

An Inexpensive Disposable Sensor for Detection of Phosphate using Ammonium Molybdate and Pyrrole Nanocomposites Drop Casting

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Abstract

Controlling phosphate levels in water is immensely crucial as it causes excessive growth of algae that creates imbalances with destroying other life forms and produce harmful toxins. Ammonium Molybdate (AM) and Pyrrole (PY) nanocomposites were used to create a distinctly sensitive and low-cost electrochemical sensor for the detection of phosphate anions in water. Using open circuit voltammetry, different concentrations of phosphate solutions (H_2PO_4) were tested with the developed sensor to determine the sensitivity and lowest detection limit. The potential response showed good characteristics with value of $R^2 = 0.9552$ (logarithm fit) in the 10^{-11} mol/L to 10^{-7} mol/L range and $R^2 = 0.9839$ (logarithm fit) in the 10^{-6} mol/L to 10^{-2} mol/L range for KH_2PO_4 . Also, $R^2 = 0.9260$ (logarithm fit) in the 10^{-11} mol/L to 10^{-7} mol/L range and $R^2 = 0.9517$ (logarithm fit) in the 10^{-6} mol/L to 10^{-2} mol/L range for NaH_2PO_4 . According to the findings, the established electrochemical sensor has the capacity to detect phosphate anion with maintaining high precision rate.

Objective

The main objective of this study is to fabricate and develop a low-cost, mobile, and disposable phosphate sensor that can be tested in aqueous solution. Also, characterization of the developed electrochemical phosphate sensor in terms of sensitivity, selectivity, stability and lower detection limit.

Methodology

The screen-printed electrode (SPE) used here has three electrodes. Before the working electrode's surface was modified, the SPE sensors were cleaned. By cyclic voltammetry (0.0 to 1.4 V, 15 cycles, scan rate 50 mV/s), the new SPE was cleaned with 0.1 M H_2SO_4 solution, followed by soaking (only the electrode portion) in 0.1 M NaCl solution and then acetone for 1 minute each to eliminate any physically adsorbed materials on the electrode surface. Between each cleaning phase, the SPE was cleaned in fresh DI water, and after cleaning, all of the sensors were dried at room temperature for 6 hours before treatment. A homogenous mixture of 8 μL of 0.2 M PY and 2×10^{-3} AM was drop-casted on the working electrode, then dried for 8 hours at room temperature.

The concentration of phosphate in the sample solution was determined using open circuit voltammetry. The potential response from the SPE phosphate sensor was recorded using the three-electrode device at room temperature using the CHI-6012E electrochemical analyzer. The potential is measured in open circuit voltammetry when there is no external current flowing in the device. After contacting H_2PO_4 solution, the formation of phosphate complexes on the SPE sensor causes a potential improvement. Figure 1 depicts a schematic of the formed phosphate sensor's measurement procedure. Various concentrations of H_2PO_4 were measured with the fabricated SPE sensor for electrochemical detection of phosphate anions. The developed phosphate sensor was tested using the dipping process. For the open circuit time potential analysis, the sensor was submerged in the sample solution. At room temperature, the testing lasted 400 seconds and data was collected every 0.1 second. For a uniform phosphate concentration in the sample vial, a magnetic stirrer was used at 750 rpm. Also, the SEM images were taken using the JEOL JSM-6460 LV with Energy Dispersive Spectroscopy and Plasma Sputter Coating equipment.

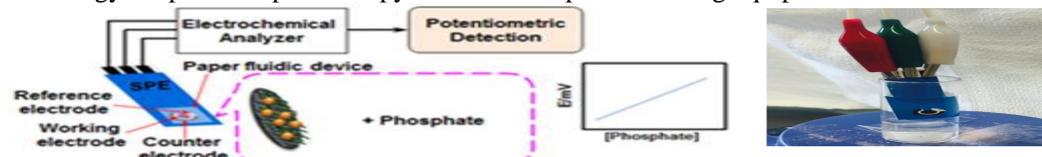
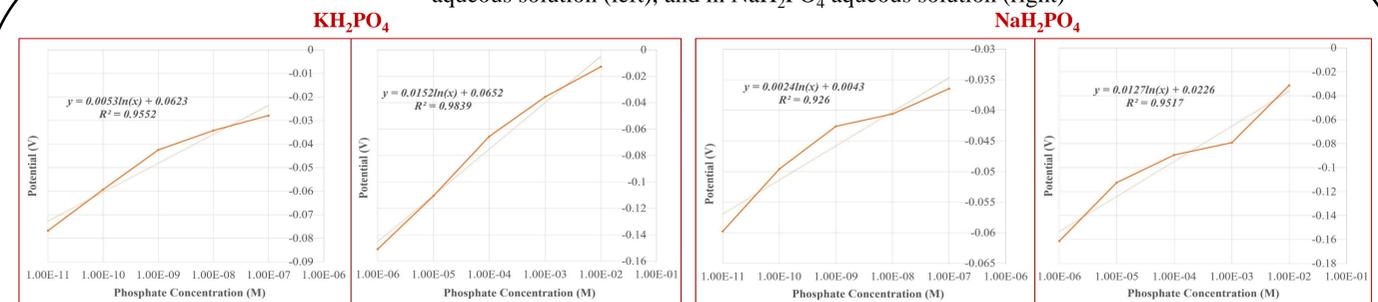


Fig 1: Working method of AM-PY fabricated SPE

Results

Fig 2: Phosphate detection using mixture of PY, and AM modified SPE in KH_2PO_4 aqueous solution (left), and in NaH_2PO_4 aqueous solution (right)

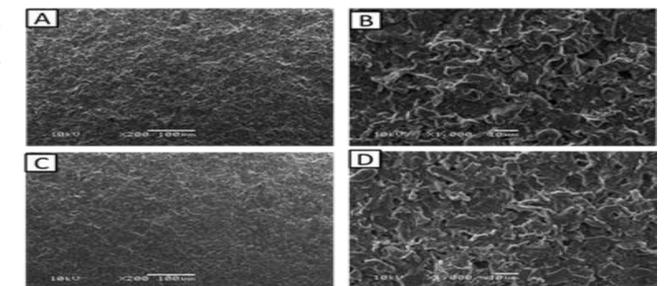


• Figure 2 depicts graph of a single calculation for each of the four measurements. After stabilization, the electrical potential of each phosphate concentration was calculated by averaging measured values from 200 to 300 seconds. Stabilization takes about 1 minute on average. The increment of the potential was in proportion as the phosphate concentration increased.

The phosphate concentrations showed good linearity with the optimized mixture of PY (0.2 M) and AM (2×10^{-3} mol/L). For both KH_2PO_4 and NaH_2PO_4 , the OCPT response in two ranges of phosphate concentration showed an improved calibration curve (logarithmic fit).

• Using different magnification level, the SEM images have been collected of the developed sensor for surface study. Before and after the experiment, the SEM images shows no significant effect on the sensor surface (Figure 3).

Fig 3: Scanning electron microscopy (SEM) images of AM-PY modified SPE (A) before experiment x200 magnification (B) before experiment x1000 magnification (C) after experiment x200 magnification (D) after experiment x1000 magnification



Conclusion & Future Work

For rapid in-situ measurement of phosphate ions in water, the developed sensor has showed promising and good results in terms of lower detection limit and sensitivity. Having a lightweight structure and convenient mobility, the proposed sensor can certainly replace the present bulk instruments and methods that has been used for detecting phosphate. Like the conventional methods, this sensor do not require skilled personnel and expensive instruments to detect phosphate level in aqueous solutions. As a result, the screen-printed electrode (SPE)-based disposable phosphate sensor has great potential for cost-effective and on-site analysis of water samples. Further experimentations are ongoing with other nanoparticles for fabricating more precise sensors in terms of detection limits, stability and potential response. The effect of PH for different concentration of phosphate solutions are also under investigation now.

References

1. W.-L. Cheng, J.-L. Chang, Y.-L. Su, and J.-M. Zen, "Facile Fabrication of Zirconia Modified Screen-Printed Carbon Electrodes for Electrochemical Sensing of Phosphate," *Electroanalysis*, vol. 25, no. 12, pp. 2605–2612, 2013.
2. S. Berchmans, T. B. Issa, and P. Singh, "Determination of inorganic phosphate by electroanalytical methods: A review," *Anal. Chim. Acta*, vol. 729, pp. 7–20, 2012.
3. US EPA, "Nutrient Pollution: The Environmental Problem." Available: <https://www.epa.gov/nutrientpollution/problem>.
4. NSF/ANSI, "Drinking Water Treatment Chemicals - Health Effects," 2013.