



POLYVINYLPYRROLIDONE AS A NEW FLUORESCENT SENSOR FOR NITRATE ION

(Polivinilpirolidon Sebagai Sensor Pendafluor Baru Bagi Ion Nitrat)

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Abstract

In this study, non-conjugated polyvinylpyrrolidone (PVP) is investigated for the first time as the potential polymeric material to sense nitrate ions by fluorescence spectroscopy. The PVP was diluted into various concentrations (3-10%) and they were used to sense the nitrate ions in different concentrations (0.1-100 mM). The PVP showed two excitation peaks at 285 and 330 nm due to the presence of C=O and N-C groups, respectively. One strong emission at 400 or 408 nm was observed with the excitation at 285 or 330 nm. The higher value of quenching constant at excitation wavelength of 285 nm indicated that C=O site was more favored for NO₃⁻ ions sensing than the N-C site. The PVP 7% gave the highest quenching constant; where the K_{SV} value was $9.89 \times 10^3 \text{ mM}^{-1}$ and $2.44 \times 10^3 \text{ mM}^{-1}$ for excitation at 285 and 330 nm, respectively. The sensing capability was evaluated in the presence of interference ions (SO₄²⁻, HCO₃⁻, Cl⁻, and OH⁻). It was observed that the interference ions interacted strongly with the C=O, but weakly with the N-C. Therefore, in the presence of the interference ions, the PVP would be a potential fluorescent sensor when it is excited at 330 nm.

Keywords: polyvinylpyrrolidone; fluorescent sensor; nitrate ions; quenching

Abstrak

Dalam kajian ini, polivinilpirolidon (PVP) yang bersifat bukan konjugat dikaji untuk kali pertama sebagai bahan polimer yang berpotensi untuk mengesan ion nitrat dengan spektroskopi pendafluor. PVP dicairkan kepada kepekatan yang berlainan (3-10%) dan digunakan untuk mengesan ion nitrat dalam kepekatan yang berbeza (0.1-100 mM). PVP menunjukkan dua puncak pengujian pada 285 dan 330 nm dengan kewujudan C=O dan N-C masing-masing. Satu puncak pemancaran yang tinggi pada 400 atau 408 nm diperolehi dengan pengujian pada 285 atau 330 nm. Pemalar pelidap kejutan dengan nilai yang lebih tinggi pada puncak pengujian 285 nm menunjukkan bahawa tapak C=O lebih cenderung untuk mengesan ion NO₃⁻ daripada tapak N-C. PVP 7% memberi pemalar pelidap kejutan yang paling tinggi, dengan nilai K_{SV} $9.89 \times 10^3 \text{ mM}^{-1}$ dan $2.44 \times 10^3 \text{ mM}^{-1}$ untuk puncak pengujian pada 285 dan 330 nm masing-masing. Kemampuan pengesanan dinilai dengan kehadiran ion gangguan (SO₄²⁻, HCO₃⁻, OH⁻, and Cl⁻). Hasil kajian menunjukkan bahawa ion gangguan berinteraksi kuat dengan C=O, tetapi lemah dengan N-C. Oleh itu, dengan kehadiran ion gangguan, PVP berpotensi menjadi pendafluor sensor pada tapak pengujian 330 nm.

Kata kunci: polivinilpirolidon; pengesan pendafluor, ion nitrat, pelidap kejutan

Introduction

Polymer consisting of repeating units of monomers is highly explored in various fields, owing to its non-toxic [1], simple fabrication methodology and low cost [2, 3], large surface-to-volume ratio [4] and easy modification [5]. The conjugated polymers have received particular attentions with their wide applications in batteries [6], organic light emitting diodes [2, 4, 7], and sensor [2, 4-6, 8-10], due to their unique metallic and semiconducting properties [4] as well as the fluorescence properties [4, 5, 11]. On the other hand, the non-conjugated polymers are less explored and still poorly understood. To date, the non-conjugated polyvinylpyrrolidone (PVP) is mostly used as a passivator or a capping agent for semiconductor such as ZnS or CdS, with the purpose to reduce the agglomeration and improve the optical property [12]. Some studies reported the application of the PVP as a sensor [14, 15]. Wang et al. reported that the PVP can be used as electrochemical sensor for acyclovir molecule [14], while Zhang et al. used PVP nanocomposite as a humidity sensor [15]. Since the PVP has been also reported to have photoluminescence property [16], it is worthy to study the possibility to use the non-conjugated PVP as the fluorescence sensor. To the best of our knowledge, there is no investigation on the application of the PVP as the fluorescence sensor. In this study, the PVP is used as the fluorescent sensor for detection of nitrate ions.

The nitrate ions are usually found in fertilizer for agriculture purpose. When the fertilizer is used excessively, the excess nitrate ions in the environmental water system will lead to algae blooms and eutrophication phenomena [17-19]. On the other hand, nitrate ions that are consumed into body may cause methemoglobinemia and the nitrate ions might become the source of carcinogenic N-nitrosamines [17, 20]. These are some of the reasons to monitor nitrate ions in the environment. Extensive studies have been explored to detect the nitrate ions using different techniques, such as ion chromatography [18], capillary electrophoresis [3, 20], electrochemical [3, 21-24], and fluorescence spectroscopy [17]. However, the detection limit and linear detection range of existing nitrate ion sensor are still not in satisfactory level [21], and this urges researchers to develop better nitrate sensors.

In this study, the feasibility to develop PVP fluorescence sensor for nitrate ions was examined using different concentrations of PVP and nitrate ions. The favorable sites to interact with the nitrate ions were discussed based on the quenching phenomena. Besides, the selectivity of the PVP to the nitrate ions was evaluated in the presence of other interference ions such as SO_4^{2-} , HCO_3^- , Cl^- , and OH^- .

Materials and Methods

Materials

The PVP solution (K 60, Aldrich, $M_w \approx 160000$, 45% in water), sodium nitrate (NaNO_3 , Merck, 99.5%), sodium sulphate (Na_2SO_4 , Fisher Scientific, > 99%), sodium hydrogen carbonate (NaHCO_3 , Fisher Scientific, 99%), sodium chloride (NaCl , Fisher Chemical, 100.1%), and sodium hydroxide (NaOH , QR&C, 99%) were used as-received without any treatments.

Preparation of PVP

A series of various concentrations of PVP were prepared from the PVP (K 60) by dilution method using deionized water. The prepared solution was shown as x% of PVP, where x showed the concentrations of the PVP (3, 5, 7, and 10%).

Fluorescence, quenching and selectivity test

The fluorescence property and sensing capability of the PVP solutions for detection of nitrate ions were studied using a Fluorescence Spectroscopy (JASCO, FP-8500) at room temperature. The excitation spectra of the PVP solutions were monitored at emission wavelengths of 400 or 408 nm, while the emission spectra were monitored at the excitation wavelengths of 285 or 330 nm. For quenching test, the PVP solution was exposed to various concentrations of nitrate ions (0.1-100 mM) and the interaction between the emission sites and the nitrate ions was measured. The sensing capability of the PVP was evaluated in the presence of interference ions (SO_4^{2-} , HCO_3^- , Cl^- , and OH^-). The concentration for the nitrate ions and each interference ions was fixed at the concentration of 100 mM.

Results and Discussion

Fluorescence property of PVP

The fluorescence property of the PVP solution was studied by investigating its excitation and emission sites. As shown in Figure 1, all the prepared PVP (3-10%) exhibited two excitation sites at 285 and 330 nm and one emission site at 400 or 408 nm when they were excited at 285 or 330 nm. The excitation at 285 nm would be attributed to the presence of C=O, while the excitation at 330 nm would be corresponded to the presence of N-C in the PVP, similar to the reported one [12]. It was clear that the excitation and emission intensity increased with the increase of the PVP concentrations. The increased intensities were reasonable since they indicated the increased amount of excitation and emission sites of the PVP with the increase of the concentrations. Figure 1 also showed that the intensity of N-C sites was higher than that of C=O sites, suggesting that the N-C sites would be the main excitation sites in the PVP and the N-C sites showed greater fluorescence quantum yield than the C=O site [25].

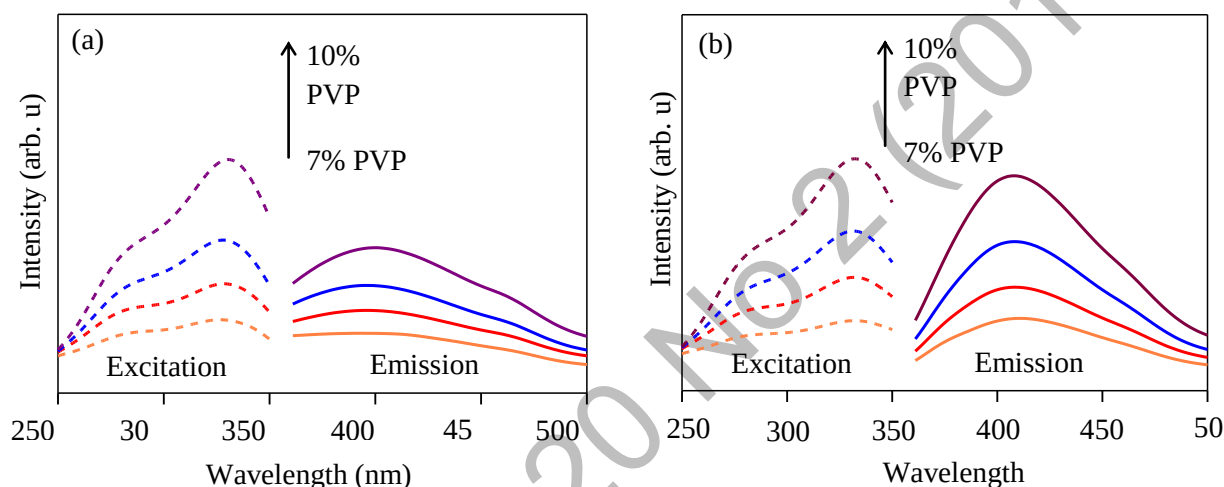


Figure 1. Excitation and emission spectra for 3, 5, 7 and 10% of PVP at (a) C=O and (b) N-C sensing sites

Quenching tests

In order to investigate the performance of the PVP to sense the nitrate ions, the interaction between emission sites and the nitrate ions were evaluated by quenching effect study. The quenching tests were evaluated by monitoring the changes in the emission intensity after addition of various concentrations of nitrate ions (0.1-100 mM). The emission spectra were monitored at two different excitation wavelengths, which were 285 nm and 330 nm. All the 3-10% of PVP showed similar results to each other, in which the emission intensities of the PVP were quenched after addition of the nitrate ions. The results of the quenching tests for the 7% of PVP are shown in Figure 2. The decrease in the emission intensity increased with the increase of nitrate ions concentrations for both emission sites, which were C=O and N-C sites. Among the prepared PVP, the 7% of PVP showed the most quenched intensity, suggesting that the 7% of PVP showed the strongest interaction with the nitrate ions (not shown).

As shown in Figure 2, quenching effects were observed on both C=O and N-C emission sites, suggesting that there were certain interactions between both the emission sites and the nitrate ions. Due to the difference of the charge between the emission sites and the nitrate ions, the most possible interactions between PVP and nitrate ions would be electrostatic interactions. Similar interactions have been proposed for the interactions between nitrates and polypyrrole [22], nitro-containing compounds with polymers [11, 26, 27]. In the presence of the same concentration of nitrate ions, especially at high concentrations, it was obviously observed that the C=O sites were more quenched than the N-C sites. This might be due to the reason that at each C=O can interact with more than one nitrate ions simultaneously and this can be more intense at higher concentration of nitrate ions. Moreover, a slight red shift in

the emission peak wavelength at high concentration of nitrate ions were also observed, suggesting that there was loss of energy through vibrational relaxation or internal conversion phenomena when the PVP interacted with nitrate ions [25].

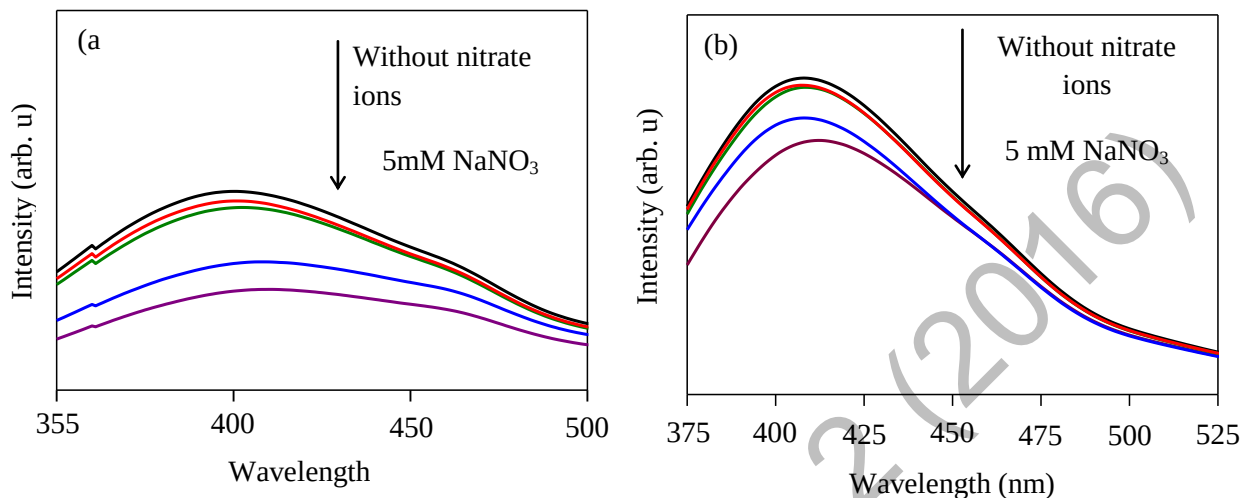


Figure 2. Emission spectra of 7% PVP with the absence and presence of nitrate ions in the 5-100 mM range for C=O sites and N-C sites, monitored at excitation wavelength of (a) 285 nm and (b) 330 nm

The interaction between the emission sites and nitrate ions can be evaluated by using the Stern-Volmer plot. When the illumination intensity and the amount of PVP are maintained to be constant, the relative emission intensity can be expressed as a function of the nitrate ions concentrations, according to the Stern-Volmer equation (Eq. 1),

$$\frac{I_0}{I} = K_{sv}[Q] + 1 \quad (1)$$

where I_0 and I are fluorescence intensities obtained in the absence and presence of nitrate ions, respectively, Q is the concentration of nitrate ions, and K_{sv} is the Stern-Volmer quenching constant.

Figure 3 shows the Stern-Volmer plots for the 7% of PVP. The plots were linear for both emission sites, suggesting that both C=O and N-C sites acted as the sensing sites for the nitrate ions. The slopes of the Stern-Volmer plots represented the quenching constant (K_{sv}), which values were $9.89 \times 10^3 \text{ mM}^{-1}$ and $2.44 \times 10^3 \text{ mM}^{-1}$ for C=O and N-C sites, respectively. The higher value of the K_{sv} for the C=O sites than that for the N-C sites indicated that the C=O sites were more favorable to sense nitrate ions than the N-C sites. This might be due to the reasons that the C=O sites have higher polarity than the N-C sites, but with less steric hindrance effect. The higher K_{sv} values obtained on the C=O sites can be observed as well on other PVP with various concentrations, as can be seen in Figure 4. It can be clearly shown that the K_{sv} values increased with the PVP concentrations up to 7%, but decreased when the PVP concentration was 10%. This result clearly suggested that 7% of PVP was an optimum concentration to get the highest quenching efficiency.

Selectivity Tests

The sensing performance of 7% of PVP towards nitrate ions was evaluated with the co-existence of interference ions. The interference ions used in current study were SO_4^{2-} , HCO_3^- , Cl^- and OH^- . The extent of interference was determined according to the equation below (Eq. 2):

$$E = \frac{I_o - I}{I_o} \times 100\% \quad (2)$$

where I_o and I show the fluorescence emission intensity for the 7% of PVP with the presence of nitrate ions only and the presence of both nitrate and interference ions, respectively. The high value of the extent of interference suggested the high interference effect of the ions towards the performance of the 7% PVP for detection of the nitrate ions.

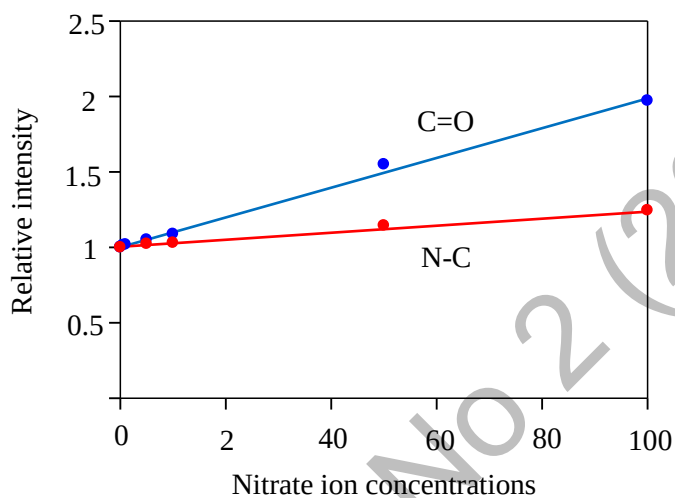


Figure 3. Linear Stern-Volmer plots for 7% PVP at C=O (●) and N-C (●)

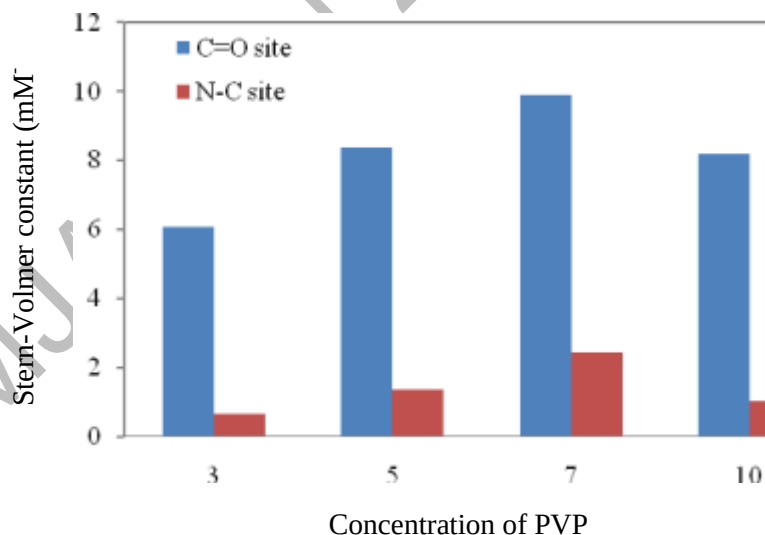


Figure 4. Stern-Volmer constants for nitrate ions detection on PVP with various concentrations for both C=O and N-C sites

The extent of interference for each interference ion was shown in Figure 5. As for the C=O sites, the presence of SO_4^{2-} , HCO_3^- , Cl^- , and OH^- ions gave extent of interferences, which values of 25, 12, 4, and 47%, respectively. This result suggested that the detection of nitrate ions by C=O sites were mostly influenced by OH^- , followed by SO_4^{2-} , HCO_3^- , and Cl^- ions. The high interference effect from OH^- would be caused by the small size and polarity of OH^- ions [27]. Therefore, the 7% of PVP would not be suitable to detect nitrate ions in the presence of OH^- ions. On the other hand, even though the co-existence of polyatom anions such as SO_4^{2-} and HCO_3^- resulted in lower effect than the OH^- , the C=O sites competitively interacted with SO_4^{2-} and HCO_3^- . Therefore, the sensing performance would be affected in the presence of these ions. It is worthy noted that the C=O sites showed much less interaction with Cl^- , suggesting that the C=O sites still could be used to detect the nitrate ions even in the presence of Cl^- ions.

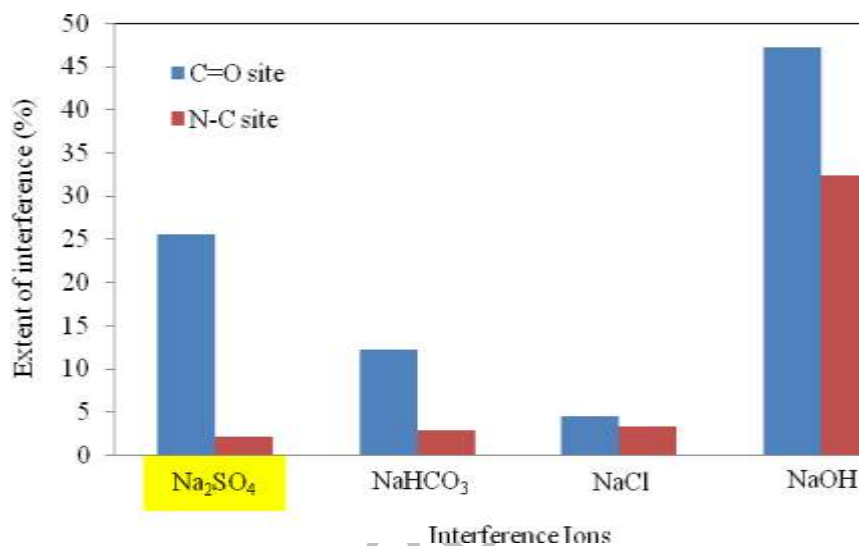


Figure 5. Extent of interferences of ions towards nitrate ions detection on 7% PVP

As for the N-C sites, the presence of SO_4^{2-} , HCO_3^- , Cl^- , and OH^- ions gave extent of interferences, which values of 2, 3, 3, and 32%, respectively. Similar to the C=O sensing sites, the N-C sites were found to be affected by the presence of OH^- . Different from the C=O sites, the performance of the nitrate sensing on the N-C sites were not much influenced by SO_4^{2-} , HCO_3^- , or Cl^- ions. These results suggested that the N-C sensing sites still can selectively interact with nitrate ions in the presence of these interfering ions.

Conclusion

The PVP showed two excitation peaks at 285 and 330 nm and one emission peak at 400 or 408 nm when excited at 285 and 330 nm. Among the prepared PVP, 7% of PVP showed the highest quenching constants toward the nitrate ions. The linear Stern-Volmer plot was observed, suggesting that the PVP can be used as a potential fluorescence sensor for nitrate ions. The C=O sites were found to show much stronger interactions with nitrate ions (four times higher) than the N-C sites, suggesting that the C=O sites were more favorable to sense the nitrate ions. The presence of interference ions were found to affect the fluorescence sensing of nitrate ions differently. As for C=O sites, it can still be used to sense nitrate ions in the presence of Cl^- ions. On the other hand, the N-C sites can selectively sense the nitrate ions in the presence of SO_4^{2-} , HCO_3^- , and Cl^- ions.

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References

1. Bourlinos, A. B., Georgakilas, V., Zboril, R., Steriotis, T. A., Stubos, A. K. & Trapalis, C. (2009). Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone for the water-soluble graphenes. *Solid State Communications*, 149 (47-48): 2172-2176.
2. Harsányi, G. (2000). Polymer films in sensor applications: a review of present uses and future possibilities. *Emerald Insight*, 20 (2): 98-105.
3. Chen, G., Lin, Y. & Wang, J. (2006). Monitoring Environmental Pollutants by Microchip Capillary Electrophoresis with Electrochemical Detection. *Talanta*, 68 (3): 497-503.
4. Ozaydin-Ince, G., Coclite, A. M. & Gleason, K. K. (2012). CVD of polymeric thin films: applications in sensors, biotechnology, microelectronics/organic electronics, microfluidics, MEMS, composites and membranes. *Report on Progress in Physics*, 75 (1): 016501
5. Fan, L.-J., Zhang, Y. & Jones, W. E. (2005). Design and synthesis of fluorescence "Turn-on" chemosensors based on photoinduced electron transfer in conjugated polymers. *Macromolecules*, 38 (7): 2844-2849.
6. Gangopadhyay, R. & De, A. (2000). Conducting polymer nanocomposites: a brief overview. *Chemistry of Materials*, 12 (3): 608-622.
7. Heeger, A. J. (2001). Semiconducting and metallic polymers: The Fourth Generation of polymeric materials. *Journal of Physical Chemistry B*, 105 (36): 8475-8491.
8. Vijayakumar, N., Subramanian, E. & Padiyan, D. P. (2012). Conducting polyaniline blends with the soft template poly(vinyl pyrrolidone) and their chemosensor application. *International Journal of Polymer Materials*, 61 (11): 847-863.
9. Akinyeye R. O., Michira, I., Sekota, M., Ahmed, A. A., Tito, D., Baker, P. G. L., Brett, C. M. A., Kalaji, M. & Iwuoha, E. (2007). Electrochemical synthesis and characterization of 1,2-naphthaquinone-4-sulfonic acid doped polypyrrole. *Electroanalysis*, 19 (2-3): 303-309.
10. Liu, S., Wang, L., Luo, Y., Tian, J., Li, H. & Sun, X. (2011). Polyaniline nanofibres for fluorescent nucleic acid detection. *Nanoscale*, 3 (3): 967-969.
11. Sam, M. S., Lintang, H. O., Sanagi, M. M., Lee, S. L. & Yuliati, L. (2014). Mesoporous carbon nitride for adsorption and fluorescence sensor of n-nitrosopyrrolidone. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 124: 357-364.
12. Minh, T. T., Van, B. P., Van, T. D. & Thi, H. N. (2013). The optical properties and energy transition process in nanocomposite of polyvinyl-pyrrolidone polymer and Mn-doped ZnS. *Optical and Quantum Electronics*, 45 (2): 147-159.
13. Nishizawa, S., Kato, Y. & Teramae, N. (1999). Fluorescence sensing of anions via intramolecular excimer formation in a pyrophosphate-induced self-assembly of a pyrene-functionalized guanidium receptor. *Journal of American Chemical Society*, 121 (40): 9463-9464.
14. Wang, P., Gan, T., Zhang, J., Luo, J. & Zhang, S. (2013). Polyvinylpyrrolidone-enhanced electrochemical oxidation and detection of acyclovir. *Journal of Molecular Liquids*, 177:129-132.
15. Thi, T. M., Tinh, L. V., Van, B. H., Ben, P. V. & Trung, V. Q. (2012). the effect of polyvinylpyrrolidone on the optical properties of the Ni-doped ZnS nanocrystalline thin films synthesized by chemical method. *Journal of Nanomaterials*, 2012:1-8.
16. Zhang, J., Shen, G., Wang, W., Zhou, X. & Guo, S. (2010). Individual nanocomposite sheets of chemically reduced graphene oxide and poly(n-vinyl pyrrolidone): Preparation and humidity sensing characteristics. *Journal of Materials Chemistry*, 20 (48): 10824-10828.
17. Taylor, C. J., Bain, L. A., Richardson, D. J., Spiro, S. & Russell, D. A. (2004). Construction of a whole-cell gene reporter for the fluorescent bioassay of nitrate. *Analytical Biochemistry*, 328 (1): 60-66.
18. Ito, K., Takayama, Y., Makabe, N., Mitsui, R. & Hirokawa, T. (2005). Ion chromatography for determination of nitrite and nitrate in seawater using Monolithic ODS columns, *Journal of Chromatography A*, 1083(1-2): 63-67.
19. Smil, V. (1997). Global population and the nitrogen cycle. *Scientific American*, 277: 76-81.
20. Moorcroft, M. J., Davis, J. & Compton, R. G. (2001). Detection and determination of nitrate and nitrite: A review. *Talanta*, 54 (5): 785-803.
21. Tu, X., Gao, Y., Yue, R., Lu, Q., Zhou, Y. & Lu, Z. (2012). An amperometric nitrate sensor based on well-aligned cone-shaped polypyrrole-nanorods. *Analytical Methods*, 4 (12): 4182-4186.

22. Bendikov, T. A. & Harmon, T. C. (2005). A sensitive nitrate ion-selective electrode from a pencil lead. An analytical laboratory experiment. *Journal of Chemical Education*, 82 (3): 439-441.
23. Jang, A., Zou, Z., Lee, K. K., Ahn, C. H. & Bishop, P. L. (2010). Potentiometric and voltammetric polymer lab chip sensors for determination of nitrate, pH, and Cd(II) in Water. *Talanta*, 83 (1): 1-8.
24. Adeloju, S. B. & Sohail, M. (2011). Polypyrrole-based bilayer nitrate amperometric biosensor with an integrated permselective poly-ortho-phenylenediamine layer for exclusion of inorganic interferences. *Biosensors and Bioelectronics*, 26 (11): 4270-4275.
25. Lakowicz, J. R. (2006). *Principles of Fluorescence Spectroscopy*. Springer: New York. 3rd edition.
26. Long, Y., Chen, H., Yang, Y., Wang, H., Yang, Y., Li, N., Li, K., Pei, J. & Liu, F. (2009). Electrospun nanofibrous film doped with a conjugated polymer for DNT fluorescence sensor. *Macromolecules*, 42 (17): 6501-6509.
27. Yang, J.-S., & Swager, T. M. (1998). Fluorescent porous polymer films as TNT chemosensors: Electronic and structural effects. *Journal of American Chemical Society*, 120 (46): 11864-11873.