Contamination of water bodies with organic and inorganic compounds caused by anthropogenic activities are a greater threat to safe potable water. Nitrate contaminants are a problem in water that are caused by leaching of the nitrate from sources like nitrate based fertilizers used in agricultural lands, improper sewage treatment facilities, by-products of industrial production of saccharin, caffeine, pharmaceuticals, decaying plants and animal residues in soil into water bodies. The nitrate content in water is measured as nitrate-nitrogen (NO$_3^−$-N). Long term safe permissible limit for nitrate (as NO$_3^−$-N) in water as suggested by environmental protection agency (EPA) is < 10 ppm and < 11 ppm by world health organization (WHO). In addition, nitrate gets converted to nitrite and in combination with amines or amides will become highly carcinogenic in nature. The drinking water sources near to the agricultural lands are more prone to nitrate contamination is found to be 10–110 ppm. In some rural areas, where agriculture and livestock are part of their daily activity, many of the wells dug up have found to be contaminated with 340 ppm NO$_3^−$-N concentration.

When concentration exceeds 11 ppm, potable water will become the major source of total nitrate intake. Hence it is imperative and practically useful to detect nitrate ion concentration range of 11–22 ppm in potable water instead of low 0.02 to 0.22 ppm which many detection techniques reports. Spectrometric and electrochemical methods are common platforms for determination of ions in water. The Central Pollution Control Board in India has set guideline to monitor the pollutant in surface and ground water in Indian states. Two methods are followed. For drinking water that is free from most of the organic contaminants UV Spectrophotometric method is followed. Here the nitrate is determined by measuring the absorbance at 220 nm. This method can determine upto 0.04 ppm NO$_3^−$-N. The possible interferents suggested are dissolved organic matter, nitrogen, hexavalent chromium and surfactants. Another method is for waste water - Phenol disulphonic acid (PDA) method. In this method, nitrate reacts with phenol disulphonic acid and produces a nitro-derivative and develops yellow color detected using a spectrometric method. The color of water is common problem encountered for spectrometric method. Hence water would be treated with aluminum hydroxide. The Standard Methods for the Examination of Water and Wastewater provide techniques for nitrate detection. Some of them are ultraviolet spectrophotometric screening method, the nitrate electrode method, the cadmium reduction method, cadmium reduction flow injection method, and ion chromatography method. Methods of detection, which rely on color change such as colorimetry, cannot be used where water test sample and the reaction product color developed are same. Electrochemical methods are used for detection of nitrate and nitrates because of their high sensitivity and selectivity. Nitrate selective electrodes that can determine the concentration of nitrate are commercially available. New ionophores are designed to increase the selectivity for binding with the nitrates. The freezing or drying up (>40 °C) of the electrolyte and leakage of the electrolyte is commonly observed issues in electrochemical sensors. In addition another challenge is that these electrodes must remain moist all the time and have to be recalibrated using standard solutions before every use.

The sensing materials used for detection of nitrate available in literature include conducting polymer, copper, biosensors, denitrifying bacteria, carbon nanotubes, nanotdots, graphene, graphene oxide, silver nanoparticles, and thiourea. The use of conjugated polymers for sensing application has gained lot of interests in recent years. The conjugation on the backbone can further amplify the response. In the present work, a conducting polymer for detection of nitrate has been designed and synthesized. A proof of concept demonstrating that designing a new conducting polymer molecule for nitrate ion detection and using them as sensing element in simple sensor architecture is presented. A new polymer poly [N'-{(4(dodecyl(phenyl)amino)benzylidene)-dithiocarbohydrazone} -poly (DATC)] is designed and synthesized which forms a complex due to specifically interacting with nitrate ions. Molecules such as thiourea and urea can bind to nitrates. Computational studies on azophenol thiourea based molecules have also been shown to exhibit an affinity for dihydrogen phosphate, acetate, fluoride, and nitrate ions. The number and distribution of thiourea moiety in the backbone of a macrocyclic receptor dictates the binding activity of nitrate and bromide ions. The size of the cavity formed by the host molecule also plays a role in specificity by capturing specific ion of the same size as that of cavity and excluding other larger ions. A macrocycle with thiourea as hydrogen bond donor was designed by Herges et al. had 2.79 Å by theoretical calculations. The size of nitrate ion is 2.06 Å had good affinity toward molecule. The bromide ion which has same size as
nitrate also showed response. The ions such as fluoride and chloride were too small and iodide was large to fit in the cavity. Cyclic and linear bis-thiourea compounds as ionophores in polymer membrane ion-selective electrodes were evaluated by Amanda et al.\textsuperscript{48} The special arrangement of the cyclic bis thiourea moiety in the compound is such that the hydrogen atom of thiourea is available for hydrogen bonding with the nitrate ion. A heteroditopic macrocyclic containing amide receptor was used for nitrate ion detection by \textsuperscript{1}H NMR technique.\textsuperscript{49} The receptor exhibited a high association constant $\sim$280 M$^{-1}$ for nitrate ion than acetate, dihydrogen phosphate or halide ions. Hence thiourea group has been incorporated into the backbone of the designed poly (DATC) polymer. In addition, the polymer backbone has conjugation that is necessary for conductivity. The nitrate ion would bind to thiourea group on the backbone of the polymer by hydrogen bonding, which consequently would trigger a change in conductivity of the sensing film. The addition of carbonaceous fillers such as carbon black and carbon nanotube have known to decrease resistance, increase sensitivity and response of sensors in addition by changing the percolation characteristics.\textsuperscript{47} Here the polymer is mixed with multi-walled carbon nanotubes (MWCNT) to increase the conductivity as well as the physical robustness of the sensor film. The polymer-MWCNT nanocomposite solution is cast as sensing film over the electrodes on a printed circuit board. The resistance of the sensor is monitored in air, in water (at pH 7) and in various concentrations of nitrate ions. The fabricated sensor shows fast response to nitrate ions in water. The interaction of nitrate ion with the thiourea moiety on poly (DATC) is elucidated with DFT and TD-DFT simulations in addition using UV visible spectroscopic technique and dynamic light scattering measurements.

Experimental

Materials.—Poly (N’-(4-(dodecyl(phenyl)amino)benzylidene)-dithiocarbonylhydrazone) - poly (DATC) and multiwalled carbon nanotube (MWCNT) are synthesized in lab. The synthesis of poly (DATC) is given elsewhere.\textsuperscript{48,49} The structure of poly (DATC) is shown in Figure 1a. Dimethyl propylene urea (DMPU) (puriss for synthesis) is obtained from Spectrochem Pvt. Ltd. Reagent grade potassium salts of nitrate, nitrite, fluoride, chloride, dihydrogen phosphate, carbonate, sodium nitrate and calcium nitrate are used as received. All solutions are prepared using de-ionized (DI) water with a resistivity of $\sim$18 M$\Omega$ cm. The pH of solutions is maintained at $\sim$7 using buffer tablets obtained from Merck Life Science Private Limited.

Detection using nitrate ion selective electrode.—The $\text{NO}_3^-$-N concentration of analyte used for testing polymer nanocomposite sensor is also tested using a Nitrate ion selective electrode (Thermo Fisher scientific) with Orion VersaStar Pro (Thermoscientific) multiparameter analyzer. This is an electrochemical method. Nitrate standard solutions (Nitrate as Nitrogen standard, Orion ionplus Application solution) is used to calibrate the electrode. The nitrate electrode is soaked in 100 ppm nitrate standard for overnight. Serial dilution of $\text{NO}_3^-$-N standard of concentration 100 ppm is carried out to obtain 10, 1 and 0.1 ppm. Nitrate ion strength adjuster (Nitrate ISA, Orion ionplus Application solution) is added in the ratio as mentioned by the supplier manual. The calibration of electrode is carried out at 25 C. The analyte for testing is prepared in the same manner as mention in Sensor fabrication and data collection from the sensor. Nitrate ion strength adjuster added to the analyte. The concentration of the analyte is measured by the nitrate electrode.

Sensor fabrication and data collection from the sensor.—10 wt% of poly (DATC)-MWCNT (9.4:0.6 wt%) is prepared in DMPU solvent. Poly (DATC) is first sonicated in DMPU for $\sim$4 min. MWCNT is added to this solution and sonicated for $\sim$30 min to get poly (DATC)-MWCNT stock solution. 4 $\mu$L of the solution is drop cast between two electrodes separated by a gap of 1 mm with an effective sensor film area of 0.6 cm$^2$. The films are dried in oven for $\sim$2 h at 70 C. The final sensor device is shown in the Figure. 1b. The sensor is connected to a data acquisition system (Model 7700 differential multiplexer with 20 channels connected to model 2700 multimeter/data acquisition (DMM), Keithley Instruments Inc.). The sensor is dipped in a 100 ml glass beaker containing DI water. The base resistance ($R_b$) is measured in DI water for 15 min. The sensor is withdrawn from de-ionized water and immediately dipped in 100 ml of water containing ions in another glass beaker. During withdrawal of DI water container and introduction of water with ions, the measurement of the sensor resistance is continued. A decrease in the resistance of the sensor is observed on introducing the water containing ions. The change in resistance is the response of the sensor. Thus, the change in resistance of the sensor is monitored. Figure. 1c shows the schematic of the sensor testing for nitrate ion in water.
Polymer characterizations.—Morphology of the film is studied by FEG scanning electron microscope Ultra 55, Zeiss. UV-Vis spectrum is recorded using Perkin Elmer - Lambda35 UV-Visible spectrophotometer. Dynamic light scattering (DLS) measurements are carried out using DynaPro MS 800 (Proterion, Protein solutions, Wyatt Technology, Santa Barbara, CA, USA).

Computational studies.—Density functional theory (DFT) calculations are executed to determine the electronic structures of the poly (DATC) for two repeating units. Ground states of poly (DATC) were optimized using density functional theory with hybrid functional B3LYP and 6–31G(d,p) basis sets in tetrahydrofuran (THF) solvent using the PCM (Polarisable Continuum Model). Time-dependent density functional theory (TD-DFT) calculations are carried out on the molecule to obtain calculated UV-Visible spectrum. The calculated UV-Visible spectrum is fitted with Gaussian fit for 2 peaks. The frontier molecular orbitals are visualized using Avogadro software.50,51

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Table I. Calculated contribution from various molecular orbital energy levels.

| Excited state | Energy (eV) | Wavelength (nm) | Oscillator strength | Percentage contributions |
|---------------|-------------|-----------------|--------------------|--------------------------|
| 1             | 3.12        | 397.35          | 1.04               | H-1→L (12%), H→L (26%), H→L+1 (58%) |
| 2             | 3.22        | 384.58          | 0.20               | H-2→L (43%), H-1→L (41%) H-2→L+1 (33%), H-2→L+2 (3%) H→L (6%) |
| 3             | 3.27        | 379.47          | 0.36               | H-2→L (22%), H-1→L (35%), H→L (10%), H→L+1 (26%) H-2→L+1 (2%) |
| 4             | 3.31        | 374.98          | 0.07               | H-2→L (12%), H-2→L+1 (11%), H→L (51%), H→L+1 (11%) H→L (7%) |
| 5             | 3.38        | 366.95          | 0.01               | H-2→L (16%), H-2→L+1 (61%) H-2→L+3 (9%), H→L+7 (2%), H-1→L+1 (3%), H→L (3%) |

Results and Discussion

Design of conjugated polymer for nitrate sensor.—Conjugated polymer designed for nitrate detection in the present work is poly [N’-(4-(dodecyl(phenyl)amino)benzylidene)-dithiocarbohydrazone] - poly (DATC) has thiourea group in the backbone of the polymer (Figure 1a). The repeating unit of poly (DATC) consists of phenylaniline and thiourea unit as shown in Figure 1a. The molecular orbitals energy levels of the poly (DATC) were determined by DFT calculations. To simplify the simulation, two repeat units to represent the polymer poly (DATC), and the alkyl chains were replaced with methyl groups. Figure 1d shows optimized structure of poly (DATC) molecule in tetrahydrofuran. The highest occupied molecular orbital (HOMO) (−5.44 eV) and lowest unoccupied molecular orbital (LUMO) (−1.89 eV) are located on phenylaniline units and thiourea moiety with a bandgap of 3.55 eV from simulations (Figure 2a). Figure 2b shows the UV-Visible spectrum from experiment and simulations. The experimental UV-Vis absorption spectrum of poly (DATC) in tetrahydrofuran (THF) shows a maximum absorption peak at ~380 nm and a shoulder at ~322 nm. 60 excited energies and oscillatory strengths were calculated and Table I presents the calculated first 5 singlet excitations. The first singlet absorption transition is at 397 nm with oscillator strength 1.04. The electronic transition is dominated by HOMO→LUMO+1 transition. Careful analysis of the frontier molecular orbital distribution diagrams, the molecular orbitals gives a clear picture of the moieties that are involved in the transition. The electron density in HOMO and HOMO-1 is located on both phenylaniline (π) and sulfur in thiourea (lone pair electron). The electron density on LUMO is extended over entire phenylaniline units and thiourea mostly on the π bonds. This molecular orbital involved in transition are shown in Figure 2a. Hence the absorption at 397 nm arises because of π and n electron transition.

Geometric shape matching of the analyte ion and host molecule in addition to the requirement of Lewis acid and hydrogen bonding functionalities in host molecule are the techniques used here.54 The nitrate ion has a trigonal planar structure with a bond angle of 120° (O-N-O).55 The negative charge is distributed evenly over the 3 oxygen atoms (Figure 1e). Anions such as chloride, nitrate, and hydrogen sulfate are weak bases and interact with receptor mainly through hydrogen bonds.56 The molecules with N-H groups such as pyrrole, urea, guanidium and thiourea when present on the backbone...
of the polymer will help in binding to nitrates. These molecules are good hydrogen bond donors and also have planar structure.\textsuperscript{57,58} Hence geometrically the nitrates can bind to these moieties when incorporated in the polymer backbone.\textsuperscript{42} Most of the thiourea and urea based receptors designed for anion recognition are reported to be suitable receptors for dihydrogen phosphate, acetate ions. It has been shown that when any other molecule is coupled to thiourea or urea moiety, the resulting effect of interaction with nitrate depends on the nature of the coupling molecule.\textsuperscript{40–42,58,59}

Phenyl aniline molecule has been used in detection of nitrate ion.\textsuperscript{60–62} In this study, phenylaniline moiety is coupled to thiourea. Phenylaniline-thiourea forms a neutral receptor molecule which is capable of hydrogen bonding with nitrate ion. Furthermore, polymerization increases the number of binding sites in addition to increase in conjugation along the backbone to signal the binding event.

Resistor architecture devices are fabricated as explained in experimental Sensor fabrication and data collection from the sensor section is shown in the Figure 1b. The sensing element here is dry film form of synthesized conjugated polymer containing thiourea functional moiety that can specifically interact with nitrate ion in water.

**Optimization of the response.—** Poly (DATC) film exhibited a resistance of 500–2500 k\(\Omega\) (is median from box plot) as seen from Figure 3a. The variation in resistance is due to the 1 mm gap between the electrodes and due thickness of film as the processing is by drop cast method. The current density is almost same for all sensors with resistance 500 and 2500 k\(\Omega\) calculated. For example, resistance \(R_1 = 2.70 \times 10^6\ \Omega\), current density \(J_1 = 4.93 \mu\text{A/cm}^2\) and \(R_2 = 4.12 \times 10^7\ \Omega\), \(J_2 = 3.24 \mu\text{A/cm}^2\). This shows that resistance varies as thickness of film and the inherent electronic property of the materials is consistent. From these results, it appears that control over the fabrication process is more critical. The nitrate ion would bind to thiourea group on the backbone of poly (DATC) by hydrogen bonding, which consequently would trigger a change in conductivity of the sensing film (Figure 3b). This event indicates the binding and sensing of nitrate ion. However, the base resistance of the neat polymer is very high (2000 k\(\Omega\)). The resistance of solid state sensors should be lower for practical measurement purposes. To obtain a lower resistance of \(\sim 150–250\ k\Omega\), multi-walled carbon nanotubes (MWCNTs) were blended with the polymer at percolation of \(\sim 6\%\) to observe the sensor response mostly due to poly (DATC).\textsuperscript{53} The comparison of resistance values and response to nitrate ion of poly (DATC) film and poly (DATC)-MWCNT nanocomposite film is shown in Figure 3a and Figure 3b. The poly (DATC)-MWCNT sensor is fabricated and used for all measurements, care is taken so that the resistances of all sensing films are in the same range. However, the agglomeration of MWCNT and the film thickness will cause change in percolation path and hence change in resistance. The morphology of poly (DATC)-MWCNT film is examined using scanning electron microscopy. The image in Figures 3c and 3d shows morphology and distribution of MWCNT in the polymer matrix.

**Stability of baseline resistance of sensor.—** Poly (DATC) is a conducting polymer based sensor. Conjugated molecules are prone to degradation. To minimize degradation and achieve stability of base resistance, the fabrication of thin films is carried out by maintaining uniform distribution of MWCNT, same size (area) and thickness of film. This will enable to obtain consistent, repeatable quality of film and hence stability of base resistance. In present work, the drop cast method is used as it is a simple technique. Care has been taken to maintain constant resistance of the sensors by maintaining the size and amount of solution drop cast on the area same every time. The base resistance of the sensors is measured over a period as shown in Figure 4. The data is analyzed using statistical method ANOVA and represented using graphical method, analysis of mean (ANOM). The

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**Figure 3.** (a) Base resistance distribution of poly (DATC) and poly (DATC)-MWCNT composite (b) The response of poly (DATC) and poly (DATC)-MWCNT for 14000 ppm. (c) and (d) Morphology of the composite film.
mean of base resistances of devices fabricated over a period of 20 months are compared. It can be observed that the base resistance of sensor is stable about a mean resistance of 83 kΩ of all sensors. All the resistance of the sensors lies within the two limits 42.7 and 123.7 kΩ. For significance level $\alpha = 0.05$. The mean of resistance lie between the two limits 60.3 kΩ and 106.1 kΩ. The difference between mean of resistance of all sensors are statistically insignificant suggesting the stability of the sensor.

**Working of the sensor.**—The resistance of polymer nanocomposite sensor decreases on binding with nitrate ion in water. The binding of nitrate ion to the polymer will push the polymer chains apart resulting in a bridge between adjacent polymer chains. The increase in the size of nitrate-polymer complex is observed as seen later in DLS measurements. The nitrate ion would facilitate the transfer of charges between the polymer molecules. This would enable the charge transportation through the polymer film others being through the conjugated along the backbone and intramolecular hopping. Poly (DATC) is a new conjugated polymer. Hence this could be the reason for the decrease in resistance.

The sensor response monitored is shown in Figure 3b. The relative change in resistance is calculated using Equation 1

$$\text{Response} (%) = \frac{R_o - R_i}{R_o} \times 100$$  \[1\]

$R_o$ is the value of the sensor resistance in DI water and $R_i$ is the sensor resistance in presence of each anion in DI water. To demonstrate the change in resistance of the sensor to various concentration of nitrate ions, the response $R_p$ of the sensor at a maximum value of resistance is taken which is denoted as $R_p$ ($i = p$).

**Response to low concentrations of nitrate ions.**—The performance of polymer nanocomposite sensor for various concentrations in DI water (pH 7) is evaluated. The response of the sensor is tested for 14–14000 ppm NO$_3^-$ -N in water. The sensor response increases with increasing concentration of nitrate ion indicates the binding of nitrate ion as shown in Figure 5a.

**Reproducibility of sensor to various concentration of nitrate ions.**—Figure 5b demonstrates the reproducibility of the sensor. Reproducibility, here, is defined as the same response of the sensor obtained for several sensors with same sensing element. To obtain reproducible sensor response the distribution of the MWCNT in the nanocomposite and thickness of the sensing film is maintained same. This is achieved by monitoring the time of mixing and dispensing same quantity of polymer nanocomposite solution in a defined area. The sensor used for testing for 14000 ppm is different from sensor used for testing 1400 ppm and so on. Different sensors were used for

![Figure 4. Stability of polymer nanocomposite sensor.](image)

![Figure 5. (a) The response to various concentrations of nitrate ions. (b) Reproducibility of the sensors. (c) Calibration curve of the sensor. Inset gives the response for all the concentrations. (d) Repeatability and reuse of the sensor.](image)
testing different concentration but the $R_o$ resistance of these were in range 150–250 kΩ (is median from box plot shown in Figure 3a). The reason for using different sensors for testing is because the residual ions in the sensor may affect the response due to another concentration. This has been carried out throughout the measurements.

Calibration curve for polymer nanocomposite sensor.—The calibration curve of the sensor is plotted and is shown in Figure 5c. The inset of the plot shows the calibration curve from 14–14000 ppm. It can be observed that in the concentration range 14–1400 ppm, the response follows a linear equation with co-efficient of regression $R^2 = 0.998 \pm 0.01$. The sensitivity of the sensor is 0.03059/ ppm. The response to the lowest concentration measured that could be discernible by this method is $\sim 14$ ppm NO$_3^-$. This is lower limit of detection by this method. This may not be the limit of detection of the material.

Repeatability and reuse of sensor.—Figure 5d demonstrates reuse and repeatability of the sensor for various concentrations of nitrate ions. For same concentration (1400 ppm). Here same sensor is tested for 140 ppm, 1400 ppm and 14000 ppm. The first response—shown in inset—is for 140 ppm. The second and third response is for 1400 ppm (2 cycles). The fourth is response for 14000 ppm. It can be observed that for 14000 ppm, there is no recovery. This could be due to the hydrogen bonding of nitrate ions with the polymer and the redistribution of nanotubes that takes place after withdrawing the nitrate ion solution.

Response time.—The response time for all sensors for various concentrations is observed to be statistically same as shown in Figure 6a. The response to the analyte happens by 2 mechanisms i) by adsorption of the analyte by the interaction with sensing molecules and ii) these adsorbed molecules physically push and disturb the alignment of the molecules consequently changing the charge percolation pathway thereby contributing toward the response. Due to this percolation pathway inconsistency, response time differs.

Cross-sensitivity of the poly (DATC)-MWCNT sensor to various ions.—The response of polymer nanocomposite sensor for various anions and cations is determined. The response of the sensor to nitrate ion in presence of interfering ion is also determined.

Anions.—Urea, calcium ammonium nitrate, and nitrate fertilizers provide nitrogen to plants, is a direct source of nitrates that would leach into water from the soil. Refuse runoff also contributes to the nitrate contamination in water. The other sources of nitrates are the decaying plants and animals produce ammonia which during nitrogen cycle is converted to nitrite and nitrate. Nitrite is more toxic than nitrate. Hence polymer nanocomposite sensor is tested to detect the presence of nitrite and ammonia along with nitrate. The sensor is also tested for other anions like fluoride, chloride, nitrite, carbonate and phosphate ions for understanding the interference effect. Figure 6b shows the response of the sensor to 1 molar potassium nitrate, potassium nitrite, ammonia, potassium fluoride, potassium chloride, potassium carbonate, potassium dihydrogen phosphate. The measurements were carried out at higher concentration because if there is no interference at higher concentration, then there cannot be any interaction at lower concentration. Figure 6c shows a box plot of maximum change in resistance of the sensors for various anions. The maximum response is observed for fluoride ions and lowest response for dihydrogen phosphate ions. The sensor interacts with all the ions but the interaction with nitrate and fluoride is predominant. This statistical difference between the response could be used by an external data.
would be a hard acid. The preferential binding of the anions to host molecule containing fluoride compounds such as fluorite (CaF2), the solubility of ammonia present in water is reduced to nitrite and then to nitrate in all pH.75 The increase in the concentration of nitrate occurs when fluoride could higher and enough to overcome the Gibbs free energy of ions. The higher the Gibbs free energy, stronger is the hydration. The anions in this study are hard bases. Hydrogen bonding molecules are borderline hard acids. Poly (DATC) is hydrogen bonding molecule and hence hard acid. The preferential binding of the anions to host molecule would be $\mathrm{F}^-$, $\mathrm{Cl}^-$, $\mathrm{PO_4}^{3-}$, $\mathrm{CO_3}^{2-}$, $\mathrm{NO_3}^-$, $\mathrm{NH_3}$, $\mathrm{NO_2}^-$. Table II gives the absolute hardness and softness values for the anions obtained from literature70 and calculated value for poly (DATC).

The interaction of various ions with polymer is explained using Pearson hard acid and soft base theory.69 According to the theory hard acids preferably bind to hard bases to form ionic complexes and soft acids to soft bases to form covalent complexes. This theory can explain the complex formation by ions with host molecules.66–69 The anions in the literature70 and calculated value for poly (DATC).

Table II. Ionic size and absolute hardness values for anions and poly (DATC).

| Anion/polymer | Ionic radius (nm) | Absolute hardness(a) (eV) | Softness(b) (eV) |
|---------------|------------------|----------------------------|-----------------|
| Fluoride      | 0.133            | 7                          | 0.14            |
| Chloride      | 0.181            | 4.7                        | 0.21            |
| Nitrite       | 0.192            | 4.5                        | 0.22            |
| Ammonia       | 0.148            | 6.9                        | 0.14            |
| Poly (DATC)   | 1.77             | 0.56                       |                 |

(a)70 (b)72 (c) Hardness $\eta = [\mathrm{LUMO-HOMO}] / 2$ Softness $\sigma = 1/\eta$.

The SNR = ($R_o$ - $R_p$) / (standard deviation of baseline taken over 1000 point) [2]

The SNR of the sensor for all ions is higher $S/N > 3$. This shows that the sensor response signal is large than the noise in the base resistance. The SNR for fluoride and nitrate ions is higher compared to the other anions as seen from Figure 6d. The large SNR for sensor signal to fluoride and nitrate indicates the clear selective response to fluoride and nitrate ions.

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Banaaski et al.71 have reported the transport of fluoride and nitrate in water and have compared the hydration radius of fluoride and nitrate ions. The hydration radius of fluoride is lower than for nitrate.72 The fluoride ion will be strongly hydrated than the nitrate molecules. The strength of hydration is quantified by Gibbs free energy of ions. The higher the Gibbs free energy, stronger is the hydration. In other words, fluoride ion is more strongly bound to water molecules than nitrate ion.72 Nitrate ion can easily move around in water (7.4 x 10^{-8} m^2/s) compared to fluoride ion (5.7 x 10^{-8} m^2/s).71 In our study, it is observed that poly (DATC) molecules attract fluoride ions higher than nitrate ions. The interaction energy of poly (DATC)-fluoride could higher and enough to overcome the Gibbs free energy of fluoride-water. Fluoride is highly electronegative and has higher possibility of formation for hydrogen bonding, and hence the apparent more interaction of polymer sensor in present work is with fluoride ion.

The regions where nitrate is present excess in groundwater, have agricultural activities. Anthropogenic sources contamination of water with fluoride occur in small amounts. Fluoride contamination of water sources along with nitrate in water is not observed frequently and has no correlation between concentration of nitrate and fluoride in water.73,74 An inorganic compound of fluoride dissociates into cation and nitrate and remains same without change in the state of ion at all pH.75 The increase in the concentration of nitrate occurs when ammonia present in water is reduced to nitrite and then to nitrate in presence of microorganisms. This occurs in the pH 6.5 to 8.5.76 In case of fluoride, an inorganic compound of fluoride on dissolving in water increase the alkalinity to be of pH 7–8.77 The geological rock containing fluoride compounds such as fluoride (CaF2), the solubility of fluoride occurs in higher alkalinity conditions 7.5 to 8.5. It is observed that fluoride contaminated water is highly alkaline. In low pH conditions, fluoride does not exist as ion, whereas nitrate can. Hence both nitrate and fluoride ion occur at the same place in very few cases. Though polymer sensor in the present work, sensor can sense both fluoride and nitrate, the sensor can be used as nitrate sensor alone in most of the places.

Cations.—The sensor response for potassium, calcium and sodium ions, is monitored (Figure 7a). Nitrate salts potassium, calcium, and sodium, is dissolved in water (pH 7). It could be observed from Figure 7b that the percent change in resistance of the sensor for sodium, potassium and calcium cations is almost same and varies between 60 and 75 percent change in resistance. This shows that the presence of cation-sodium, potassium and calcium along with nitrate ion does not alter the sensor response to nitrate.

Response for nitrate ion in presence of interfering ion.—The response of the sensor to 14000 ppm NO3^- –N in the presence of various ions is also determined (Figures 7c and 7d). On comparison of Figures 7c and 6c, it may be noted that the percent change in resistance of carbonate and dihydrogen phosphate has increased in the presence of nitrate ions. This could be because the nitrate ion would have occupied the sites that have not been occupied by the other ion and hence has contributed to increased response. The response of the sensor for mixture of two ions is because of two types of ion available at the binding site. Figure 7d shows that the response of the sensor to nitrate ion remains unaltered in presence of two types of cations.

Comparison of sensor response with nitrate ion selective electrode and current method available.—The response of polymer sensor is tested for nitrate ion concentration 14000–14 ppm. The same analyte is tested with a commercial nitrate ion selective electrode using a multiparameter analyser as mentioned in Detection using nitrate ion selective electrode section. The nitrate ion selective electrode is calibrated using Nitrate ion standards for 0.1, 1, 10, 100 ppm NO3^- –N. Figure 8 shows the comparison between the calculated and measure concentration of nitrate ions expressed as NO3^- –N. From the calibration curve, it is observed that from 0–1400 ppm the sensor follows linear relationship Equation 3

$$y = -0.0777 + 0.03059x$$

The nitrate ion solution of various concentration - 14, 140 and 1400 ppm of NO3^- –N is prepared by standard analytical method. The response of polymer sensor is collected (as mentioned in experimental Materials section). The actual concentration of the analyte is then calculated using calibration curve is given in Table III. The same solution is measured using nitrate ion selective electrode. From the Table III, it can be observed that the concentration of nitrate ion measured by the ion selective electrode and polymer sensor are in good agreement.

The present work detection limit and the materials used are compared with the current literature available for detection of nitrate ion in water (Table IV).

Sensing mechanism.—The interaction mechanism of nitrate ion with poly (DATC) is investigated using UV-Vis spectroscopy and dynamic light scattering techniques.

The UV-Vis spectrum of poly (DATC) in THF/water (50:50 v/v) in Figure 9a shows absorbance at 368 nm. The decrease in intensity of absorption peak at 368 nm is because of binding of nitrate ion of thiourea group. The UV-Visible transition at 368 nm involves of absorption peak at 368 nm is because of binding of nitrate ion. Figure 8 shows the comparison between the calculated and measure concentration of nitrate ions expressed as NO3^- –N. From the calibration curve, it is observed that from 0–1400 ppm the sensor follows linear relationship Equation 3

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Figure 7. (a) Response of sensor to cations with nitrate as anion (b) Reproducibility of the sensor response to cations. (c) Reproducibility of the sensor response to 1 molar nitrate ion in presence of 1 molar of other anions. (d) Reproducibility of the sensor in presence of two types of cations.

UV-Visible absorption spectrum for 14, 140, 1400, 14000 ppm of nitrate ion concentration in THF/water (50:50 v/v) is provided Figures 9b.

The hydrodynamic radius of poly (DATC) in absence and presence of nitrate ion is determined from dynamic light scattering (DLS) measurements (Figures 10a and 10b). Figure 10a shows a broad distribution in hydrodynamic size of the polymer in solution from 4 to 86 nm. The radius of poly (DATC) in obtained from simulation results indicated 3 to 10 nm (Figure 10c). The simulation results assume the polymer to be a single chain of 70 repeat units. Poly (DATC) has a medium polydispersity of 1.33 which suggests that, in the polymer, each chain has different lengths. The slightly higher molecular globule’s size observed in DLS measurements is attributed to the intertwined polymer chain in solution rather than separated chain. The hydrodynamic radius for poly (DATC) after interaction with nitrate ion is observed to increase to about 100–238 nm. This increase in size of the molecules suggests the complex formation of polymer with nitrate ions. The nitrate ion interacts with thiourea sites on polymer backbone. This interaction could also be between thiourea moieties and nitrate on the same chain or between various chains. The interaction will result in complex formation of nitrate ion with polymer. The proximity of all the chains which form this complex leads to increase in globule size which reflects in the increase in hydrodynamic radius. DLS results indicate that complex formation between thiourea moieties on poly (DATC) and nitrate ions.

Conclusions

In summary, a conducting polymer poly (DATC) is designed and synthesized, is used for detection of nitrate ion by chemiresistor architecture. The receptor for nitrate ion is chosen considering the geometric shape of analyte ion and receptor in addition to hydrogen bonding ability of receptor. The synthesized polymer has a strategically placed thiourea moiety which can bind to nitrate ion by hydrogen bonding. The base resistance stability of polymer sensor is studied and is observed that it is stable for more than 20 months. The polymer sensor has shown repeatable and reproducible behavior. The lower limit of detection of the sensor is observed to be \( \sim 14 \) ppm \( \text{NO}_3^- \) which is a more useful and practical detection range (11–22 ppm) in potable water. The sensor is tested for various interfering ions separately and mixture of ions. The sensor shows higher SNR to nitrate ions indicating that it is selective to nitrate ion. From the calibration
Table III. Comparison of present work with commercial ion selective electrode.

| Sensor Response (%) | Solution prepared according to analytical methods | Obtained from calibration curve of polymer sensor in this present work $y = -0.0777 + 0.03059x$ | Measured with multi-parameter analyzer using nitrate ion selective electrode |
|---------------------|--------------------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| 1.11 ± 0.4          | 14                                               | 39 ± 13                                                                         | 26                                                                            |
| 4.3 ± 1.4           | 140                                              | 143 ± 47                                                                         | 165                                                                          |
| 42.9 ± 6.5          | 1400                                             | 1406 ± 213                                                                       | 1627                                                                         |

Table IV. Comparison of methods of detection for nitrate ion and their detection limit.

| Method of detection | Material                                                      | Detection range (ppm) |
|---------------------|---------------------------------------------------------------|------------------------|
| Electrochemical method$^9$ | Ag@iron oxide nanocomposite powders                           | 0.42                   |
| Electrochemical method$^18$ | Copper nanostructures                                        | 0.008                  |
| Extended gate organic field effect transistor$^{20}$ | Nitrate reductase with bipyridinium derivative               | 0.01                   |
| Impedance spectroscopy$^{20}$ | PEDOT nanofibers and Graphene oxide                        | 0.1–100                |
| Electrochemical method (Ion selective electrode)$^{32}$ | Cyclic bis thiourea compound                           | 0.09                   |
| Electrochemical method$^{28}$ | Ag-doped zeolite-expanded graphite-epoxy composite electrode | 1.4–14                 |
| Electrochemical method$^{70}$ | Palladium-tin bimetallic composite                         | 0–11                   |
| Electrochemical method$^{69}$ | Silver                                                        | 0.045                  |
| Colorimetric detection$^{61}$ | p- dimethylaminocinnamaldehyde (p-DMAC) dispersed in poly(acrylamide) hydrogels | 0.45                   |
| Colorimetric method (Greiss test) Cayman chemical Nitrate/Nitrite Colorimetric assay | N-(1-naphthyl ethylenediamine (Greiss reagent 2) | 0.5                     |
| SUNA V2 UV Nitrate sensor$^{83}$ | UV lamp                                                     | 0.007 to 56             |
| UV Nitrate sensor YSI 701/705 IQ NitraVis UV/VIS Sensor$^{84}$ | UV-VIS spectral measurement (200–720 nm)                  | 0–68                    |
| Commercially available Electrochemical method (Ion selective electrodes)$^{85}$ | Nitrate ion selective ionophores                        | 0.1 ppm to 14,000 ppm   |
| Ion chromatography$^{66}$ | Conductivity of ions                                        | 0.0045 to 225           |
| Resistive method (present work) | Poly(DATC)-MWCNT                                          | 14–14000                |

Figure 9. Measured UV Vis spectra in THF/water (50:50 v/v) for various concentration nitrate ion of (a) with poly (DATC) (b) without poly (DATC).

Figure 10. Hydrodynamic size distribution of poly (DATC) by dynamic light scattering measurements and simulation. (a) measured polymer (b) measured poly (DATC)-nitrate ion complex and (c) simulation polymer.
curve, it is inferred that the sensor can detect up to ~14 ppm. The sensor performance is further compared with a nitrate selective electrode for real-world sample applications. The electronic property of poly (DATC) is calculated using density functional theory. The calculated UV-Visible spectrum agrees well with the experimentally observed absorption wavelength of 368 nm. Analysis of the calculated UV-Visible spectrum and molecular orbital diagrams provides insight to the molecular orbitals that are involved in the transition. The first excited state has major contribution HOMO levels to LUMO+1 level. The HOMO and HOMO-1 involve sulfur atom contribution for delocalization of electron. The absorption spectrum (experiment) of poly (DATC)-nitrate complex shows a decrease in absorbance at 368 nm on the addition of nitrate ions. This indicates the binding of nitrate to thiourea moiety. The dynamic light scattering experiments indicated the increase in the hydrodynamic size on the interaction of nitrate ion with poly (DATC) suggesting the polymer nitrate complex formation. This interaction has been shown to use as a sensor which detects practically useful concentration of nitrate in potable water.

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