International Journal of
Advances in Scientific Research and Engineering (ijasre)

E-ISSN : 2454-8006

DOI: http://doi.org/10.31695/IJASRE.2018.33004

Volume 4, Issue 12
December - 2018

Synthesis of Nitrate Doped Polypyrrole Conducting Polymer Membrane and Fabrication of Passive Sampler to Determine Diffusion of Nitrate and Chloride Through Membrane in Aquatic Ecosystem

S. Arasaretnam[1*], S. Keerthanan[2] and Hasitha Sulochani Wickramasinghe[3]

[1-3] Department of Chemistry
Eastern University, Sri Lanka
Chenkalady
Sri Lanka.

ABSTRACT

Nitrate is the most considerable substance in the hydrosphere and high concentration of nitrate can be harmful to the healthy life of creatures and human being. The removal of nitrate from the water is very essential. Therefore this study was focused to synthesis the nitrate doped polypyrrole polymer membrane (PPy-N) and the diffusion of nitrate in the presence of high chloride concentration through the membrane for samples obtained in 5th, 7th, 9th, 11th, 13th days in synthetic freshwater was also studied. Passive samplers have been developed in order to assess water quality over the period of time they have been deployed and also to simplify sampling and sample preparation processes. Nitrate doped polypyrrole film was synthesized through chemical polymerization process using Pyrrole and HNO_3*. The characterization of the membrane was performed by Fourier Transform Infrared Spectroscopy (FTIR). The amount of nitrate and chloride diffused through a nitrate doped polypyrrole films (*$PPy\text{-}N_1$*) were determined using cadmium reduction method and chloride ion selective electrode technique respectively. In order to improve the diffusion of nitrate through the membrane, the laboratory filter paper was used to prepare another nitrate doped polypyrrole films (*$PPy\text{-}N_2$*). The same techniques that used for* $PPy\text{-}N_1$ *were used to determine diffused nitrate and chloride through* $PPy\text{-}N_2$ *membrane. The results revealed that, membrane* $PPy\text{-}N_2$ *has exhibited 13.102 ± 0.469 %, 42.969 ± 5.107 %, 55.932 ± 1.579 %, 64.096 ± 2.171 %, and 77.826 ± 1.752 % diffusion of nitrate and 36.989 ± 3.177 %, 43.922 ± 1.823 %, 46.223 ± 0.817 %, 49.042 ± 0.908 %, and 49.679 ± 0.119 % diffusion of chloride through the membrane after 5 days, 7 days, 9 days, 11 days and 13 days respectively. Whereas membrane* $PPy\text{-}N_1$ *exhibited that 11.497 ± 0.715 %, 14.899 ± 1.431 %, 33.932 ± 0.469 %, 35.066 ± 0.592 %, and 42.917 ± 1.875 % diffusion of nitrate and 25.612 ± 1.683 %, 38.959 ± 1.201 %, 36.075 ± 2.151 %, 37.004 ± 2.989 %, and 38.495 ± 1.341 % diffusion of chloride after those days respectively.*

Keywords: *Passive sampler, Nitrate doped - Polypyrrole membrane, Nitrate, Chloride, Freshwater.*

---

1. INTRODUCTION

Nitrogen is one of the most abundant elements in the atmosphere and it is found in cells as a major component of proteins. Inorganic nitrogen exists in free N_2, nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+). Nitrate is important and commonly occurring nitrogen species in the environment. Nitrate ions are highly soluble in water, which cause animal wastes, fertilizers to wash off land and into rivers. Then rivers drain to the ocean or lakes and the high nitrate level affects the aquatic life of those ecosystems. High nitrate concentration effects on both human and animals as which cause methemoglobinemia or blue baby syndrome, gastric problems, urinary system problems and many health problems. The increased flux of nutrients has leads to eutrophication or increased production of plant organic carbons and growth rate of green algae increased on the surface water [2]. Because of its role in ecosystem dynamics and its impacts on human health, nitrate levels in water are regulated carefully and monitored. Use of passive sampler is interest because of cost saving and ability to collect samples over an extended period of time [7]. Doped polypyrrole films can be used as highly selective membranes in ion selective membrane material in potentiometric ion selective electrode fabrication [3].

There are several types of passive sampler have been constructed in order to monitor the water quality over the last 30 years [8]. Among these passive sampler, some types are commonly used in monitoring the quality of water such as semipermeable membrane devices [9], polar organic chemical integrative samplers [10], diffusion gradient in thin-films [11], and Chemcatcher samplers [12], Passive samplers which covering a wide range of inorganic and organic compounds (e.g. polycyclic aromatic hydrocarbons, herbicides, heavy metals) [13-14]. However, this work has been carried out to develop nitrate doped polypyrrol polymer membrane (PPy- N) sampler to monitor the diffusion of nitrate and chloride in freshwater.

In passive sampling technique it is diffusion induced by concentration gradient. Most passive sampling devices typically consist of a receiving phase separated from the aquatic environment by a diffusion membrane. For the fabrication of passive sampler to analysis nitrate in coastal and estuarine ecosystems, it is essential to concentrate nitrate using an effective nitrate selective membrane, due to the high chloride concentration [1]. The membrane can be defined essentially as a barrier which separates two phases and restricts transport of various chemicals in a selective manner. Transport through a membrane can be affected by convection or by diffusion of individual molecules [7].

Nitrate analysis can be done by cadmium reduction method or in order words colorimetric method using Griess reaction assay. In this method nitrate in the sample is reduced to nitrite by treating the sample with chemical reductant such as cadmium. Here cadmium is exposed to $CuSO_4$ solution and then Cu^{2+} is reduced on cadmium surface to form a porous metalic copper “coat”. The metalic copper layer has been shown to catalyze the reduction process of nitrate to nitrite. The copper layer facilities electron transfer from cadmium to nitrate. The overall reaction in a mild alkaline solution can be described as follows.

$$NO_3^- + H_2O + Cd \rightarrow NO_2^- + Cd^{2+} + 2OH^-$$

The nitrate formed is treated with diazotizing reagent like sulphanilamide (SA) in acidic media and then allowed to react with coupling reagents, N-napthyl-ethylenediamine (NED) to form a stable azo compound which is purple in colour. The absorbance of this adduct at 540 nm is linearly proportional to the nitrate concentration in the sample. [5]

This study aimed to determine nitrate concentration in the presence of high salt (Chloride) concentration and how the passive sample works and develops in laboratory and external environments.

2.MATERIALS AND METHODS

Analytical grade chemicals and reagents were used in this study. Pyrrole (AR grade) was distilled at 130 °C and stored at 4 °C. All solutions were prepared using deionized water.

2.1 Chemical polymerization of Pyrrole doped with Nitrate.

25 ml of 1 M Pyrrole solution was prepared in 1 M HNO_3 solution and the pH of the solution was brought to 1.0 using conc. HNO_3 acid. The temperature of solution was maintained at 0 °C and 25 ml of 0.5 M $(NH_4)_2S_2O_8$ solution was added drop wisely while stirring. The polymerization was carried out for a period of three hours. After that the solution was poured into two petri dishes about 2 mm of thickness and one petri dish was allowed to complete the polymerization reaction. A filter paper (Whatman® No 1, pore size 11 μm) was dipped into second petri dish. The two petri dished were allowed to stand for two days to form polymer membranes. After 2 days, the film that formed on the petri dishes was peeled off and was named as PPy- N_1 and PPy- N_2 respectively.

2.2 Passive sampling experiments.

The membranes were washed successively by methanol followed by distilled water to remove excess pyrrole monomers and other impurities. The synthesis was performed without agitation and in the minimum oxygen atmosphere. These membranes were dried at room temperature (32 °C). The membranes PPy- N_1 and PPy- N_2 were placed on the hole of sample bottles containing deionized water. The sample bottles with membranes were sealed using Teflon tapes. The bottles were dipped into the synthetic freshwater containing nitrate ions and chloride ions which were prepared by dissolving $NaNO_3$ and NaCl in deionized water. The sample bottles were taken out on 5th, 7th, 9th, 11th, 13th days and the solution in it was tested for nitrate and chloride ions to obtain the percentage of ions diffusion through the both membranes.

$$\text{Diffused \%} = \frac{\text{Amount of ion species } (NO_3^- \text{ or } Cl^-) \text{ in the sampler bottle after time period.}}{\text{Initial amount of ion species in outer solution}} \times 100\ \%$$

2.3 Nitrate analysis using cadmium reduction method.

Nitrate analysis was done as by standardization method by using cadmium reduction column as given below. [6] The pH of the sample was adjusted to between 8 and 9 with adding either conc. HCl or conc. NH_4OH. 75 ml of Ammonium chloride - EDTA

DOI: 10.31695/IJASRE.2018.33004

solution was added to 25.0 ml of sample and mixed. Sample was poured into column and collected sample at a rate of 7-10 ml per minute. The first 25 ml was discarded and the rest of the sample (approximately 70 ml) was collected in to the flask. In order to prevent the oxidation by air, the reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent (NED). 2.0 ml of color reagent was added to 50.0 ml of sample. It was Allowed 10 minutes for color development. The absorbance was measured within 2 hours at 540 nm against a reagent using UV-visible spectrophotometer. The two membranes (PPy- N_1 and PPy- N_2) were tested with two samples (sample 01 and sample 02). Percentage of Nitrate diffused through both PPy- N_1 and PPy- N_2 were calculated by using the calibration curve (Figure 2) and determined their efficiency.

2.4 Chloride analysis using chloride ion selective electrode

Chloride selective electrode was used for the following experiments.

1 ppm, 10 ppm, 100 ppm of standard chloride solution was prepared using NaCl. The Volta meter was adjusted to measured millivolts (mV). 100 ml of standard Chloride solutions (1 ppm) were measured in to a 150 ml beaker and 2 ml of Ionic Strength Adjustor (ISA) was added to it and stirred. Then the electrode was rinsed with distilled water and placed it in to the above solution. After a stable reading was obtained in mV value and the corresponding standard concentration was recorded. Then the electrode was rinsed with distilled water and placed it in to the second beaker which contains the second solution and then third solution. A calibration curve was prepared by plotting the mV value on the y-axis and the standard concentration value on the x-axis. Then, 100 ml of testing sample was measured in to a 150 ml beaker and 2 ml of ISA was added to it and stirred. Then the mV value was recorded as above techniques. Concentration of samples was determined by using the calibration curve (Figure 3).

2. RESULTS AND DISCUSSION

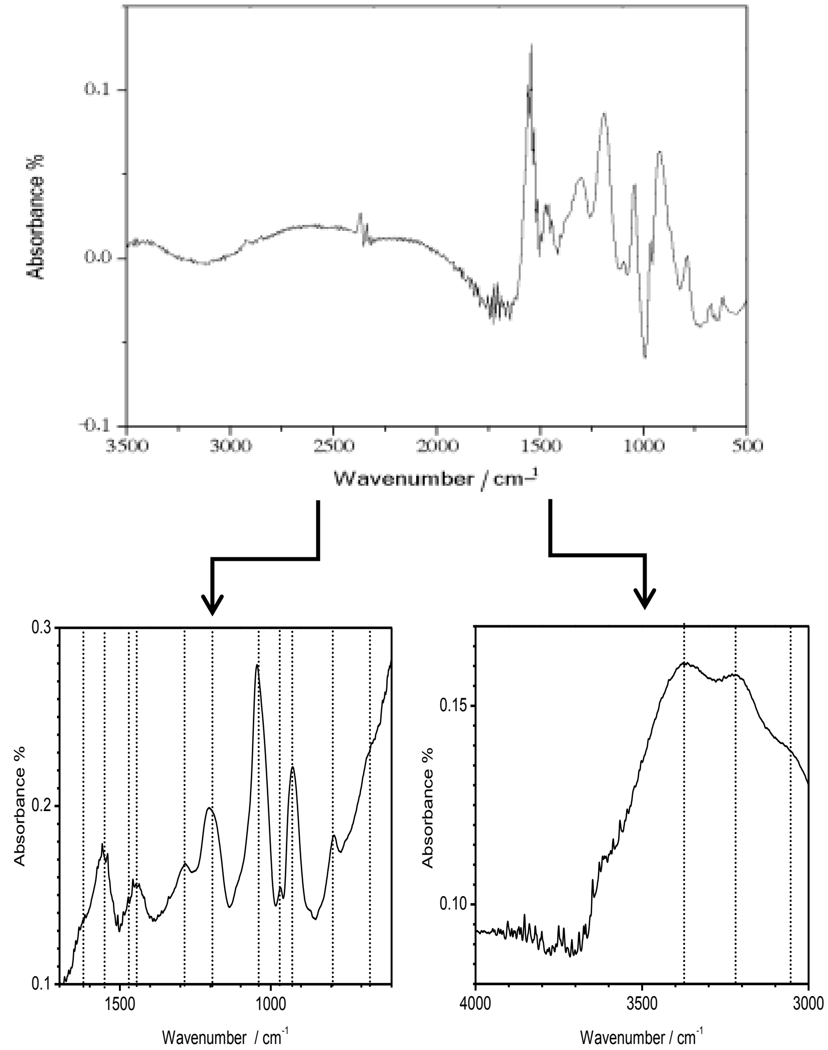

Figure 1: FTIR analysis spectrum of Polypyrrole.

In the above Figure.1 shows the FTIR spectra of Polypyrrole and the peaks at 811 cm^{-1}, 920 cm^{-1} are attributed to C-H wagging. The characteristic peaks at 1558 cm^{-1} and 1487 cm^{-1} correspond to the C=C stretching, whereas peaks at 1685 cm^{-1} and 1315 cm^{-1} represent to respectively, C=N and C-N bonds. The occurrence of small peaks at 3522 cm^{-1} is assigned to presence of N-H stretching vibrations. The peak observed in this study resembled with a previous reported work for conforming the formation of polypyrrole [4].

Absorbance of standard solutions of nitrate is plotted on the y-axis against their concentration on the x-axis as given below Figure 2.

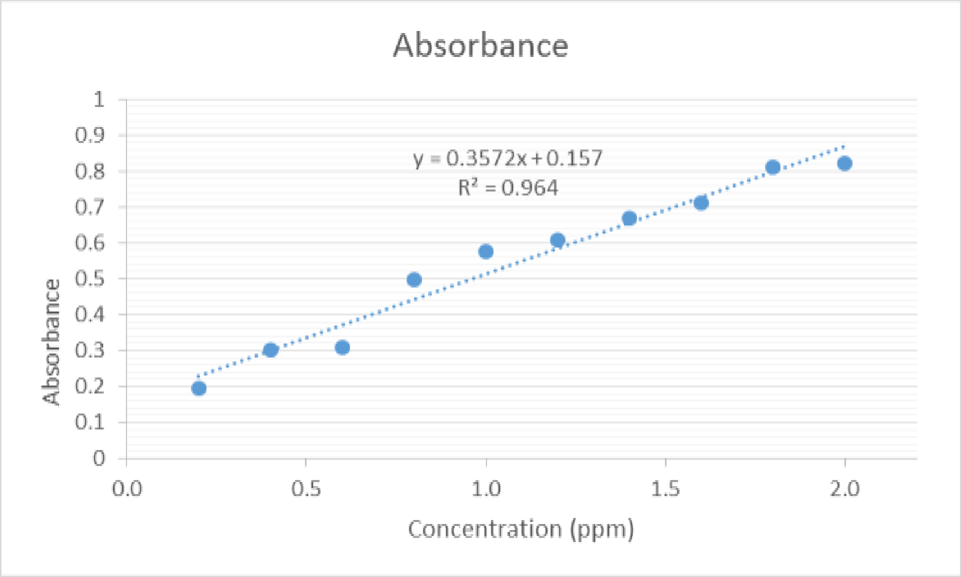

Figure 2: Calibration curve for nitrate analysis.

To determine Chloride concentration, a calibration curve was constructed. In calibration curve electrode potential of standard solutions are plotted on the y-axis against their concentration on the x-axis as given below Figure 3.

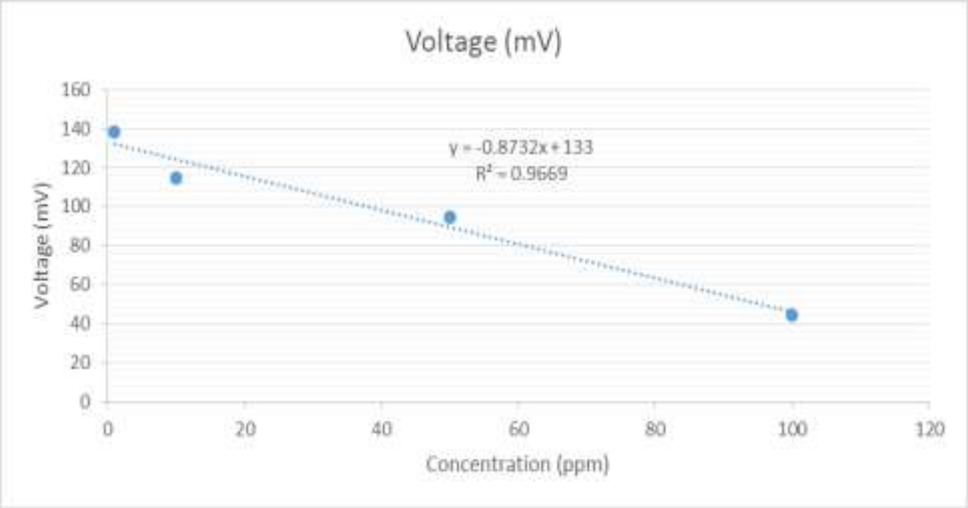

Figure 3: Calibration curve for chloride analysis.

According to the results obtained by chemical polymerization process, a thin dark brown color polymer film PPy- N_1 was formed on the surface of the solution which was difficult to peel off. When a filter paper was dipped in the solution to fabricate PPy- N_2, blackish brown color membrane was formed on the filter paper. The diffusion of nitrate and chloride through these both membranes (PPy- N_1 and PPy- N_2) were tested for sample 01 and sample 02.

Tabble 1: Percentages of diffused Nitrate through the both membranes (PPy- N_1 and PPy- N_2) from sample 01.

Percentages of diffused Nitrate through the membranes from sample 01					
diffused through PPy- N_1			diffused through PPy- N_2		
Days	$[NO_3^-]$ inner solution (ppm)	Diffused percentage (%)	Days	$[NO_3^-]$ inner solution (ppm)	Diffused percentage (%)
5	0.344	12.003	5	0.366	12.770
7	0.456	15.911	7	1.335	46.581
9	0.982	34.264	9	1.635	57.048
11	0.993	34.648	11	1.881	65.632
13	1.268	44.243	13	2.266	79.065

Concentration of nitrate ions outside the sampler bottles = 2.866 ppm.

Table 2: Percentages of diffused Nitrate through the both membranes (PPy- N_1 and PPy- N_2) from sample 02.

Percentages of diffused Nitrate through the membranes from sample 02					
diffused through PPy- N_1			diffused through PPy- N_2		
Days	$[NO_3^-]$ inner solution (ppm)	Diffused percentage (%)	Days	$[NO_3^-]$ inner solution (ppm)	Diffused percentage (%)
5	0.315	10.991	5	0.385	13.433
7	0.398	13.887	7	1.128	39.358
9	0.963	33.601	9	1.571	54.815
11	1.017	35.485	11	1.793	62.561
13	1.192	41.591	13	2.195	76.588

Concentration of nitrate ions outside the sampler bottles = 2.866 ppm.

Table 3: Percentages of diffused Chloride through the both membranes (PPy- N_1 and PPy- N_2) from sample 01.

Percentages of diffused Chloride through the membranes from sample 1					
diffused through PPy- N_1			diffused through PPy- N_2		
Days	$[Cl^-]$ inner solution (ppm)	Diffused percentage (%)	Days	$[Cl^-]$ inner solution (ppm)	Diffused percentage (%)
5	2.714	26.802	5	3.973	39.236
7	4.031	39.808	7	4.317	42.633
9	3.499	34.555	9	4.622	45.645
11	3.533	34.890	11	4.901	48.400
13	3.802	37.547	13	5.022	49.595

Concentration of chloride ions outside the sampler bottle = 10.126 ppm.

Table 4: Percentages of diffused Chloride through the both membranes (PPy- N_1 and PPy- N_2) from sample 02.

Percentages of diffused Chloride through the membranes from sample 2					
diffused through PPy- N_1			diffused through PPy- N_2		
Days	$[Cl^-]$ inner solution (ppm)	Diffused percentage (%)	Days	$[Cl^-]$ inner solution (ppm)	Diffused percentage (%)
5	2.473	24.422	5	3.518	34.742
7	3.859	38.110	7	4.578	45.210
9	3.807	37.596	9	4.739	46.800
11	3.961	39.117	11	5.031	49.684
13	3.994	39.443	13	5.039	49.763

Concentration of chloride ions outside the sampler bottle = 10.126 ppm.

DOI: 10.31695/IJASRE.2018.33004

The analyzed results concluded that the diffusion of nitrate and chloride through the both membranes were increased with time. It was taken nearly two weeks (13 days) to diffuse about 78 % of nitrate and about 50 % of chloride through the membrane PPy-N_2 and about 43 % of nitrate and about 39 % of chloride through the membrane PPy-N_1. The synthetic freshwater contains nitrate in 2.866 ppm and chloride in 10.126 ppm. Although the synthetic freshwater contains higher concentration of chloride than concentration of nitrate, the diffused percentages of nitrate through the both membrane PPy-N_1 and membrane PPy-N_2 were higher than diffused percentages of chloride. However, the diffusion of both nitrate and chloride through the membrane PPy-N_2 were higher than that of through the membrane PPy-N_1 hence the PPy-N_2 membrane was made up with using polypyrrol polymer and laboratory filter paper.

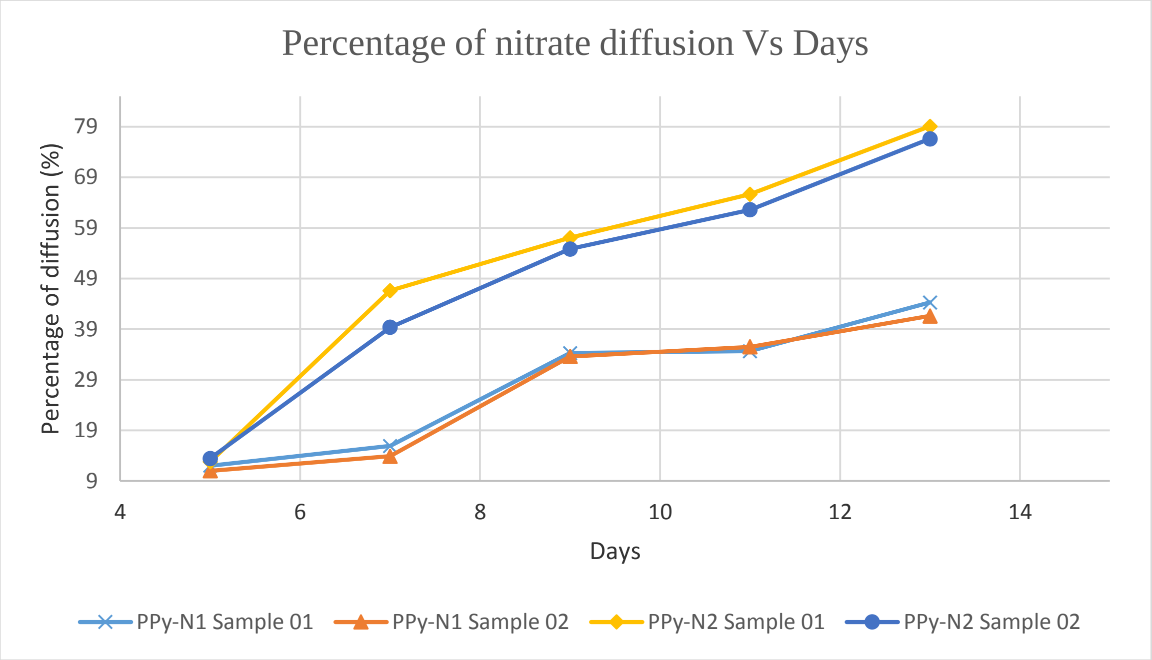

Figure 4: The diffused percentage of nitrate through both membranes with days.

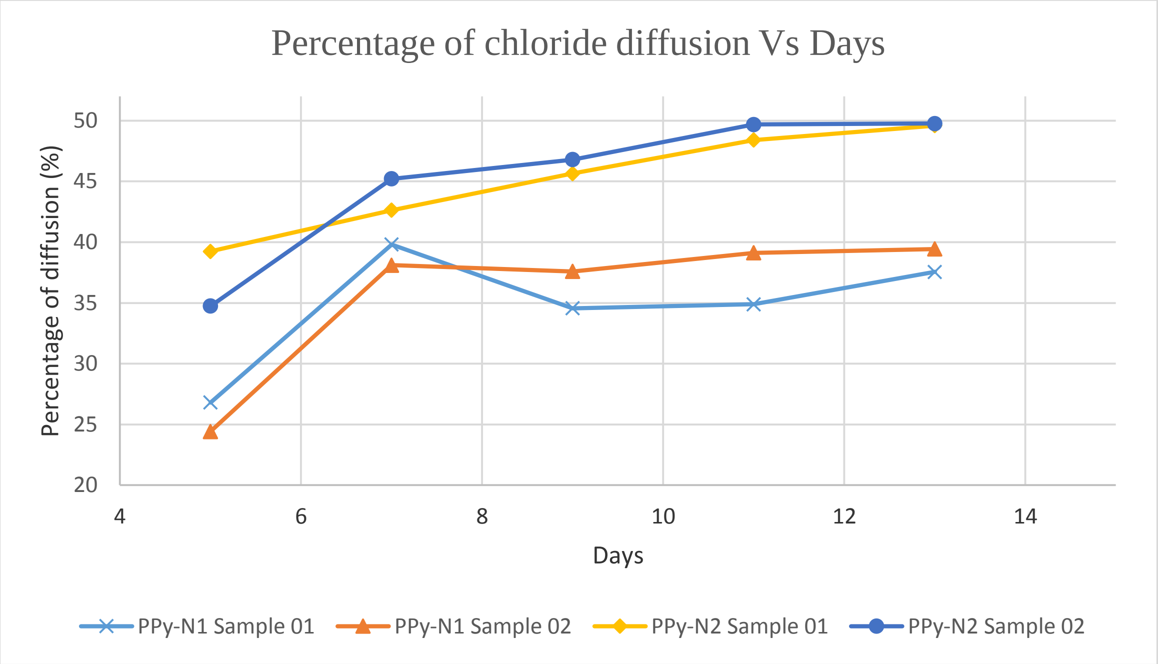

Figure 5: The diffused percentage of chloride through both membranes with days.

3. CONCLUSION

This studies can be done to synthesis a nitrate doped polypyrrole polymer membrane and tested how it allow to diffuse the nitrate and chloride through synthesized membrane to reduce the nitrate and chlorate level in aquatic environment. Based on the obtained

DOI: 10.31695/IJASRE.2018.33004

result, the PPy-N_2 membrane allowed to diffuse comparability high percentage of nitrate and chloride than PPy-N_1 membrane. PPy-N_2 polypyrrole polymer membrane could be recommended to reduce the nitrate and chloride level in aquatic system. Although significant amount of nitrate has diffused through PPy-N_2 even under high chloride concentration. It is difficult to handle these membranes as they are fragile. Passive samplers can be left unattended over long periods of time, help to avoid changes in the sample composition while transported to the laboratory and also to reduce analysis costs.

REFERENCES

[1] Adornato, L., Cardenas-Valencia, A., Kaltenbacher, E., Byrne, R. H., Daly, K., Larkin, K., and Garçon, V. C. (2009). In situ nutrient sensors for ocean observing systems. In *Proceedings of the Oceanobs' 09: Sustained Ocean observations and Information for Society Conference* (Vol. 2), 20.

[2] An alliance for coastal technologies. State of Technology in the development and Application of Nutrient Sensors, Savannah, Georgia, March 10-12, 2003.

[3] Bendikov, T. A., & Harmon, T. C. (2005). A sensitive nitrate ion-selective electrode from a pencil lead. An analytical laboratory experiment. *J. Chem. Educ*, *82*(3), 439.

[4] Manic, A, C., Shailesh,G, P., & Shashwati, S. (2011). Synthesis and characterization of polypyrrole (PPy) thin films. *Soft Nanoscience Letters*, *2011*.

[5] Official methods of analysis of the Association of Official Analytical Chemists (AOAC), 15th edition 1990..

[6] Ridnour, L. A., Sim, J. E., Hayward, M. A., Wink, D. A., Martin, S. M., Buettner, G. R., & Spitz, D. R. (2000). A spectrophotometric method for the direct detection and quantitation of nitric oxide, nitrite, and nitrate in cell culture media. *Analytical Biochemistry*, *281*(2), 223-229.

[7] Rivera, C. (2003). Performance of a passive sampler system for nitrate and phosphate monitoring. Chalmers University of Technology, Sweden.

[8] Vrana B, Mills GA, Allan IJ, Dominiak E, Svensson K, Knutsson J, et al. Passive sampling techniques for monitoring pollutants in water. *Trends Anal Chem*. 2005;24:845–68.

[9] Esteve-Turrillas FA, Yusa V, Pastor A, de la Guardia M. New perspectives in the use of semipermeable membrane devices as passive samplers. *Talanta*. 2008;74:443–57.

[10] Harman C, Allan IJ, Vermeirssen ELM. Calibration and use of the polar organic chemical integrative sampler—a critical review. *Environ Toxicol Chem*. 2012;31:2724–38.

[11] Davison W, Zhang H. Progress in understanding the use of diffusive gradients in thin films (DGT) back to basics. *Environ Chem*. 2012;9:1–13.

[12] Ahkola H, Herve S, Knuutinen J. Overview of passive Chemcatcher sampling with SPE pretreatment suitable for the analysis of NPEOs and NPs. *Environ Sci Pollut* Res. 2013;20:1207–18.

[13] Stuer-Lauridsen F. Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. *Environ Pollut.* 2005;136:503–24.

[14] Kot-Wasik A, Zabiegala B, Namiesnik J. Passive sampling for long-term monitoring of organic pollutants in water. *Trends Anal Chem*. 2000;19:446–59.

DOI: 10.31695/IJASRE.2018.33004