POLYVINYLPYRROLIDONE, GRAPHENE OXIDE AND THEIR COMPOSITES AS POTENTIAL FLUORESCENCE SENSING MATERIALS FOR NITRATE AND NITRITE IONS

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemistry)

Faculty of Science
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MAY 2017

To my beloved family

ACKNOWLEDGEMENT

Thanks God for leading me go through my PhD journey.

Thanks to my project supervisors, Dr. Leny Yuliati and Dr. Hasmerya Maarof, for their very great efforts in guiding me and encouraging me when I felt lost and down during my research journey. They really showed great patience in leading me to complete my research project and great kindness to share their knowledge with me.

Thanks to my beloved family for their continuous moral supports and financial supports in my PhD journey. Without them, I might give up halfway due to financial constraint.

Thanks UTM for offering me PhD study and thanks to MyBrain 15 MyPhD Scolarship for sustaining me financially for 3.5 years. Thanks to Center for Sustainable Nanomaterials (CSNano), Ibnu Sina Institute for Scientific and Industrial Research for providing most of the facilities for my research. Thanks to all laboratory staffs in CSNano, Department Chemistry, Faculty of Science, UTM who offered their helping hand during my study. Thanks to my colleagues and friends for their willingness to share their knowledge, experience and great moral support in my study.

ABSTRACT

The existence of toxic nitrate (NO_3^-) and nitrite (NO_2^-) ions above the permissible level causes environmental pollution and human health hazard. Therefore, many studies have been carried out to improve sensitivity and selectivity of sensors for the ion detections. In this study, polyvinylpyrrolidone (PVP), graphene oxide (GO), and polyvinylpyrrolidone-graphene oxide (PVP-GO) were prepared, characterized, and tested for their ability to detect nitrate and nitrite ions. A series of PVP with concentration of 1-10% was prepared by dissolvation in deionized water. The PVP has –C=O and –N–C sensing sites, with excitation wavelength of 285 nm and 330 nm and emission wavelength of 408 nm and 410 nm, respectively. All the PVP sensing materials showed greater sensitivity towards nitrite than nitrate. It was found that 7% PVP showed the best sensitivity for the analytes detection at both sensing sites. Nitrate preferred the –C=O site, while nitrite preferred the –N–C site. The selectivity tests demonstrated that 7% PVP gave great selectivity towards analytes even in the presence of SO_4^{2-}, HCO_3^-, or Cl^-, but not OH^- ion. The high interference from OH^- could be due to hydrogen bond formation. Computational simulation for PVP and analytes was investigated using B3LYP/6-311G(d,p). The simulation studies revealed that PVP formed greater interaction with nitrite than nitrate. Characterization results showed that the GO was successfully prepared by the improved Hummers' method. GO showed greater sensitivity for the detection to nitrite than nitrate in the range of 0-100 mM. Selectivity tests found that GO showed great selectivity tawards analytes even in the presence of SO_4^{2-} or Cl^-, but low selectivity in the presence of HCO_3^- or OH^- ion, due to the formation of hydrogen bond. Simulation results demonstrated that GO formed greater interaction with nitrite compared to nitrate. The high binding energies between hydroxyl or carboxyl site and the analytes showed that they might be the possible sensing sites in GO. A series of PVP-GO(x) composite was prepared by mixing and sonication treatment of 7% PVP (100 mL) and various amounts of GO (x = 0.0075-0.03 g). The characterizations supported the successful formation of the composites. All composites showed superior sensitivity towards nitrite than nitrate. Among the composites, the PVP-GO(0.01) showed the highest sensitivity for the detection of both analytes. For the selectivity tests, PVP-GO(0.01) showed great selectivity for the detection of analytes even in the presence of SO_4^{2-}, HCO_3^-, or Cl^-, but not for OH^- ion. The simulation tests exhibited that the –C=O site of PVP interacted with hydroxyl site of GO to form PVP-GO composite. The PVP-GO showed greater interaction with nitrite compared to nitrate. All computational results matched with the experimental results. The addition of GO to the PVP was found to increase the sensitivity and selectivity for nitrate detection, but not for nitrite detection. However, the composite gave better limit of detection (LOD) than the 7% PVP and GO. This study showed that among all the investigated materials, 7% PVP was the most potential fluorescence sensor for nitrate detection with LOD of 4.00 mM at –C=O site, while PVP-GO(0.01) was the most potential one for nitrite detection with LOD of 0.26 mM at –N–C site. Real sample testing using UTM lake water demonstrated the potential application of 7% PVP as a fluorescence sensor.

ABSTRAK

Kewujudan ion nitrat (NO_3^-) dan nitrit (NO_2^-) yang bertoksik di atas paras dibenarkan telah menyebabkan pencemaran alam sekitar dan membahayakan kesihatan manusia. Justeru, banyak kajian telah dijalankan untuk meningkatkan kepekaan dan kepilihan pengesan bagi pengesanan ion. Dalam kajian ini, polivinilpirolidon (PVP), grafina oksida (GO) dan polivinilpirolidon-grafina oksida (PVP-GO) telah disediakan, dicirikan, dan diuji keupayaan mereka untuk mengesan ion nitrat dan nitrit. Satu siri PVP dengan kepekatan 1-10% telah disediakan dengan pemelarutan di dalam air ternyahion. PVP mempunyai tapak pengesanan –C=O dan –N–C, masing-masing dengan panjang gelombang pengujaan pada 285 nm dan 330 nm dan panjang gelombang pemancaran pada 408 nm dan 410 nm. Kesemua bahan pengesanan PVP menunjukkan kepekaan yang lebih terhadap nitrit berbanding nitrat. Didapati 7% PVP menunjukkan kepekaan yang terbaik untuk pengesanan analit di kedua-dua tapak pengesanan. Nitrat lebih suka tapak –C=O, manakala nitrit lebih suka tapak –N–C. Ujian kepilihan menunjukkan bahawa 7% PVP memberikan kepilihan yang baik terhadap analit walaupun dengan kehadiran ion SO_4^{2-}, HCO_3^-, atau Cl^-, tetapi bukan ion OH^-. Gangguan yang tinggi daripada OH^- mungkin disebabkan oleh pembentukan ikatan hidrogen. Simulasi berkomputer untuk PVP dan analit telah disiasat dengan menggunakan B3LYP/6-311G(d,p). Kajian simulasi mendedahkan bahawa PVP membentuk interaksi yang lebih baik dengan nitrit berbanding nitrat. Keputusan pencirian menunjukkan bahawa GO telah berjaya disediakan dengan kaedah peningkatan Hummers'. GO menunjukkan kepekaan yang lebih tinggi bagi pengesanan nitrit berbanding nitrat dalam julat 0-100 mM. Ujian kepilihan mendapati bahawa GO menunjukkan pemilihan yang baik terhadap analit walaupun dengan kehadiran SO_4^{2-} atau Cl^-, tetapi kepilihan yang rendah dengan kehadiran ion HCO_3^- atau OH^-, disebabkan oleh pembentukan ikatan hidrogen. Keputusan simulasi menunjukkkan bahawa GO membentuk interaksi yang lebih baik dengan nitrit berbanding nitrat. Tenaga pengikat yang tinggi antara hidroksil atau tapak karboksil dengan analit menunjukkan bahawa kemungkinan ia adalah tapak pengesanan di dalam GO. Satu siri komposit PVP-GO(x) telah disediakan dengan pencampuran dan rawatan sonikasi antara 7% PVP (100 mL) dan pelbagai jumlah GO (x = 0.0075-0.03 g). Pencirian telah menyokong bahawa komposit telah berjaya dibentuk. Semua komposit menunjukkan kepekaan yang unggul terhadap nitrit berbanding nitrat. Antara komposit-komposit, PVP-GO(0.01) menunjukkan kepekaan tertinggi bagi pengesanan kedua-dua analit. Bagi ujian kepilihan, PVP-GO(0.01) menunjukkan kepilihan yang baik bagi pengesanan analit walaupun dengan kehadiran SO_4^{2-}, HCO_3^-, atau Cl^-, tetapi bukan OH^-. Ujian simulasi mempamerkan bahawa tapak –C=O daripada PVP berinteraksi dengan tapak hidroksil daripada GO untuk membentuk komposit PVP-GO. PVP-GO menunjukkan interaksi yang lebih baik dengan nitrit berbanding dengan nitrat. Semua keputusan simulasi berkomputer sepadan dengan keputusan eksperimen. Penambahan GO kepada PVP didapati meningkatkan kepekaan dan kepilihan bagi pengesanan nitrat, tetapi bukan bagi pengesanan nitrit. Bagaimanapun, komposit memberi had pengesanan (LOD) yang lebih baik berbanding 7% PVP dan GO. Kajian ini menunjukkan bahawa antara semua bahan kajian, 7% PVP adalah pengesan pendaflour yang paling berpotensi bagi pengesanan nitrat dengan LOD 4.00 mM di tapak –C=O, manakala PVP-GO(0.01) adalah paling berpotensi bagi pengesanan nitrit dengan LOD 0.26 mM di tapak –N–C. Ujian sampel sebenar menggunakan air tasik UTM menunjukkan potensi aplikasi 7% PVP sebagai pengesan pendaflour.

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LIST OF ABBREVIATIONS

EPA - Environmental Protection Agency
NMR - Nuclear Magnetic Resonance
GCE - Glassy Carbon Electrode
SPE - Screen Printed Electrode
PPy-NaR-NADH - Polypyrrole-Nitrate Reductase-Nicotinamide Adenine Dinucleotide
P-*o*-PDA - Poly-ortho-Phenylenediamine
EDTA - Ethylenediaminetetraacetic Acid
1,4-DNT - 1,4-dinitrotoluene
2,6-DNT - 2,6-dinitrotoluene
1,3-DNB - 1,3-dinitrobenzene
4-NT - 4-nitrotoluene
HOMO - Highest Occupied Molecular Orbital
LUMO - Lowest Unoccupied Molecular Orbital
PVP - Polyvinylpyrrolidone
DMF - *N*,*N*-dimethylformamide
NMP - *N*-Methyl-2-Pyrrolidone
BASF - Badische Anilin-und Soda-Fabrik
GO - Graphene Oxide
HOPG - Highly Ordered Pyrolytic Graphite
UV - Ultraviolet
Vis - Visible
NIR - Near-Infrared
DMSO - Dimethyl Sulfoxide
AP-AuNPs - Amino-Pyrene-grafted Gold Nanoparticles
CRG/PVP - Chemical Reduced Graphene/ Polyvinylpyrrolidone

PVA - Polyvinyl Alcohol
PVP-GO - Polyvinylpyrrolidone- Graphene Oxide
HPLC - High Performance Liquid Chromatography
IC - Ion Chromatography
DFT - Density Functional Theory
PM3 - Parameterized Model number 3
FTIR - Fourier Transforms Infra Red
XRD - X-ray Diffraction
TEM - Transmission Electron Microscopy
TGA - Thermogravimetric Analysis
B3LYP - Becke, three-parameter, Lee-Yang-Parr
PCM - Polarizable Continuum Model
K*sv* - Stern-Volmer constant
R.S.D - Relative standard deviation
L.O.D - Limit of Detection
a. u. - Arbitrary unit
g - Gram
M_w - Molecular weight
mL - Mili Liter
min - Minute
mM - Mili Molar
rpm - Revolutions per minute
wt/V - Weight per volume
kV - Kilo Volt
℃ - Degree Celsius
nm - Nano meter
ΔE_{int} - Difference in binding energy
E_S - Binding energy of the sensing site
E_A - Binding energy of the analyte

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Nitrate (NO_3^-) and nitrite (NO_2^-) are negatively charged inorganic ions that have high solubility in water. Unfortunately, they are toxic and hazardous to human and aquatic creatures. Both inorganic ions are the major constituents in fertilizer production. Poor management in conventional agricultural practices and use of massive dosage of chemical fertilizer to land and crops led to the presence of excessive nitrate and nitrite ions in the environment. The high level of nitrate and nitrite ion concentrations in the aquatic environment of agriculture area has led to serious environmental problems, such as eutrophication, and algae blooms (Moorcroft *et al*., 2001, Smil, 1997). Besides, if ingested, they also cause life-threatening methemoglobinemia (blue baby syndrome) to baby infants, abdominal pain and diarrhea (Hord *et al*., 2009, Namasivayam and Sangeetha, 2005). In addition, the ingested nitrate can be converted to nitrite, a precursor for carcinogenic compound nitrosamines (Kyrtopoulos, 1988). The previous reports claimed that nitrite is highly hazardous to human as it can impair our nervous system, spleen and kidney (Liu *et al.*, 2013). Since the presence of high level of nitrite and nitrate ions can cause environmental and human health problems, it is important to monitor the level of nitrate and nitrite ions in the environment. To date, numerous efforts have been carried out to obtain excellent materials to be employed as nitrite and nitrate sensor.

Many materials have been explored for sensitive detection of hazardous nitrate and nitrite ions. In 1879, Peter Griess developed an assay to detect nitrate and nitrite ions (Griess, 1879). With his great effort, he successfully developed a sensitive and simple assay, which was able to detect nitrite directly and nitrate indirectly to certain sensitivity. Since different amounts of nitrite will cause different absorbance, the colour observed indicate the amount of nitrite present in a sample. Though Griess reagent is a simple and widely used until today, the assay contains toxic sulfonamides reagent and yet produces toxic diamine product (Guevara *et al.*, 1998, Miranda *et al.*, 2001, Sastry *et al.*, 2002, Senra-Ferreiro *et al.*, 2010, Wang *et al.*, 2016).

Previous studies investigated various types of metals for nitrate or nitrite ion detection. For example, metal such as silver has been employed as sensor for simultaneous detection of nitrate and nitrite ions (Madasamy *et al.*, 2014, Manea *et al.*, 2010). Further, multivalency transition metal such as copper (Shariar and Hinoue, 2010) or copper complex (Shiddiky *et al.*, 2006) has been employed for nitrate and nitrite ions detection. Though metal has been widely explored as sensing material, but they could be easily suffered from corrosion which will lead to attenuation in their sensitivity. Moreover, some of the transition metal are expensive

Other than the simple Griess assay and metal sensing materials, some efforts have also been carried out to design and synthesize macromolecule complex for selective detection of nitrate and nitrite ions. The complex molecule with suitable cavity shape and size has been designed for selective sensing of nitrate or nitrite ion. The complex sensing molecule seems to bring a promising material to detect nitrate or nitrite, but it involves extensive and complex synthesis protocol (Işıklan *et al.*, 2011, Singh and Sun, 2012, Strianese *et al.*, 2013, Whittington *et al.*, 2012). Therefore, a more environmental friendly material with less complex synthesis method such as biomolecule has also been developed for nitrate or nitrite ion detection (Adeloju and Sohail, 2011, Almeida *et al.*, 2010, Ho *et al.*, 2009, Quan *et al.*, 2005). Inspired by the natural detection in the environment, the use of biomolecule can bring selective detection (Saleem, 2013). For example, polypyrrole-nitrate reductase-nicotinamide adenine dinucleotide (PPy-NaR-NADH) has been used to convert nitrate to nitrite ion for sensitive detection of both nitrate and nitrite ions (Adeloju and Sohail, 2011). The biomolecule normally is incorporated with polymer to improve the detection for nitrate or nitrite ion (Albanese *et al*., 2010, Cosnier *et al*., 2008, Madasamy *et al*., 2014, Plumeré, 2013, Wang *et al*., 2013b). Though this combination is expected to give sensitive yet selective detection, but this sensitive material still suffers from thermal instability and could be easily affected in the presence of heat and interference material, respectively.

Another type of material, which is polymeric material, has been explored vastly due to its tunable properties and robustness. There are varieties of organic scaffolds containing polymer that have been tested for their feasibilities to be used as sensing materials in anion recognition. It has been reported that the nitrogen containing moieties showed rather good selectivity for anion binding. For instance, the positively charged ammonium salts such as quaternized amines (Bianchi *et al*., 1996, Hossain *et al*., 2003b, Sisson *et al*., 2003, Späth and König, 2010) and imidazolium cation (Chellappan *et al*., 2005) have found their application in anion binding. Besides, the neutral species such as amide (Amendola *et al*., 2010, Chen *et al*., 2007, Choi and Hamilton, 2003, Hossain *et al*., 2003b, Hossain *et al*., 2003a, Kang *et al*., 2006, Kang *et al*., 2003, Qu *et al*., 2009, Singh and Sun, 2012), urea (Custelcean *et al*., 2008, Zhu *et al*., 2008), pyrrole (Aldakov and Anzenbacher, 2004, Sessler *et al*., 2003, Späth and König, 2010, Wu *et al*., 2006a, Yoon *et al*., 2008), and thioamide (Devaraj *et al*., 2009, Hossain *et al*., 2003a) also showed great affinity for anion binding. Particular attention has been made on the use of amide moieties containing compound for anion recognition owing to its good selectivity and sensitivity. In this study, amide moiety containing polyvinylpyrrolidone (PVP) was explored for its feasibility to be used as a fluorescence sensor.

PVP is a long chain polymer consisting of tertiary amide functional group and vinylpyrrolidone monomer that makes up to different molecular weight polymer. PVP is a bio-compatible polymer which is soluble in many solvents such as water and other organic solvents. From literature, PVP has been applied as sensor for glucose (Mano and Heller, 2005), acyclovir (Wang *et al.*, 2013a), alcohol (Lee *et al.*, 2011), hydrazine (Li and Wang, 1997), ascorbic acid (Han *et al.*, 2010), gold nanoparticle (Behera and Ram, 2012), hydrogen (He *et al.*, 2010), and humidity (Zhang *et al.*, 2010a). It is worth noting that PVP contains electron lone pair in tertiary amide vinylpyrrolidone structure, and this structure makes PVP has remarkable luminescence property (Minh *et al.*, 2013). Though PVP shows great luminescence property, up to date PVP has never been reported as nitrate and nitrite sensor.

On the other hand, graphene oxide (GO) possesses a large surface area with a great number of oxygenated functional groups, and fascinated electronic properties. Due to the distinct properties of GO, it has been used as electronic devices, energy storage, and sensor (Georgakilas *et al.*, 2012, Gilje *et al.*, 2007, Huang *et al.*, 2011, Zhu *et al.*, 2010). Particularly in sensing application, GO has been used to quench the intensity of fluorescence material (Liu *et al.*, 2011, Wang *et al.*, 2009b) and has been applied as gas sensor (Schedin *et al.*, 2007), pH sensor (Chen and Yan, 2011, Mohanty and Berry, 2008, Ohno *et al.*, 2009), pressure sensor (Kazemzadeh *et al.*, 2015), and temperature sensor (Sahoo *et al.*, 2012). Incorporation or functionalization of polymeric material on GO is known to improve mechanical, thermal, electrical, and optical properties of GO (Du and Cheng, 2012). The produced polymer-GO composite has been developed to improve the sensing performance in many aspects especially on the sensitivity and selectivity (Al-Mashat *et al.*, 2010, Eswaraiah *et al.*, 2012, Kundu *et al.*, 2012, Wang *et al.*, 2011, Zhang *et al.*, 2014, Zhang *et al.*, 2010a). In this study, a novel PVP-GO composite was synthesized as a fluorescence sensor for nitrate and nitrite detection.

Apart from the lack of sensitive material from the aspect of sensitivity and selectivity, the employed sensing technique also gives a different extent of sensitivity and selectivity in sensing performance. The commonly used conventional techniques in detection of nitrate and nitrite ions include high performance liquid chromatography (HPLC), ion chromatography (IC) and Griess colorimetric assay. However, these techniques come with several shortcomings. In HPLC measurement, several tedious purification steps are required to eliminate the interfering such as chloride and biogenic amines (El Menyawi *et al.*, 1998, Jobgen *et al.*, 2007, Stratford *et al.*, 1997). While for the IC method, extensive maintenance and sample pretreatment are needed prior to sample measurement (Blount and Valentin-Blasini, 2006, Ito *et al*., 2005, Moorcroft *et al*., 2001, Stalikas *et al*., 2003). In Griess assay, all the nitrate ions are converted to nitrite ion which later are transformed to colored azo dye, but this method lacks sensitivity (Badea *et al.*, 2001). Therefore, a sensitive and simple detection technique is still highly required. In this study, fluorescence spectroscopy was applied as a sensitive and simple detection method for the nitrate and nitrite ions.

With the great evolution of technology, computational study has been exploited in aiding researcher to predict the experimental results. Vast simulation techniques have been developed to match with its purpose. The selection of simulation technique would be based on the properties of interest. The calculation for computational simulation was done by solving a bunch of mathematical equations, with Schrödinger equation as the basic for almost all calculation (Young, 2004). Particularly, the generally used technique to simulate the sensing condition is the density functional theory (DFT). It is a calculation technique based on electron density which able to give superior accuracy when calculating the involved energy in a system (Ghosh *et al*., 2010, Ghosh *et al*., 2004, Jose *et al*., 2007). Semi-empirical Parameterized Model number 3 (PM3) is another well-known technique with faster calculation that is good for geometry optimization (House, 2003). Both techniques were employed in this study to support the experimental results.

1.2 Statement of Problem

Nitrate and nitrite ions are toxic and hazardous compounds to human. Furthermore, the simultaneous existence of both anions led to environmental pollution and yet there is still a lack of material which is good in both sensitivity and selectivity for both analytes. Though there are some sensitive materials being proposed, there are still some limitations on those reported sensitive materials. For instance, the Griess reagent consists of toxic compounds and produces toxic diamine products during the detection process (Griess, 1879, Guevara *et al*., 1998, Miranda *et* *al*., 2001, Sastry *et al*., 2002, Senra-Ferreiro *et al*., 2010, Wang *et al*., 2016). On the other hand, the macromolecule complex involves complicated synthesis procedures (Işıklan *et al*., 2011, Singh and Sun, 2012, Strianese *et al*., 2013, Whittington *et al*., 2012) and biomolecules cannot stand with interference materials (Adeloju and Sohail, 2011, Almeida *et al*., 2010, Ho *et al*., 2009, Quan *et al*., 2005). The later means that the existing sensitive material still showed low selectivity for the detection of nitrate and nitrite ions in the presence of foreign ions. Therefore, simple synthesis of sensitive materials that are non-toxic, environmentally safe, and having good selectivity is still highly required.

In this study, three novel materials were proposed, which were PVP, GO, and PVP-GO composites that were prepared by a simple mixing method. PVP has been reported to act as a good sensor for several organic compounds (Han *et al*., 2010, He *et al*., 2010, Lee *et al*., 2011, Li and Wang, 1997, Mano and Heller, 2005, Wang *et al*., 2013a), gold nanoparticle (Behera and Ram, 2012), and humidity (Zhang *et al*., 2010a). PVP has been also recognized to give fluorescence emission property when being illuminated by light energy (Thi *et al*., 2012). On the other hand, GO has been employed as a sensor for organic materials (Chen and Yan, 2011, Mohanty and Berry, 2008, Ohno *et al*., 2009, Schedin *et al*., 2007), pressure (Kazemzadeh *et al*., 2015), and temperature (Sahoo *et al*., 2012). It is known that GO has fluorescence property which enabled it to be used as biosensor (Dong *et al*., 2010, Jung *et al*., 2010, Loh *et al*., 2010). Despite these, PVP and GO materials have never been reported yet as fluorescence sensors for nitrate and nitrite detection. Since these PVP and GO materials are highly potential as fluorescence sensors for nitrate and nitrite detection, the important sensing sites for high sensitivity and selectivity towards nitrate and nitrite ions need to be clarified. In order to improve the performance of these materials, a novel composite of PVP-GO was also synthesized by a simple mixing method.

Even though the development of novel materials with high sensitivity and selectivity has been investigated, the important factors determining the sensitivity and selectivity of the sensor materials are sometimes neglected. Yet, the sensing process when the analyte presents have not yet been clearly understood. This limitation can be overcome with the aid of computational simulation. In recent years, the fast development in computer software has aided researchers to visualize the molecule in multi-aspects via state of art of computational program. This includes the geometry of molecule, molecular bonding, interaction energy, or binding energy of a design system (Adejoro *et al*., 2012, Adejoro *et al*., 2013, Ghosh *et al*., 2004, Ghosh *et al*., 2010, House, 2003, Mohammed, 2014, Momany *et al*., 2005, Odiaka *et al*., 2012). Numerous programs have been designed with different theories to aid researchers to gain better understanding on their experimental works. In current work, two simulation methods, namely semi empirical and density functional theory (DFT) methods were used to configure the molecular geometry with the lowest energy. Moreover, the interaction between the sensing sites and the analytes was also investigated computationally by calculating the binding energy and interatomic distance between the sensing sites and the analytes.

1.3 Objectives

There are several objectives in this current study as stated below.

(a) To prepare and characterize PVP, GO, and PVP-GO composites as novel fluorescence sensors.
(b) To examine the sensitivity ad selectivity of the PVP, GO, and PVP-GO composites for detection of nitrate and nitrite ions.
(c) To investigate the interaction between the sensitive materials and the analytes by computational simulation.

1.4 Scope of Study

This research can be divided into three parts. The first part discussed about the preparation, characterizations, and performance of PVP as also supported by computational study. The PVP was prepared by dilution method, where the concentration was fixed at 1, 3, 5, 7, and 10%. The characterizations were carried out by Fourier transform infra red (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and fluorescence spectroscopy. The performance of PVP was evaluated via sensitivity and selectivity tests by fluorescence spectroscopy. The excitation wavelengths were fixed at 285 and 330 nm, while emission wavelength was monitored at 408 and 410 nm. Sensitivity tests were carried out on all PVP samples by evaluating the quenching study in the presence of nitrate (0-100 mM) and nitrite (0-100 mM) ions. Selectivity tests were carried out only on the best sample, which was 7% PVP, in the presence of Na_2SO_4, $NaHCO_3$, NaCl, or NaOH foreign ions. For selectivity tests, the concentration for nitrate and nitrite was fixed at 100 mM and 10 mM, respectively. Gaussian 09 program was used for computational simulation study. B3LYP/6-311G(d,p) level of theory was implemented to calculate the binding energy between the PVP and nitrate or nitrite ions with water induced polarizable continuum model (PCM).

In the second part, GO was used as sensitive material for nitrate and nitrite ion detection. Overall, the preparation, characterization, and performance of GO were discussed, supported by computational simulation. GO was synthesized using an improved Hummers' method and further ground to get GO fine powder. The properties of GO were studied using FTIR, XRD, TEM, TGA, and fluorescence spectroscopy. The sensing performance of GO was examined from two aspects, sensitivity and selectivity, using fluorescence spectroscopy. GO was excited at wavelengths of 367 nm, and its emission was monitored at 567 nm. The sensitivity tests were evaluated from quenching study in the presence of nitrate or nitrite ion at 0-100 mM. On the other hand, the selectivity tests were conducted in the presence of Na_2SO_4, $NaHCO_3$, NaCl, or NaOH foreign ions. For the selectivity of GO to nitrate, the concentration of nitrate and foreign ion were fixed at 100 mM while for nitrite selectivity test, the concentration of nitrite and foreign ion were fixed at 10 mM.

Further support from computational simulation was carried out using Gaussian 09 program. B3LYP/6-311G(d,p) level of theory was implemented to calculate the binding energy between the GO and nitrate or nitrite ions with PCM.

In the third part, the PVP-GO composites were prepared for nitrate and nitrite ion detection. The composites were prepared by simple mixing between 100 mL 7% PVP and various mass of GO, where the weight per volume percent of the composites was fixed at 0.0075, 0.01, 0.02, and 0.03%. The prepared composites were further put under sonication for 30 min. In this context, the preparation, characterizations, and sensing performance of PVP-GO were discussed, with support from computational simulation. The properties of the PVP-GO were studied using FTIR, XRD, TEM, TGA, and fluorescence spectroscopy. The sensing performance of PVP-GO to analyte ion was examined from sensitivity and selectivity via fluorescence spectroscopy. The excitation wavelengths were set at 285 and 330 nm, whereas the emission wavelengths were monitored at 408 and 410 nm respectively. The sensitivity of PVP-GO composites was interpreted from quenching study in the presence of nitrate or nitrite ion at concentration of 0-100 mM. The selectivity tests were conducted in the presence of Na_2SO_4, $NaHCO_3$, NaCl, or NaOH foreign ions. For the selectivity tests, the concentration of nitrate and foreign ions were fixed at 100 mM, while for nitrite selectivity test, the concentration of nitrite and foreign ions were fixed at 10 mM. The interaction site between PVP and GO was pre-optimized from PM3, and further optimized using Gaussian 09 program. The interaction between PVP-GO and analyte was further computed using B3LYP/6-311G(d,p) level of theory via calculation of the binding energy with PCM.

1.5 Significance of the Study

This study proposed novel sensitive materials, which were PVP, GO, and PVP-GO composites as fluorescence sensor for the detection of nitrate and nitrite ions. Those sensitive materials are non-toxic and can be synthesized by a simple methodology without generating any toxic products. Therefore, this study will be very important for improving the development of environmentally friendly materials. In the point of view of material science, this study will also contribute significantly to the development of fluorescence sensor materials.

This study demonstrated that the PVP, GO, and PVP-GO composites showed good sensitivity particularly towards nitrite ion detection and they gave good selectivity in the presence of foreign ions, such as sulphate, bicarbonate, and chloride ions. Moreover, these materials also showed good reproducibility and acceptable limit of detection. It is expected that they can be used as potential fluorescence sensor for detection of hazardous nitrate and nitrite ions, and this will be very important for environmental studies.

Since they have not been reported yet, the interactions between these potential fluorescence sensors and the analytes need to be clarified to understand the important factors that lead to high sensitivity and good selectivity. This study also investigated the computational simulation where the interaction strength, orientation and the position of the involved molecules were predicted by solving certain mathematical equations. These computational techniques are important in predicting the feasibility of the sensor to interact with the analytes by investigating the bonding between them.

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