ESKİŞEHİR TECHNICAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY
A- APPLIED SCIENCES AND ENGINEERING

2020, 21(3), pp. 464-476, DOI: 10.18038/estubtda.583923

RESEARCH ARTICLE

PHENANTHROIMIDAZOLE-AZO DERIVED POLYMER BASED FLUORESCENCE SENSOR DESIGN FOR MONITORING OF Fe (III) IONS

Sibel GÜLLE[1, *], **Seçil ÇELİK ERBAŞ** [2]

[1] Manisa Celal Bayar University, Faculty of Arts and Science, Department of Chemistry, Campus of Şehit Prof. Dr. İlhan Varank, 45140, Manisa, Turkey
[2] Manisa Celal Bayar University, Faculty of Engineering, Department of Metallurgy and Materials Engineering, Campus of Şehit Prof. Dr. İlhan Varank, 45140, Manisa, Turkey

ABSTRACT

Dye doped polymer films which are sensitive to Fe (III) ions have been developed for using in the aqueous medium. PVC films were obtained by spreading the cocktail mixture onto a mylar film used as a supporting material. PMMA films were prepared with solvent casting method. Cation responses were examined for two different polymer films. Emission bands were obtained at different concentrations of Fe (III) ions. Because polymer films had the highest response to them. The calibration graphics were plotted for emission values at different Fe (III) concentrations. Besides, interference effects of Cr (III) and Fe (II) ions to Fe (III) ions were studied. Additionally, regeneration studies were carried out to examine application properties of the dye doped polymer films developed as a sensor for Fe (III) cations.

Keywords: Dye doped polymer film, Cation sensor, Phenanthroimidazole, Conjugated system, Fluorescence studies

1. INTRODUCTION

Determination of transition metal ions is an issue that must be taken into consideration because of their potential effects on human health and environmental protection [1-3]. For this purpose, fluorescence spectroscopy technique is widely used for a selective and sensitive sensor design. This technique is one of the most powerful and widespread technologies used in life sciences, from basic research to clinical applications [4-7]. It is also used in analytical applications because of its simplicity and sensitivity for determination of trace amounts of metal ions [8-9].

Fluorescence dyes are used as solid state sensor materials when doped into a polymer matrix. These materials' portable, reusable, cheap and eco-friendly properties make them possible to detect metal ions quickly and efficiently [10, 11]. Solid state fluorescence sensors provide instant and in-situ detection of trace elements in aqueous environments compared to fluorescence probes prepared by dissolving in solvent. These sensors are used in many applications such as organic light emitting diodes, non-linear optic materials and analyses of anionic, cationic and neutral species [12-14].

Among transition metals, iron is one of the vital elements for human health. Iron, also used in industrial, biological, environmental and medical applications, has +2 and +3 oxidation steps. Both Fe (II) and Fe (III) ions take part in many important mechanisms in the biosphere as well as playing a key role in metabolic reactions. Determination of Fe cations by using fluorescence technique is based on detection of signal changes involved in interaction between a metal sensitive molecule (fluorophore) and Fe cations [15].

---

*Corresponding Author: sibel.gulle@cbu.edu.tr
Received: 28.06.2019 Published: 30.09.2020

Due to their paramagnetic properties, Fe ions undergo non-radiative deactivation when they interact with a fluorophore, resulting in the quenching of fluorescence intensity [16].

Although there are some studies to develop an iron sensor in the solvent environment, they show limitations in dye-doped polymer films [17-20].

In this study, 4-((4-(1*H*-phenanthro[9,10-d]imidazol-2-yl)phenyl)diazenyl)-*N*,*N*-dimethylaniline (PA) compound, which was synthesized by our group [21], was doped to PVC and PMMA polymer media. Cation responses of these dye doped polymer films were investigated and these films displayed selective and sensitive responses to Fe (III) ions. It is thought that determination of certain concentration of Fe (III) ions with using PA doped polymer films in wastewater or biological medium can be performed accurately and sensitively.

2. MATERIALS AND METHODS

2.1. Instrument and Reagents

Fluorescence emission spectra were measured using Perkin Elmer Instrument LS55 spectrofluorimeter. Excitation wavelength used for emission measurements was 375 nm. Two emission bands were obtained at 410 and 435 nm. Calculations were performed using the fluorescence intensity at 435 nm which have the highest R^2 values at the calibration graphs.

Tetrahydrofuran (THF) was used as a solvent for cocktail mixture and provided from Sigma-Aldrich. High molecular weight polyvinyl chloride (PVC) and polymethyl methacrylate (PMMA) used as polymer media and dibutylphtalate (DBP) used as a plasticizer were purchased from Aldrich. Potassium tetrakis-(4-chlorophenyl) borate (PTCPB) (%98) was used as a lipophilic anionic site in constructing fluorescent optode for cations and supplied from Alfa Aesar. Mylar film used as a polyester supporting material was provided from Du Pont. The solutions of metal salts were prepared with ultra-pure water obtained from Merck. 4-((4-(1*H*-phenanthro[9,10-d]imidazol-2-yl)phenyl)diazenyl)-*N*,*N*-dimethylaniline (PA) was used as a fluorescence dye. Schematic structure of PA is shown in figure 1.

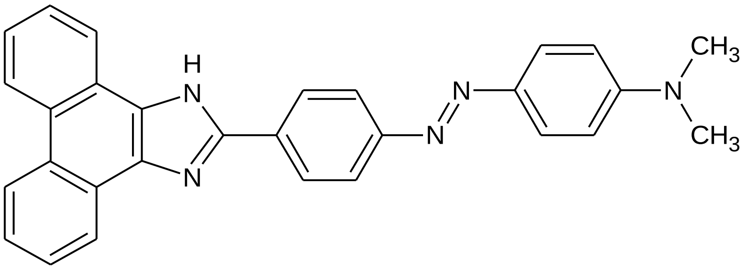

Figure 1. The structure of 4-((4-(1*H*-phenanthro[9,10-d]imidazol-2-yl)phenyl)diazenyl)-*N*,*N*-dimethylaniline (PA).

2.2. Preparation of Polymer Films

120 mg PVC, 240 mg plasticizer (DBP), PA dye (approximately 2.0 mmol dye=kg polymer), potassium tetrakis (4-chlorophenyl) borate (4.0 mmol) and 1.5 mL THF were used for cocktail mixture. PVC films were prepared by spreading of dye-polymer cocktail over a Mylar film and dried in a desiccator [18].

PMMA films were prepared with solvent casting method. In this process PMMA was dissolved in THF and PA dye was added to that solution. This solution stirred until all dye dissolved. The homogeneous solution were poured to a petri dish. After the solvent evaporation and drying in the oven, the films were stripped out.

The prepared films were cut into a suitable form (1.2 cm-3.0 cm) and placed diagonally in a quartz cuvette. Emission studies were performed for each PA doped polymer films in aqueous medium.

3. RESULTS AND DISCUSSION

3.1. Sensitivity Studies

Responses of PA doped polymer films to pH change were examined in different buffer solutions at pH 1-10. This pH range was chosen to avoid precipitation of cations with hydroxide ions. For this purpose, CH_3COOH/CH_3COO^-, NaH_2PO_4/HPO_4^{2-}, NH_4^+/NH_3 buffer solutions were prepared and also 0.10 M HCl solution was used for pH 1. It was observed that PA doped polymer films didn't give significant response to pH change. Figure 2 shows pH responses of PA doped PMMA films. The cation studies were performed at pH 7 except for Fe^{3+} ions because of the fact that the solubility coefficient of $Fe(OH)_3$ is too low ($K_{sp}=2.0 \times 10^{-39}$ at 25 °C). So, $FeCl_3$ solution was prepared at pH 1.

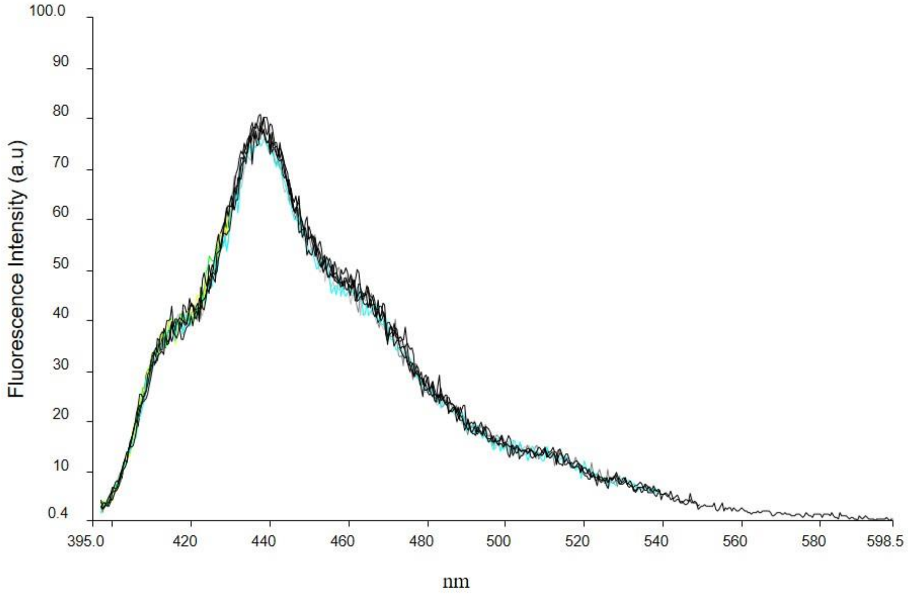

Figure 2. pH responses of PA doped PMMA films at pH 1-10.

The relative signal changes of PA doped PMMA and PVC films to different cations at the concentration of 1.50×10^{-3} M were shown in Figure 3 and 4. In these graphs; I_0 and I indicate emission intensities of PA doped polymer films in pure water and cation solutions, respectively. Cation studies showed that PA doped polymer films gave high responses to Fe^{3+}, Fe^{2+} and Cr^{3+}. These cations gave responses in the same order for both PVC and PMMA films. Some of the other cations showed different responses for PVC and PMMA films. Very low affinity of the dye molecules to these cations could be caused to positive or negative relative signal changes as seen in figure 3 and 4.

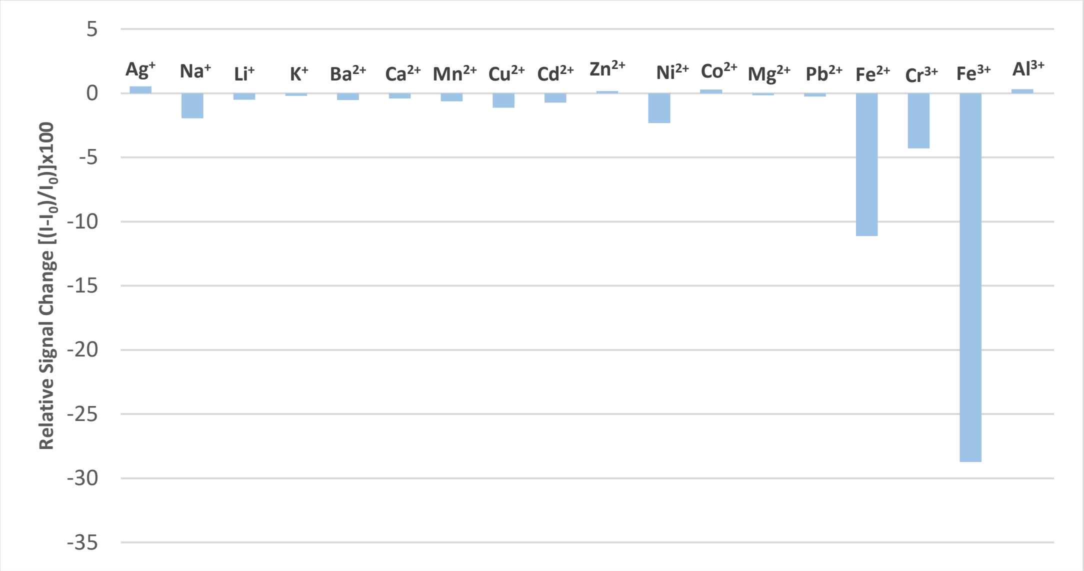

Figure 3. Relative signal changes of PA doped PMMA film to different cations at the concentration of 1.50x10^{-3} M.

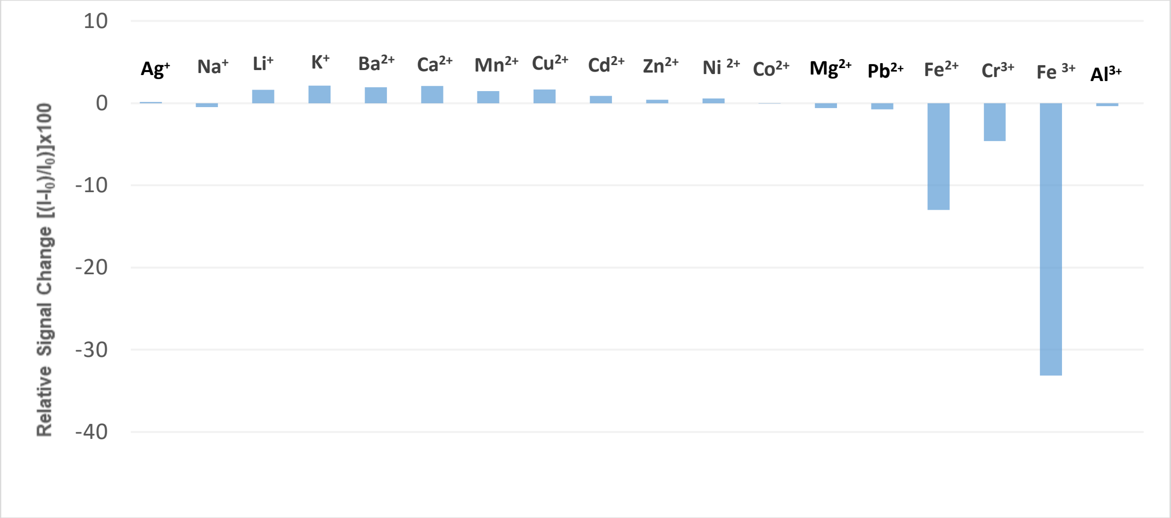

Figure 4. Relative signal changes of PA doped PVC film to different cations at the concentration of 1.50x10^{-3} M.

The fluorescence responses of PA doped PVC and PMMA films to Fe^{3+}, Fe^{2+} and Cr^{3+} cations were shown in figure 5 and 6 respectively. The fluorescence intensities of PA doped polymer films to the other cations were very close to each other and nearly found in the same area. So, these cation responses weren’t showed in figure 5 and 6.

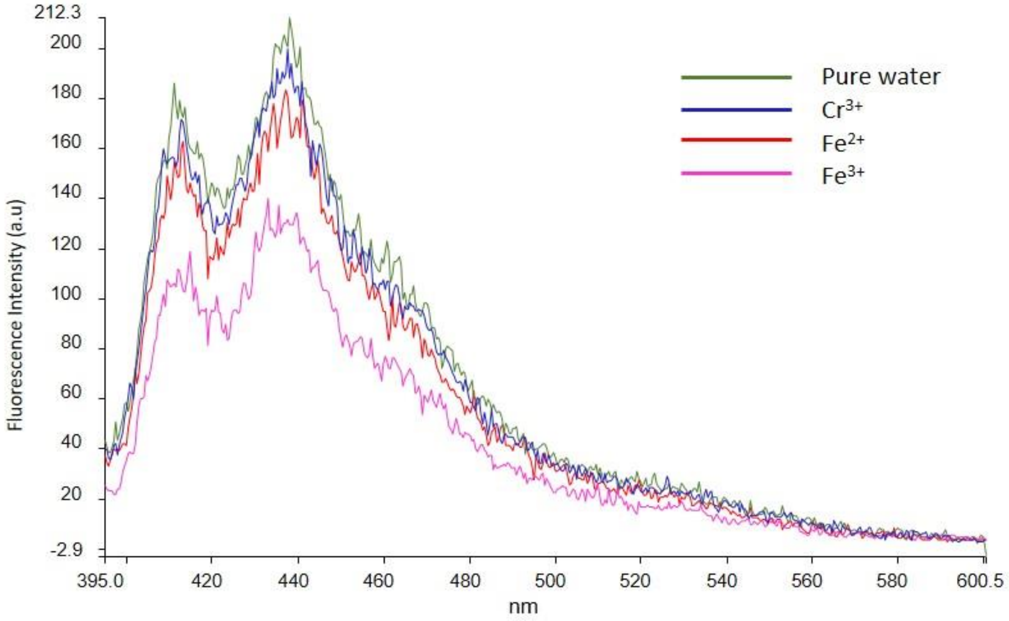

Figure 5. Fluorescence responses of PA doped PVC film to Fe^{3+}, Fe^{2+} and Cr^{3+} cations at the concentration of 1.50×10^{-3} M.

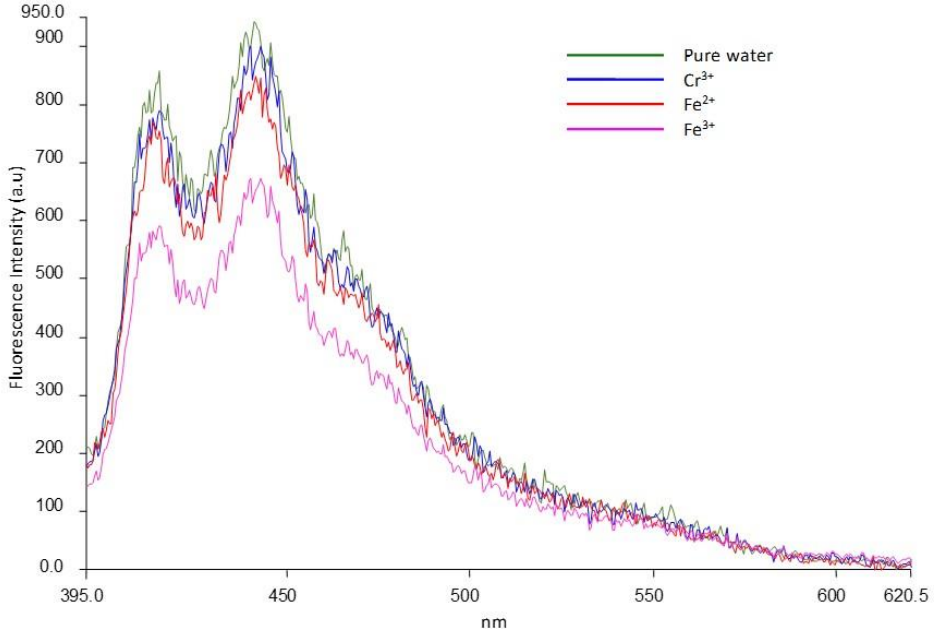

Figure 6. Fluorescence responses of PA doped PMMA film to Fe^{3+}, Fe^{2+} and Cr^{3+} cations at the concentration of 1.50×10^{-3} M.

3.2. Fluorescence responses of PA doped polymer films at different concentrations of Fe^{3+}

The calibration graphics of PA doped PVC and PMMA films were plotted for Fe^{3+} emission values at the concentration ranges between 1.0×10^{-2} – 5.0×10^{-4} M. The relative signal changes had logarithmic correlations for both polymer films as shown in figure 7 and 8. R^2 values were obtained as 0.9811 and

0.9813 in PMMA and PVC media respectively. Concentration values of Fe^{3+} used on calibration graphics are shown in Table 1. As indicated in figure 9 and 10, the emission intensities of PA doped PMMA and PVC film decreased with the rise in the concentration of Fe^{3+}.

Table 1. Concentrations of Fe^{3+} and relative signal changes for both polymer media used on calibration graphics.

PMMA		**PVC**	
Concentrations (M) of Fe^{3+}	**Relative Signal Change $\lvert I-I_0\rvert/I_0$**	**Concentrations (M) of Fe^{3+}**	**Relative Signal Change $\lvert I-I_0\rvert/I_0$**
$5.0x10^{-4}$	0.0700	$5.0x10^{-4}$	0.0469
$1.0x10^{-3}$	0.1522	$1.0x10^{-3}$	0.1670
$1.25 x 10^{-3}$	0.2466	$1.25 x 10^{-3}$	0.3398
$3.0x10^{-3}$	0.4970	$2.5x10^{-3}$	0.5178
$4.0x10^{-3}$	0.6428	$3.75x10^{-3}$	0.7084
$5.0x10^{-3}$	0.7276	$5.0x10^{-3}$	0.8397
$7.5x10^{-3}$	0.8678	$7.5x10^{-3}$	0.8823
$1.0x10^{-2}$	0.9365	$1.0x10^{-2}$	0.9606

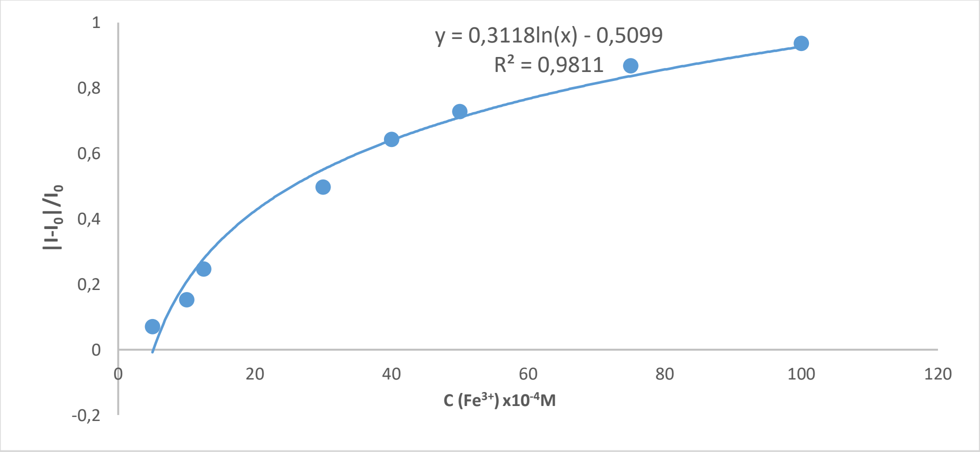

Figure 7. Calibration graphic of Fe^{3+} for PMMA medium.

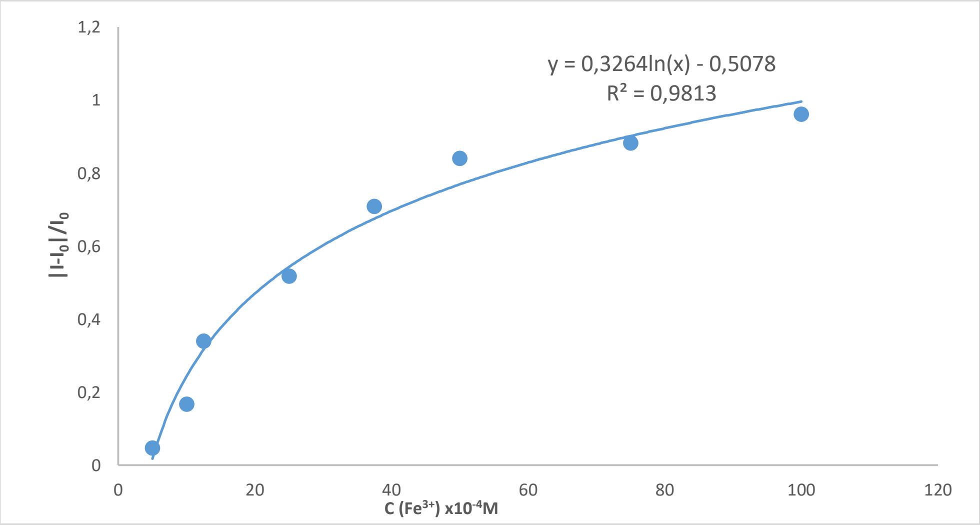

Figure 8. Calibration graphic of Fe^{3+} for PVC medium.

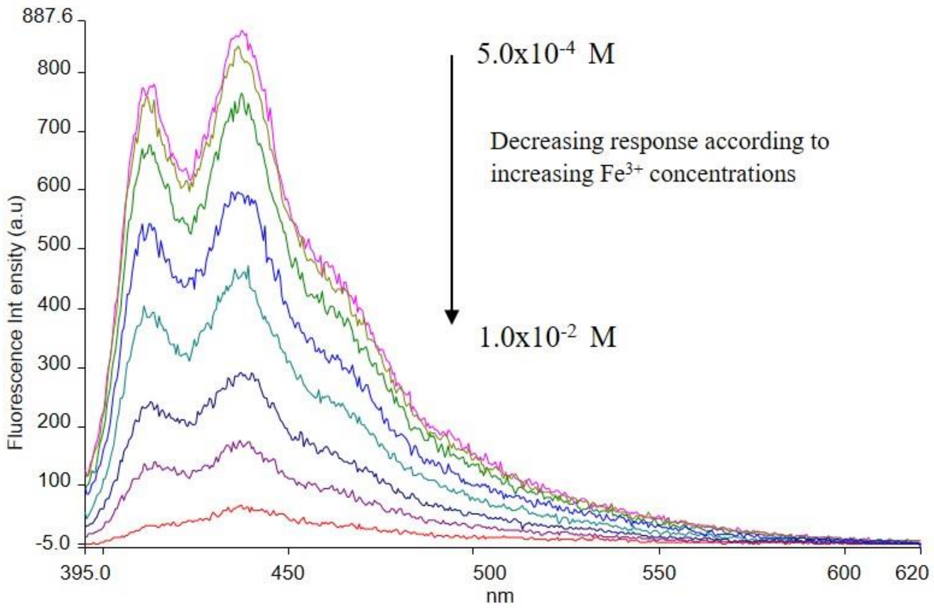

Figure 9. Emission spectrum of PA doped PMMA film depending on Fe^{3+} concentrations.

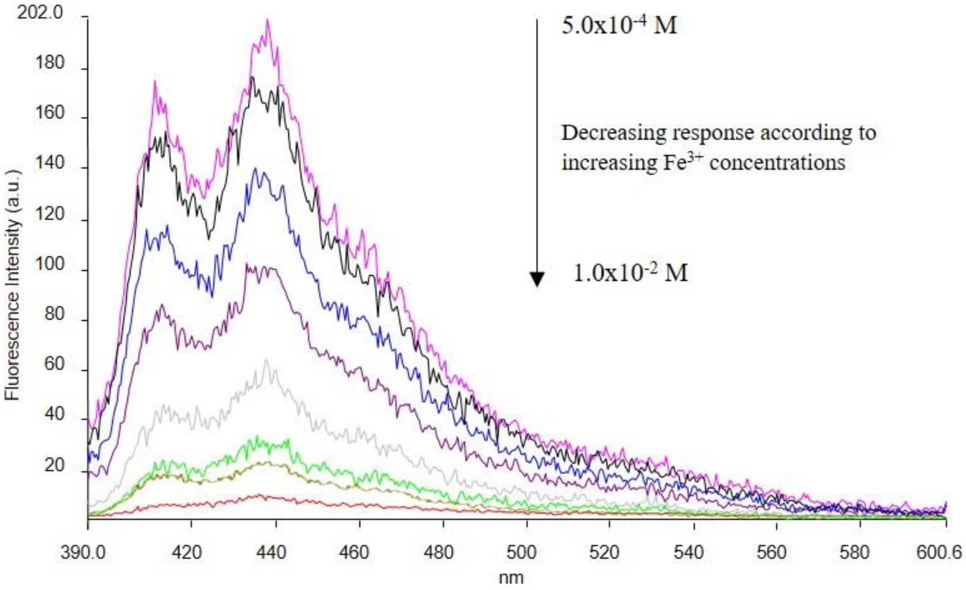

Figure 10. Emission spectrum of PA doped PVC film depending on Fe^{3+} concentrations.

3.3. Interference Studies

PA doped PMMA and PVC films gave the highest responses to Fe^{3+}, Fe^{2+} and Cr^{3+} among the studied ions. Emission intensity variations of the other ions were too low. Therefore, interference effects of Fe^{2+} and Cr^{3+} in the presence of Fe^{3+} were examined. Certain volumes of concentrated Fe^{2+} and Cr^{3+} solutions were added with a micropipette to Fe^{3+} solution found in a quartz cuvette and emission studies were performed.

Interference effects of Fe^{2+} and Cr^{3+} in the presence of 1.0×10^{-2} M and 1.0×10^{-3} M Fe^{3+} were investigated. Figure 11 and 12 showed that there wasn't any interference effect between Fe^{3+} and Fe^{2+}

or Fe^{3+} and Cr^{3+} at the concentrations of 1.0 x 10^{-3} M. Contrary, there were some interference effects when the concentrations of Fe^{2+} and Cr^{3+} were ten times higher than Fe^{3+}. The interference effects of Fe^{2+} and Cr^{3+} ions were too low in the presence of 1.0x10^{-2} M Fe^{3+} as seen in figure 13 and 14.

Fe^{2+} and Cr^{3+} ions were added simultaneously or subsequently to 1.0 x 10^{-2} M Fe^{3+} solution and their interference effects were examined to identify selectivity of PA doped polymer films to Fe^{3+}. It was considered that the interference effects of Cr^{3+} and Fe^{2+} ions were not clearly observed when these ions were added subsequently to the quartz cuvette in which Fe^{3+} already existed. It was estimated that Fe^{3+} could interact with the surface of PA doped polymer film. But, there wasn't observed any significant difference for adding Fe^{2+} and Cr^{3+} ions simultaneously or subsequently to Fe^{3+} (Figure 13, 14).

These compatible results can be attributed to high selectivity of the dye doped polymer films to Fe^{3+}.

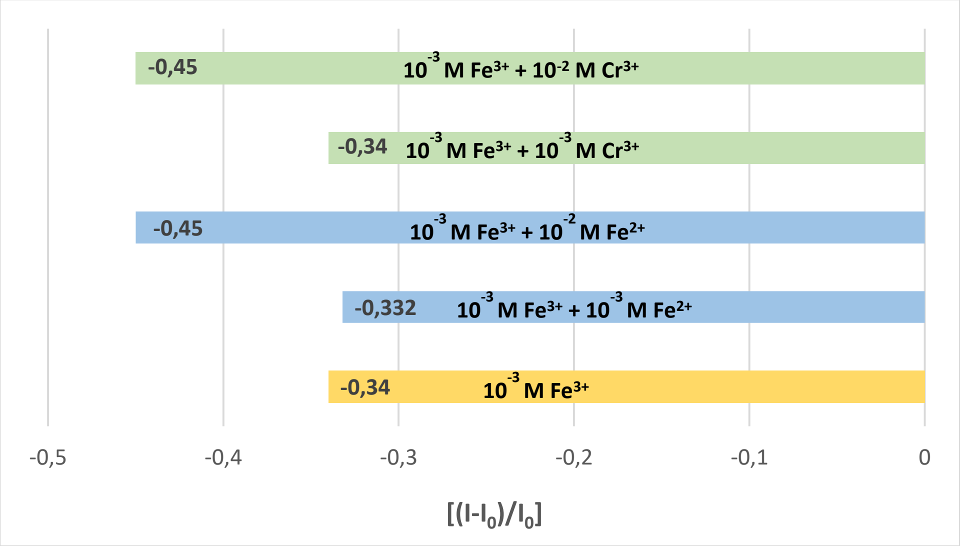

Figure 11. Interference effects of Fe^{2+} and Cr^{3+} to Fe^{3+} in PMMA medium.

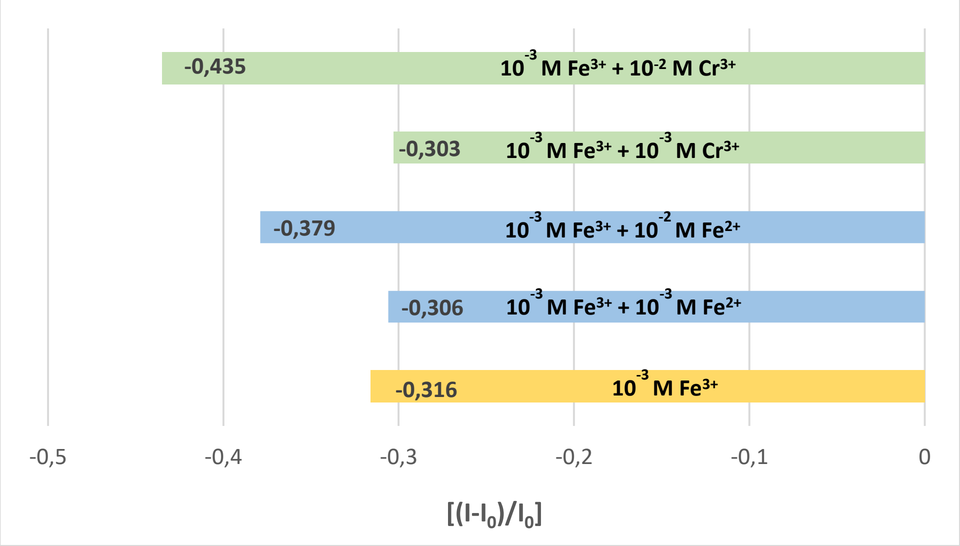

Figure 12. Interference effects of Fe^{2+} and Cr^{3+} to Fe^{3+} in PVC medium.

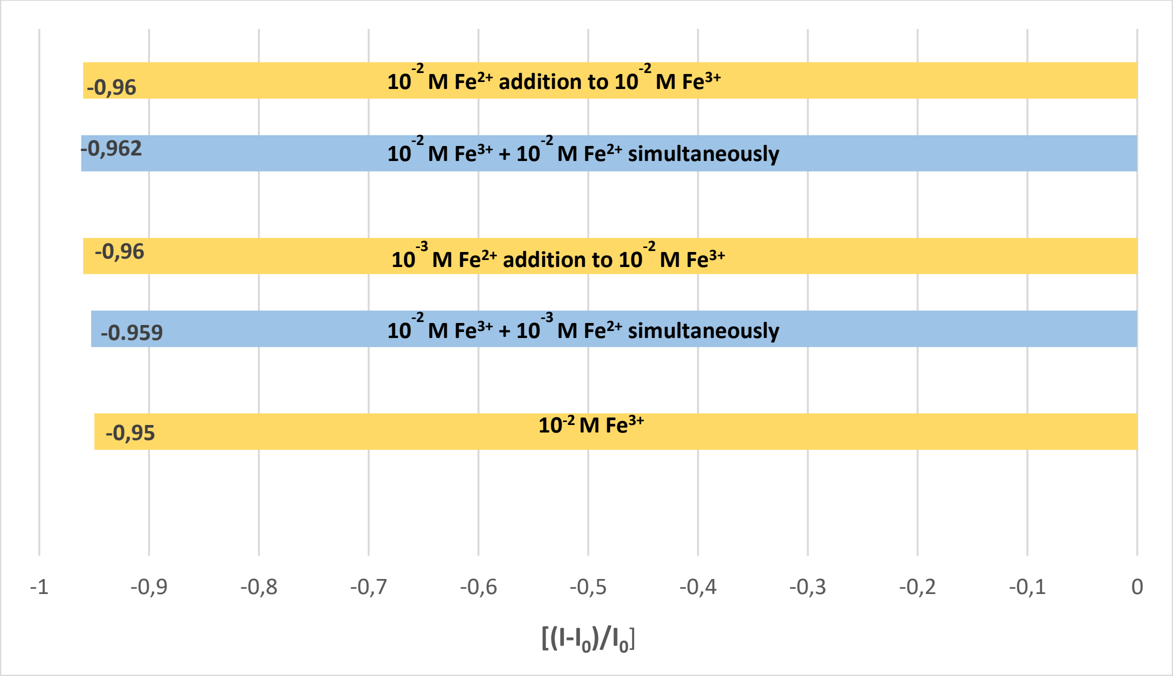

Figure 13. Interference effects of Fe^{2+} to Fe^{3+} in PMMA medium.

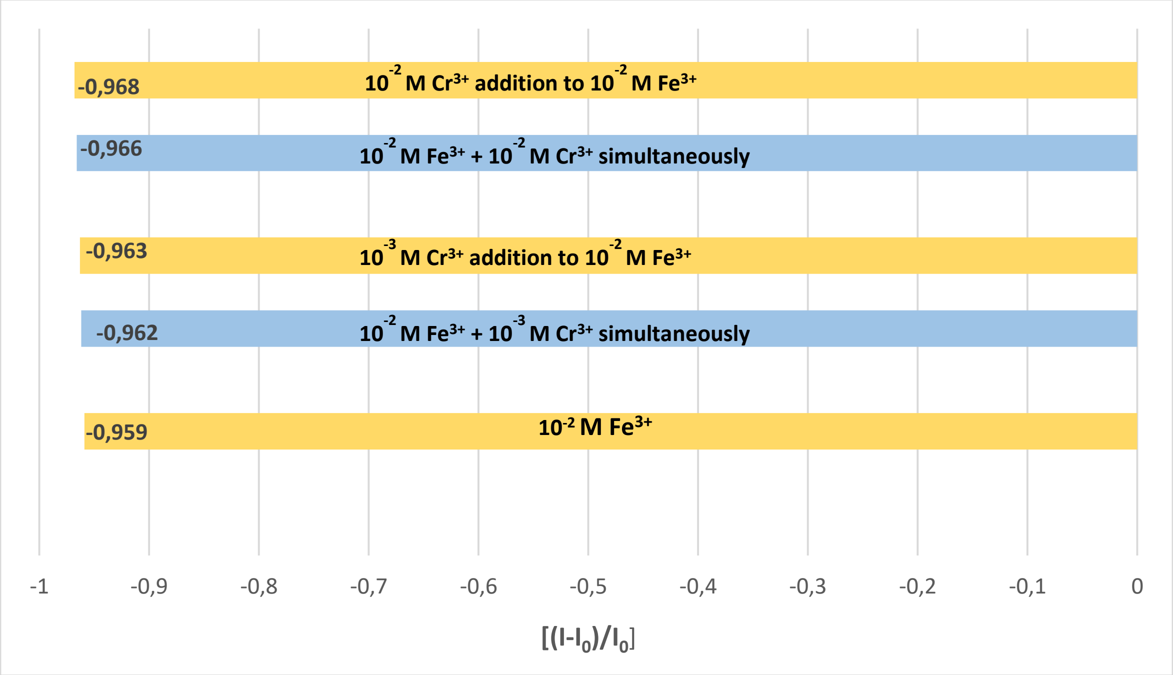

Figure 14. Interference effects of Cr^{3+} to Fe^{3+} in PVC medium.

3.4. Regeneration Studies for PA doped PMMA and PVC Films

Emission measurements of PA doped polymer films were repeated three times in both cation solutions and pure water. Average values of these measurements were used in this study. It was observed that PA doped polymer films showed similar results for each emission measurements. Figure 15 and 16 show examples of emission responses of PA doped polymer films to 5.0x10^{-3} M Fe^{3+} ion. Standard deviation and relative standard deviation of emission values at the concentration of 1.0 x 10^{-2} M Fe^{3+} were calculated. These values were found as 0.662 and 0.02 for PVC medium and 0.778 and 0.003 for PMMA medium respectively.

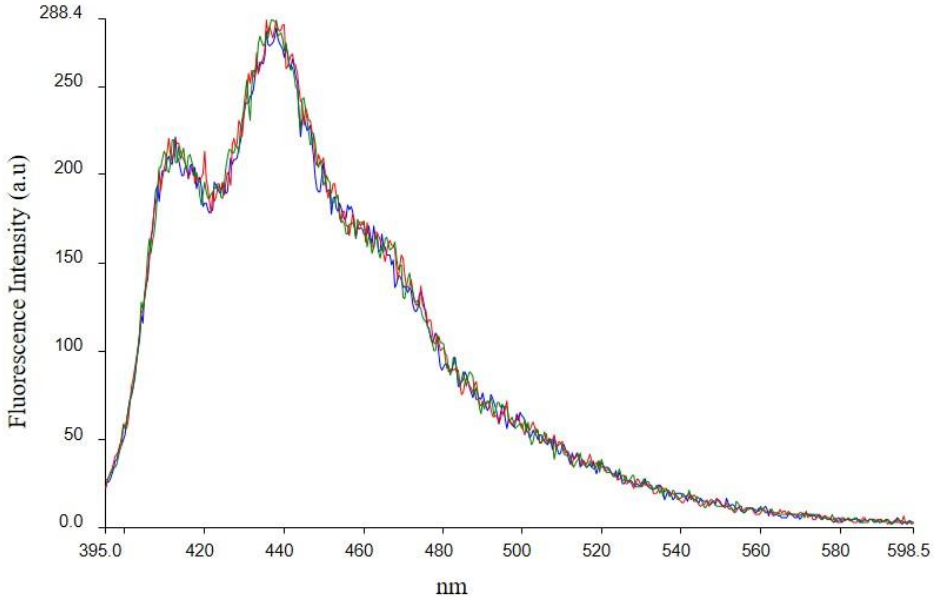

Figure 15. Fluorescence responses of PA doped PMMA films to 5.0x10^{-3} M Fe^{3+}.

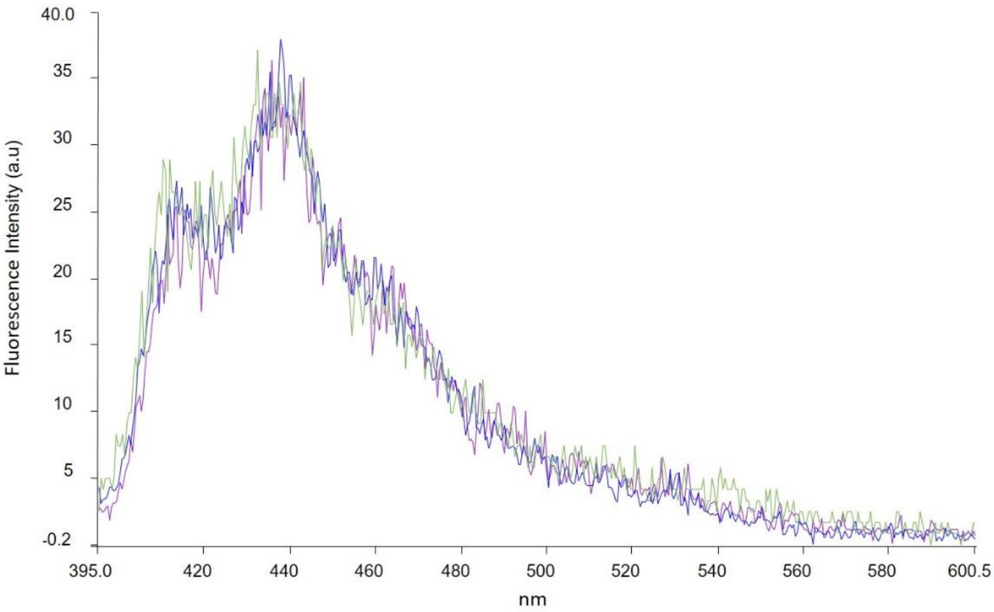

Figure 16. Fluorescence responses of PA doped PVC films to 5.0x10^{-3} M Fe^{3+}.

Regeneration results for both PA doped polymer media were shown in Figure 17 and 18. PA doped polymer films were washed with pure water after each cation response. Emission results of the polymer films in pure water showed that both dye doped polymer films could be highly regenerated.

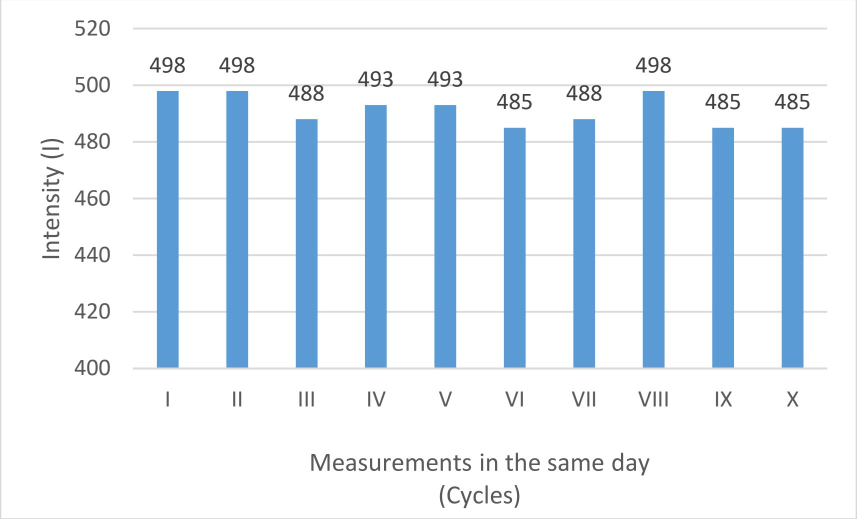

Figure 17. Emission responses of PA doped PVC film after washing with pure water in the same day.

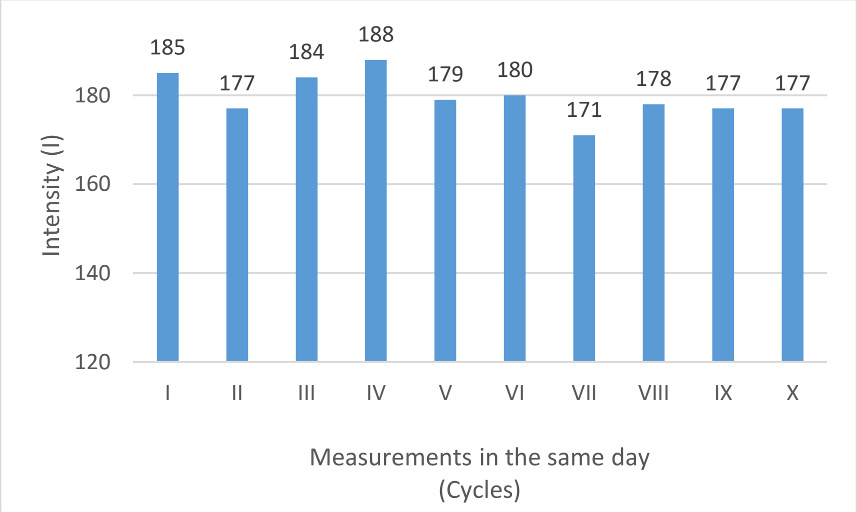

Figure 18. Emission responses of PA doped PMMA film after washing with pure water in the same day.

4. CONCLUSIONS

The aim of this study is usage of different polymers to develop a cationic sensor. PVC and PMMA polymers were chosen because of their flexible, transparent, thermoplastic character and compatibility with aqueous medium.

Emission responses of PA doped polymer films to different cations were investigated and these films showed the highest responses to Fe^{3+}, Cr^{3+} and Fe^{2+} ions. It was thought that metallic cations could be interact with N donor atom in aromatic heterocycle or azo bridge of PA structure via dipol-ion (coordinate covalent bond) interactions. Emission results of PA doped PVC and PMMA films to different cations were compared. The highest relative signal changes for both polymer media were sequenced as Fe^{3+}>Fe^{2+}>Cr^{3+}.

Calibration graphs of the polymer films were plotted ($1.0x10^{-2}$-$5.0x10^{-4}$ M). Logarithmic variations were observed.

Interference effects of Fe^{3+}, Cr^{3+} and Fe^{2+} ions were investigated due to their higher relative signal changes compared with other ions. The interference effect was too low in the presence of $1.0x10^{-3}$ M Fe^{3+} - $1.0x10^{-3}$ M Fe^{2+} or $1.0x10^{-3}$ M Fe^{3+}- $1.0x10^{-3}$ M Cr^{3+}. When the concentrations of other two ions were 10 times higher than $1.0x10^{-3}$ M Fe^{3+}, the interference effect was approximately 11%. The interference effects of Cr^{3+} and Fe^{2+} were very low at the concentration of $1.0x10^{-2}$ M Fe^{3+} (0.9-1.2 %).

Also Cr^{3+} and Fe^{2+} ions, which thought to have interference effect were added simultaneously or subsequently to $1.0x10^{-2}$ M Fe^{3+} solution and the emission responses were studied. Similar results showed that PA doped polymer films were selective to Fe^{3+} ions.

The regeneration studies were performed for PA doped polymer films. The emission studies were repeated three times with the same polymer films and similar results were obtained. Cation responses were given as the average of these three values. Polymer films were washed with pure water before every measurement. The emission responses of polymers films were taken in pure water after their cationic measurement and it was seen that they have been highly regenerated. As a result, interference effects of Fe^{2+} or Cr^{3+} ions were too low to Fe^{3+} at the concentration of 1.0×10^{-2} M. These films may be used in environmental or biomedical applications due to their reusable, portable and simple qualifications.

ACKNOWLEDGMENTS

This work was financially supported by Manisa Celal Bayar University Research Fund (MCBU BAP: 2013- 096)

REFERENCES

[1] Bilcikova J, Fialkova V, Kovacikova E, Miskeje M, Tombarkiewicz B, Knazicka Z. Influence Of Transition Metals On Animal And Human Health: A Review. Contemporary Agriculture 2018; 67: 187-195.

[2] Aydemir B, Kızıler AR, Onaran İ, Alıcı B, Özkara H, Akyolcu MC. Impact of Cu and Fe Concentrations on Oxidative Damage in Male Infertility. Biol Trace Elem Res 2006; 112: 193-203.

[3] Ando K, Ogawa K, Misaki S, Kikuwaga K. Increased Release of Free Fe Ions in Human Erythrocytes During Aging in the Circulation. Free Radical Res 2002; 36: 1079-1084.

[4] Borst JW, Visser AJVG. Fluorescence lifetime imaging microscopy in life sciences. Meas Sci Technol 2010; 10: 1-21.

[5] Wagnieres GA, Star WM, Wilson BC. In Vivo Fluorescence Spectroscopy and Imaging for Oncological Applications. Photochem Photobiol 1998; 68: 603-632.

[6] Gillenwater A, Jacob R, Richards-Kortum R. Fluorescence spectroscopy: A technique with potential to improve the early detection of aerodigestive tract neoplasia. Head Neck-J Scı Spec 1998; 20: 556–562.

[7] Müller MG, Valdez TA, Georgakoudi I, Backman V, Fuentes C, Kabani S, Laver N, Wang Z, Boone CW, Dasari RR et al. Spectroscopic detection and evaluation of morphologic and biochemical changes in early human oral carcinoma. Cancer 2003; 97: 1681-1692.

[8] Carter KP, Young AM, Palmer AE. Fluorescent Sensors for Measuring Metal Ions in Living Systems. Chem Rev 2014; 114: 4564-4601.

[9] Cabaniss SE, Shuman MS. Combined ion selective electrode and fluorescence quenching detection for copper-dissolved organic matter titrations. Anal Chem 1986; 58: 398-401.

[10] Wolfbeis OS. Materials for fluorescence-based optical chemical sensors. J Mater Chem 2005; 15: 2657-2669.

[11] Rakow NA, Suslick KS. A colorimetric sensor array for odour visualization. Letter 2000 ; 406: 710-713.

[12] Hebner TR, Wu CC, Marcy D, Lu MH, Sturm JC. Ink-jet printing of doped polymers for organic light emitting devices. Appl Phys Lett 1998; 72: 519-521.

[13] Sun Y-F, Wang H-P, Chen Z-Y, Duan W-Z. Solid-state Fluorescence Emission and Second-Order Nonlinear Optical Properties of Coumarin-based Fluorophores. J Fluoresc 2012; 23: 123-130.

[14] Mahanta, D, Madras G, Radhakrishnan S, Patil S. Adsorption and Desorption Kinetics of Anionic Dyes on Doped Polyaniline. J Phys Chem B 2009; 113: 2293-2299.

[15] Espósito BP, Epsztejn S, Breuer W, Cabantchik ZI. A Review of Fluorescence Methods for Assessing Labile Iron in Cells and Biological Fluids. Anal Bıochem 2002; 304: 1-18.

[16] Zeng Z, Jewsbury RA. Fluorimetric determination of iron using 5-(4-methoxyphenylazo)-8-(4-toluenesulfonamido)quinoline. The Analyst 2000; 125: 1661-1665.

[17] Khalil R. Optical Properties of Rhodamine - B Dye Doped in Transparent Polymers for Sensor Application. Chinese J Phys 2013; 51: 570-580.

[18] Oter O, Ertekin K, Kirilmis C, Koca M, Ahmedzade M. Characterization of a newly synthesized fluorescent benzofuran derivative and usage as a selective fiber optic sensor for Fe(III). Sensors and Actuators B: Chemical 2007; 122: 450-456.

[19] Gülle S, Çelik Erbaş S. A Selective Fluorescence Sensor for Fe (III) Based on Phenanthroimidazole Imine Compound. J Fluoresc 2017; 28: 445-451.

[20] Tofiño PP, Moreno JM, Pérez-Conde MC. A flow-through fluorescent sensor to determine Fe (III) and total inorganic iron.Talanta 2000; 51:537–545.

[21] Erbaş SÇ, Gülle S. Synthesis and Photophysical Behaviours of Novel Phenanthro [9,10-d] Imidazole Substituted Azo Dyes in Solvent Media. CBUJOS 2018; 14: 285-289.