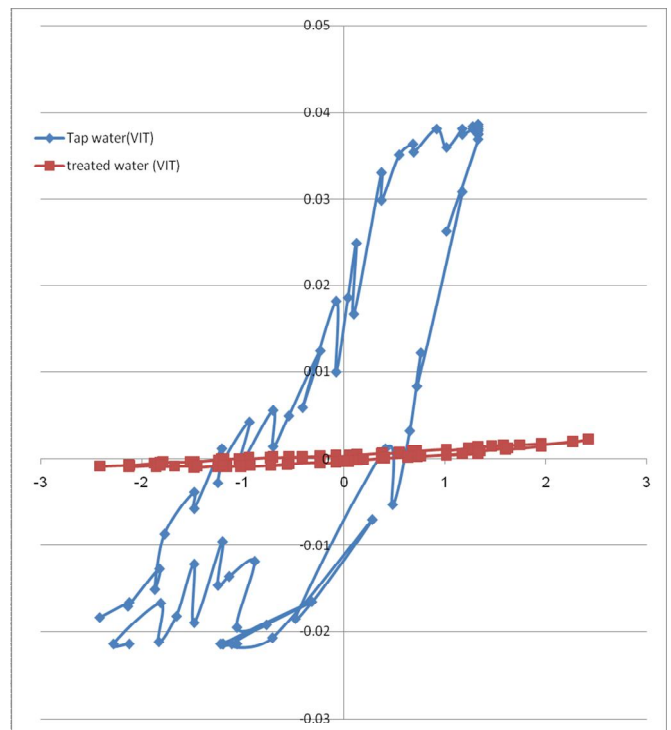


Table 1. Current response of different water samples

Type of water sample	Max. current response in Amps	Applied voltage sweep in volts
Double distilled water (D.D)	0.0002	+/-2
D.D with Salt (1000:5) ratio.	0.0006	+/-2
VIT Treated Water	0.002	+/-2
Packaged Purified Mineral water Bottle -1	0.003	+/-2
Packaged Purified Mineral water Bottle -2	0.0005	+/-2
Packaged Purified Mineral water Bottle -3	0.001	+/-2
VIT Tap Water	0.04	+/-2

Voltammetry on Treated Water

Voltammetry on treated water is carried out at different scan rates. Electrodes are separated by a distance and dipped at 8 cm depth. Voltammograms of treated water at different scan rates are shown in Fig. 9. It confirms that the variation of scan rates does not produce any drastic change in the response of the solution. Fig.10 compares the D. D water, treated water and D.D water with salt (1000:5). The area under the voltammogram of treated water is more since it contains more species compared to the other two. Fig.11 shows the graphical display of the voltammogram of the treated water by JHD12864E(1) 128 x 64 pixel display.

Voltammetry on different bottled water samples

Voltammetry of different bottled water available in market are conducted. Voltammograms of different bottled waters are compared with Double Distilled water (D.D water) and treated water (VIT) as shown in Fig.12. Here all readings are taken with a scan rate of 156.25 mV/sec.

The voltammogram of Bottled Water -2 is similar to that of D.D water with almost zero area. This indicates that, it may be the pure bottled water among the other three but might lack in essential minerals in it. The voltammogram of treated water (VIT) and Bottled Water - 1 (natural mineral water) is almost similar. The comparison of voltammograms of treated water and bottled water-1 is given in Fig.13.

Effect of electrode gap and depth on voltammogram

Voltammetry is conducted in treated water with electrodes kept at different separation and depth. The voltammograms are shown in Fig.14. It is seen that the current is independent of the separation between electrodes and dependent upon the depth of the electrodes. According to Randles-Sevcik equation peak current, $i_p = (2.69 \times 10^5) n^3/2 ACD^{1/2} v^{1/2}$ is dependent on area of electrodes and independent of the separation between them. The voltammograms of electrodes kept at: 8 cm depth , 2cm gap, 4 cm depth , 2cm gap and 8 cm depth , 4 cm gap. From the voltammograms it is clear that

the current through electrode is independent of the separation between the electrodes. However the change in depth varies the area of contact and the electrode current differs.

Voltammetry on tap water

The voltammogram obtained after voltammetry on tap water (VIT) is as shown in Fig.15. A large amount of current (around 40 mA) is seen for tap water and the area covered is large. This indicates the presence of contaminants like heavy metals.

Conclusion

The consolidated response of all the different water samples is listed in the Table 1. The area and the maximum current response of the voltammogram is directly proportional to the level of contamination. The small intermittent peak currents appearing at different biasing voltages during the voltage sweep indicate the presence of different minerals in the solution. By using this voltammogram as the reference guide, we can easily distinguish the different water solutions. The important feature of the new model electrochemical sensor is, it can graphically display the amount of contamination which makes it easy for the user to compare different samples and it can be used as a low cost water impurity sensor.

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