Luminescent Probe for Crotoxyphos Pesticide Detection Based on Eu (III) Complex with 7-Hydroxy-Coumarin-4-Acetic Acid

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Abstract: Luminescent Europium complex based on7-hydroxy-coumarin-4-aceticas ligand was investigated as a probe for the detection of organophosphorus pesticides. The complex exhibited an interesting action towards Crotoxyphos pesticide. The luminescence of the Eu(III)-7-hydroxy-coumarin-4-acetic was remarkably enhanced by gradual addition of Crotoxyphos. Limit of detection (LOD) = 1.86 µM and limit of quantitation (LOQ) = 6.19µM. Binding constant at different temperatures was calculated according to Benesi-Hildebrand equation. The thermodynamic parameters ΔH, ΔS and ΔG were calculated for characterization of the nature of force due to interaction of the complex with Crotoxyphos. Finally, the effect of interfering anion and cations that naturally occur in water and soil was studied, in addition; interference of some pesticides was studied.

Keywords: Luminescence probe, Europium, Coumarin derivative, Crotoxyphos.

INTRODUCTION

Organophosphorous pesticides are the most widely used group of insecticides, worth nearly 40% of the market sales (Singh and Walker 2006;Anonymous, 1996). Organophosphorous pesticides are acetylcholinesterase (AChE) inhibitors. These pollutant move in environment by volatilization, leaching and runoff (Sawhney *et al.,* 1989). Monitoring pesticides in environment depended on expensive chromatographic methods for decades, new novel methods has been submitted to achieve the fast, reliable, cheap and selective qualitative and quantitative detection of pesticides *e.g.* AChE-based biosensors (Carlo *et al.,* 2004; Vakurov *et al.,* 2004; Bucura *et al.,* 2006), Lateral field excited acoustic sensor with polymer coating (Yihe Hu*et al.,* 2005), Carbon paste electrochemical transducer (Liu and Lin, 2005), Fluorescence (Jenkins*et al.,* 1999; Russell *et al.,*1999; Viveros *et al.,* 2006), Potentiometric ion-selective electrode (Rainina *et al.,* 1996; Ristori *et al.,* 1996), pH-sensitive field-effect transistor (Simonian *et al.,* 2001), Amperometric microbial detection (Doick*et al.,* 2005, Mulchandani*et al.,*2006), Quantum dots (Tang *et al.,* 2016; Zhang *et al.,* 2010), Surface enhanced Raman spectroscopy (Nguyen *et al.,* 2014;Bin Liu*et al.,* 2013) and Nanoparticle-Based Chemiluminescent Sensor (Yi He *et al.,*2015).

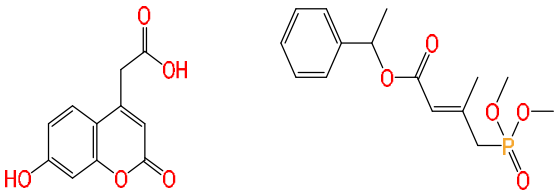
In this work, we study and improve a selective probe for Crotoxyphos pesticide based on Eu(III)-7-hydroxy-coumarin-4-acetic, this probe based on lanthanide as approach in Analytical sensors (Bünzli and Eliseeva, 2011).7-hydroxy-coumarin-4-acetic (Figure 1) is a comarin base derivative, they are sensors for ions (El-Shekheby *et al.,* 2014), pesticides (Obare *et al.,* 2010). Although comarins are good lanthanide sensitizers (Hussein*et al.,*2016; Féau *et al.,* 2009). This work shows the selectivity of luminesncet Eu(III)-7-hydroxy coumarin-4-acetic acid toward Crotoxyphos pesticide.

MATERIALS AND METHODS

Materials

Europium chloride hexahydrate ($EuCl_3.6H_2O$) was analytical grade and purchased from Sigma-Aldrich. The stock solution was prepared in Ethanol. Solvents were purchased from Sigma-Aldrich and Fisher chemicals HPLC grade.

Material used in organic synthesis and salts used in work were AR grade and used without further purification included: Heavy metals (Nitrate of Ni^{2+}, $Cd^{2+}$and Pb^{2+}), Alkali metals (Chlorides of Ca^{2+}, Na^{+} and K^{+} also NH_4^{+}), Anions (Sodium salt of CO_3^{2-}, NO_3^{2-}, $H_2PO_4^{-}$, HPO_4^{2-}, Br^{-}, and I^{-}).Pesticides used in work included Dichlorvos (P1), Malathion (P2), Crotoxyphos (P3), Chlorpyrifos (P4), Paraoxon (P5), Profenofos (P6), Endosulfan (P7) and Heptachlor (P8). All pesticides are analytical standard brought from Sigma-Aldrich.



7-Hydroxy Coumarin-4-acetic acid Crotoxyphos (P1)

Figure (1): Chemical structure of 7-Hydroxy coumarin-4-acetic acid and Crotoxyphos

Chemical and physical measurements

^{1}H-NMR performed on Bruker Ascend 850 MHz. Infrared spectra were obtained on 4100 JASCO Japan FT-IR. Fluorescence spectra were performed on Jasco FP-6300 spectrofluorometer 1.0 cm path using Hellmaquartz cell type 111-QS with a 150W xenon lamp for excitation. Absorbance spectra (UV-VIS) were carried out using Shimadzu UV-1800, Double Beam photometric system, and 1.0 cm path length cell.

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Methods

Preparing complex and testing samples were achieved by using stocks solutions of materials and adding a precise volume of them to solvent, then stir using vortex action, the desired measurement was taken at room temperature 22-24°C or using a water bath to rise sample temperature. UV-Absorption measurements in 1 cm quartz cell. Fluorescence measurements in 1cm quartz cell and excitation wavelengths based on excitation and absorption spectra.

RESULTS AND DISCUSSION

UV Absorption Spectra

Absorption spectra of 7-hydroxy coumarin-4-acetic acid (C_1) areillustrated in figure (2) in ethanol where two absorption bands observed at 219 and 325 nm, the first one may be attributed to $\pi\rightarrow\pi^*$ and the second one could be assigned to $n\rightarrow\pi^*$ transition. Eu(III)-C_1complex exhibit two absorption bands at 220and 326 nm, where there is a very small shift in absorption peaks to red in comparison to the free C_1 ligand. Two broad weak peaks are observed at 244 and 245 nm. This indicative of complex formation.

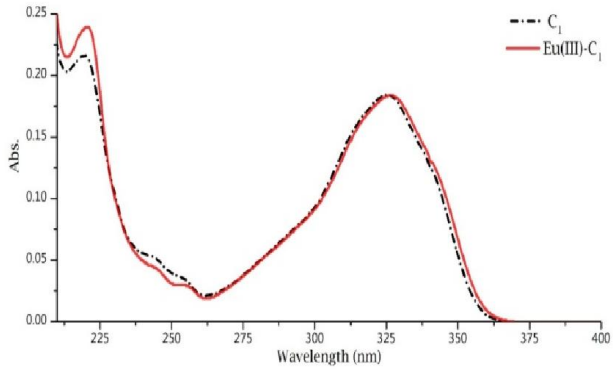

Figure (2): UV-absorption spectra of [10µmol/L] C_1 and with [10µmol/L] Eu^{3+} in ethanol.

Fluorescence of Eu(III)-C_1 and Interactions with Pesticides

Fluorescence of Eu(III)-C_1.

Like majority of Coumarins (Féau *et al.,* 2009), C_1 has strong fluorescence and upon complexation with Europium with C_1 in molar ratio 1:1 make a noticeable change in fluorescence spectra of coumarin (C_1) which interpreted due to complex formation and energy transfer to Eu(III) center. Two characteristic bands of Eu(III) were observed; one at λ_{Eu1}=592nm correspond to $^5D_0\rightarrow{}^7F_1$ and λ_{Eu2}= 617nm correspond to $^5D_0\rightarrow{}^7F_2$ transition of Eu(III) (Cotton, 2006) in ethanol, methanol, and DMF. The sequence of increasing of intensity of the main characteristic emission peak for Eu(III) at 617nm in Eu(III)-C_1 complex is Ethanol ≈ DMF > Methanol, for rest of the solvents ethyl acetate, acetonitrile, acetone and water no observed emission peaks of Eu(III) bands (Figure 3). This behavior interpreted according to solvent effect, in case of DMF and Ethanol both solvents have strong solvation power protecting Eu(III). While in Water, not only the stronger O-H oscillator and high coordinating tendency to Eu(III) but also water effect on excited state of C_1 decreasing energy gap between $^3T^*$ and Eu(III) predicted from red shift in fluorescence spectra of C_1 band, this decrease in energy gap may either cancel energy transfer to Eu(III) or complete quench of Eu(III) by non-radiative vibrations of water molecule.

C_1 shows strong emission peak in Eu(III)-C_1 complex. This band differs in intensity and wavelength from solvent to another. In water coumarin exhibits extremely strong emission peak at λ_{C1}=462nm at low sensitivity the fluorescence in rest of solvents was taken at medium sensitivity. In case of other solvents, the emission peak for coumarin in the complex is observed at 388, 392, 393 and 397nm in acetonitrile, DMF, ethanol and acetone respectively. The sequence of increasing of C_1 emission peak intensity in Eu(III)-C_1 complex is water >>> DMF > Methanol > Ethanol >Acetonitrile > Acetone >> Ethyl acetate. Interpretation according to solvent effect as mentioned before that typically, the fluorophore has a larger dipole moment in the excited state (μ_E) than in the ground state (μ_G) (Lakowicz, 2007). Following excitation, the solvent dipoles can reorient or relax around μ_E, which lowers the energy of the excited state. As the solvent polarity is increased this effect becomes larger, resulting in emission at lower energies or longer wavelengths which make. In this case polarity order water >Methanol> Ethanol> Acetonitrile> DMF> Acetone, this explain why water appeared in much lower energy and much intense intensity. DMF even It lower polar but it has no H-X quenchers like Methanol and Ethanol so C_1 intensity stronger in DMF.

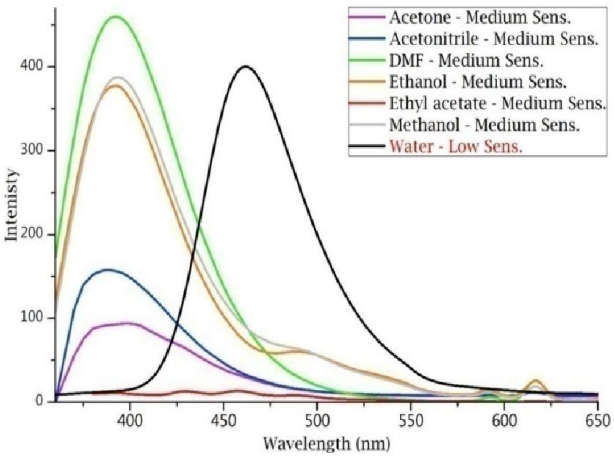

Figure (3): Fluorescence spectrum of 10µmol/L of Eu(III)-C_1 [1:1] in different solvents, excitation at 330nm at medium sensitivity except in water at low sensitivity and excited at 340nm.

Interaction of Pesticides with Eu(III)-C_1

Figure (4) illustrates the fluorescence spectra for the interaction of 10µmol/L Eu(III)-C_1 complex with 10µmol/L of pesticides: Crotoxyphos (P1), Malathion (P2), Dichlorvos (P3), Chlorpyrifos (P4), Paraoxon (P5), Profenofos (P6) and Endosulfan (P7) in ethanol. Two Fluorescence bands are effected differently the C_1 band at λ_{C1}=392nm and Eu(III) characteristic band at λ_{Eu}=617nm. Table 1 illustrated the effect on intensity of Eu(III) band at λ_{Eu}=617nm. Quenching by Chlorpyrifos (P4) and enhancement by Crotoxyphos (P1), Dichlorvos (P3), Malathion (P2), Paraoxon (P5) and Endosulfan (P7). Not effect by Profenofos (P6). The effect on Eu(III) band not tangible enough to consider the interaction unique for specific pesticide. While C_1 emission peak in Eu(III)-C_1 affected by pesticides in two manner, first is shift in peak and most interested red shift by Crotoxyphos (P1) where λ_{C1} shifted from 392nm to 412nm and rest of pesticide has no change in peak position. The second effect on peak intensity where it is quenched by Paraoxon (P5) and Endosulfan (P7), while it is enhanced by Chlorpyrifos (P4), Crotoxyphos (P1), Dichlorvos (P3) and Profenofos (P6), then Malathion (P2) has no effect on intensity.

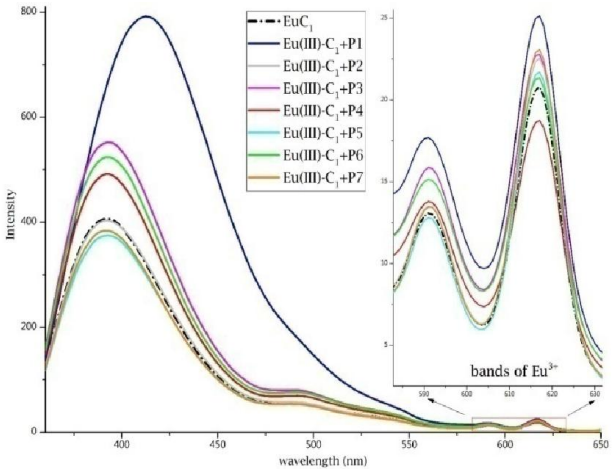

Figure (4): Fluorescence spectra for the interaction of [10µmol/L] Eu(III)-C_1 complex with [10µmol/L] of different pesticides Crotoxyphos (P1), Malathion (P2), Dichlorvos (P3), Chlorpyrifos (P4), Paraoxon (P5), Profenofos (P6) and Endosulfan (P7) in ethanol, λ_{exc}=330nm at medium Sensitivity.

Table (1): Interaction of 10µmol/L of pesticide on fluorescence of 10µmol/L Eu(III)-C_1 in ethanol, the change if intensity and shift of C_1 band.

Sample	C_1 [λ_{C1}=392nm]				Eu^{3+}[λ_{Eu}=617nm]		
	$\Delta\lambda$	$I_{C_1}/I^0_{C_1}$*	Effect	%	I_{Eu}/I^0_{Eu}**	Effect	%
Eu(III)-C_1+P1	+20	1.95	Enh.	95%	1.19	Enh.	19%
Eu(III)-C_1+P2	0	1.00	Nill	0%	1.10	Enh.	10%
Eu(III)-C_1+P3	+1	1.36	Enh.	36%	1.10	Enh.	10%
Eu(III)-C_1+P4	0	1.19	Enh.	19%	0.95	Q.	-5%
Eu(III)-C_1+P5	+1	0.92	Q.	-8%	1.05	Enh.	5%
Eu(III)-C_1+P6	0	1.29	Enh.	29%	1.00	Nill	0%
Eu(III)-C_1+P7	0	0.95	Q.	-5%	1.10	Enh.	10%

*,** I/I_0 if <1 mean quenching, >1 enhancement

Fluorescence of Eu(III)-C_1 with Crotoxyphos P1

Comparison between Fluorescence Spectra of P1 with C_1 in Presence and Absence of Eu(III)

The interaction of Crotoxyphos with Eu(III)-C_1 complex observed with respect to C_1 emission peak λ_{C1}=392nm where it is more interesting than Eu(III) emission band because of the red shift in C_1 peak from 392nm to 412nm with large enhancement (F/F_0=1.95). Figure (5) shows the difference between interaction of P1 on C_1 emission peak in absence Eu^{3+} and on Eu(III)-C_1 complex. The interaction of C_1 with Crotoxyphos (P1) which shows shift of λ_{C1} from 389nm to 403nm ($\Delta\lambda_{C1}$=14) and increase in intensity by 7.5% while in Eu(III)-C_1 complex the $\Delta\lambda_{C1}$=22 and enhancement by 108%, this shows more sensitivity to P1 in presence of Eu(III)-C_1 complex. In this work rest of studies focus on the effect of P1 on emission peak of C_1in Eu(III)-C_1 complex based on pervious publish work (El-Shekheby *et al.,* 2014; Féau *et al.,* 2009).

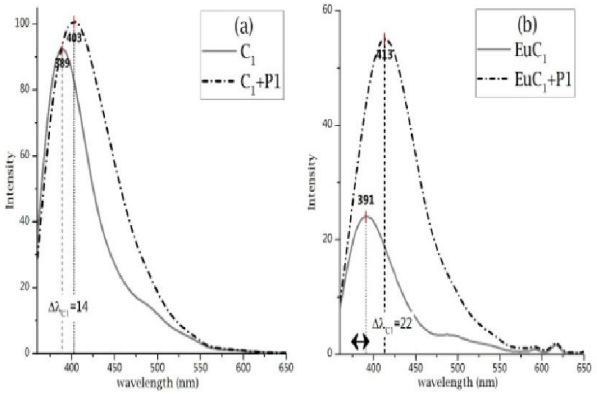

Figure (5): Interaction of 10µmol/L Crotoxyphos P1 with fluorescence of (a) 10µmol/L C_1 and (b) 10µmol/L Eu(III)-C_1 in ethanol, λ_{ex}=330nm, low sensitivity.

Calibration Curve and LOD-LOQ

Relation between intensity of C_1 band at λ_{C1}=392nm versus the concentration of P1 is shown in Figure (6). From calibration plot the correlation coefficient R^2= 0.926 which an indicative that regression line perfectly fits the data. The limit of detection (LOD) = 1.86 µmol/L and limit of quantitation (LOQ) =6.19 µmol/L calculated from calibration plot (Shrivastava and Gupta, 2011).

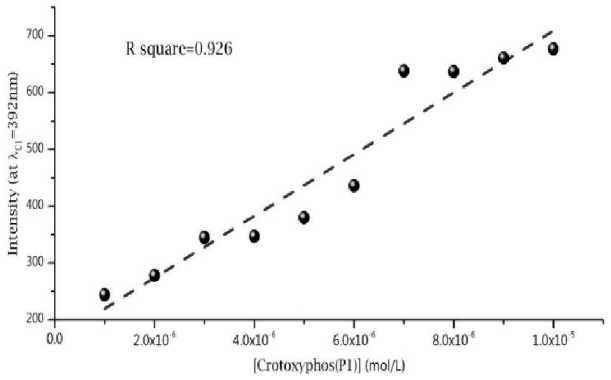

Figure (6): Calibration plot for estimating P1 using Eu(III)-C_1 at 22°C.

Determining Binding Constant (K_b)

The binding constants (K_b) at different temperatures were calculated based on Benesi-Hildebrand equation (eq. 1) (El-Shekheby *et al.,* 2014; Dalapati *et al.,*2011).

$$\frac{1}{F - F_0} = \alpha + \frac{\alpha}{K_b[Q]} \text{ , where } \alpha = \frac{1}{F_L - F_0} \qquad (1)$$

Where [Q] represents the analytical concentration of P1, F_0 and F are the fluorescence intensities in the absence and presence of Crrotoxyphos pesticide and $\alpha = \frac{1}{F_L - F_0}$.

Figure (7) illustrates the relation 1/[P1] versus 1/F-F_0 at three temperatures; 22, 30 and 40°C. From slope and intercept the binding constant was calculated at each temperature. K_d= 4.2×10^3, 15.6×10^3, 52×10^3L.mol^{-1} at 22, 30 and 40°c respectively (Table 2).

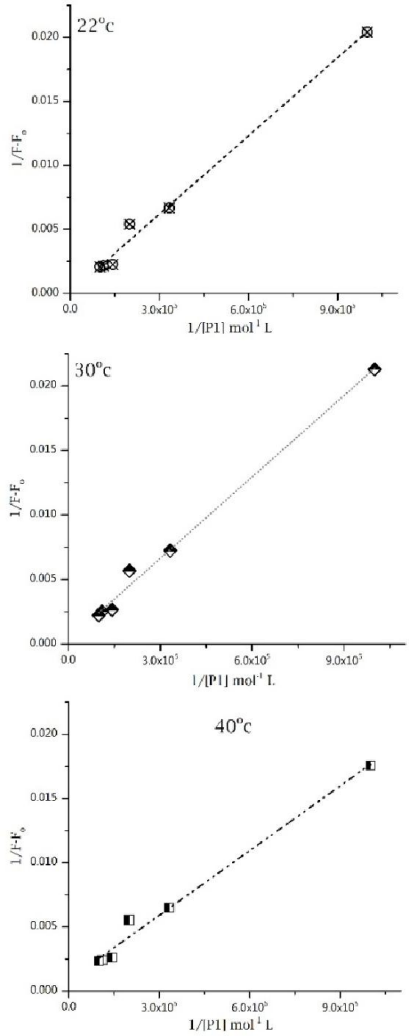

Figure (7): Benesi-Hildebrand and relation plot1/F-F_0 versus 1/[P1] in ethanol at different temperature 22, 30 and 40 °c with correlation coefficient (R^2) 0.991, 0.993 and 0.986 respectively.

Thermodynamic Parameters and the Nature of the Binding Forces

The binding constant values dependence on temperature was calculated in order to get more information about the forces acting between P1 and Eu(III)-C_1.The thermodynamic parameters, enthalpy change (ΔH), entropy change (ΔS) and Gibbs energy change (ΔG) are the main quantities utilized to determine the binding mode. The thermodynamic parameters were deduced using Eq. 2-3. The ΔH and ΔS of the binding reaction were the main thermodynamic parameter to determine binding modes. From The thermodynamic standpoint, where ΔH>0 and ΔS>0 reflects a hydrophobic interaction; ΔH<0 and ΔS<0 reflects the Vander Waals force or hydrogen bond formation and ΔH<0 and ΔS>0 suggesting an electrostatic force (Ross and Subramanian, 1981). The binding constant K_b was deduced utilizing Benesi-

Hildebrand equation, then using Van't Hoff equation (eq. 2) (Azab *et al.,*2013).

$$LnK_b=-[\Delta H/RT]+[\Delta S/R] \qquad (2)$$

Figure (8) shows Van't Hoff plot for P1 with Eu(III)-C_1 with correlation coefficient R^2=0.995. The plot is linear relationship with negative slope, the reaction is endothermic interaction between P1 with Eu(III)-C_1. The thermodynamic parameters are collected in Table 2, where the enthalpy ΔH=107 KJ.mol^{-1}, accompanied with entropy ΔS=432 J.K^{-1}mol^{-1}. In this case the interaction could be attributed to hydrophobic type. Gibbs free energy calculated at different temperatures using standard Gibbs free energy equation (eq. 3) (Atkins *et al.,* 2009), the negative values of free energy change ΔG^0 associated with the reaction indicated that the interaction of Eu(III)-C_1 complex with pesticide is spontaneous (ΔG_{295}=-20.6, ΔG_{303}=-24.07, ΔG_{313}=-28.39 KJ.mol^{-1}).

$$\Delta G = \Delta H - T\Delta S \quad \text{(Error! Bookmark not defined.)}$$

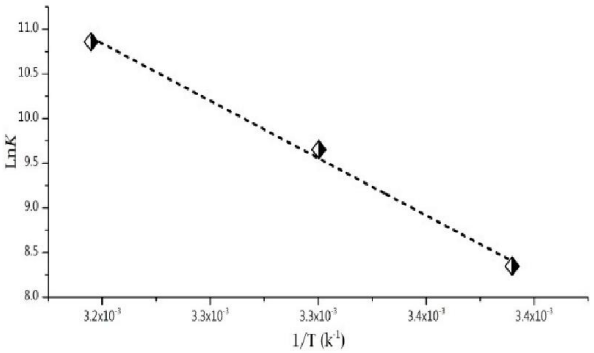

Figure (8): Van't Hoff plot for interaction of Eu(III)-C_1 with Crotoxyphos (P1) in Ethanol.

Table (2): Thermodynamic parameters involve the interaction of Eu(III)-C_1 with Crotoxyphos.

Thermodynamic Parameter	Temperature		
	295 K	303 K	313K
K_b (L·mol^{-1})	4.2×10^3	15.6×10^3	52×10^3
ΔH (KJ.mol^{-1})		107	
ΔS (J·mol^{-1}K^{-1})		432	
ΔG (KJ.mol^{-1})	-20.6	-24.1	-28.4

Effect of interfering ions on estimation of Crotoxyphos using Eu(III)-C_1 complex:

Pesticides in environment present with varieties of natural occurring salts and may be other contaminates(Manahan, 2010).In order to develop selective probe for detection of Crotoxyphos using Eu(III)-C_1complex the effect of interfering anions and cations present in environment must be studied. Table (4) summarizes the data obtained from studying most important anion, cation and also the interference of other pesticides.

Table (3): Effect of interfering Anions, Cations, and Pesticides on fluorescence spectra of Eu(III)-C_1 complex with Crotoxyphos.

Interfering Anion Tolerance 5% (mg/L)		Interfering Cation Tolerance 5% (mg/L)		Interfering Pesticides Tolerance 5% (mg/L)	
HPO_4^{2-}	0.01	Ni^{2+}	0.09	Dichlorvos	5.52
NO_3^-	0.1	NH_4^+	0.27		
CO_3^{2-}	0.54	Na^+	0.29	Chlorpyrifos	17.53
$H_2PO_4^-$	0.01	K^+	0.39		
Br^-	0.4	Pb^{2+}	1.06	Paraoxon	6.88
		Cd^{2+}	0.34		
I^-	0.69	Ca^{2+}	0.6	Endosulfan	4.07

CONCLUSION

7-hydroxy coumarin-4-aceticacid reacts rapidly with Eu(III) in solution and also rapidly interacted with pesticides under study. Promising selectivity toward Crotoxyphos in μM-range. Future study focus on introducing allyl group to C_1 ligand in order to prepare molecularly imprinted polymers (MIP) for detection of Organophosphorous pesticides specially Crotoxyphos able to be used commercially in environmental analysis.

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الكشف الومضي لمبيد الكروتوكسيفوس بإستخدام متراكب الأوروبيوم مع مشتق الكومارين

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متراكب الاوروبيوم الوامض مع مركب ٧- هيدروكسي- كومارين -٤- حامض الاسيتيكتم، تم دراسة ككاشف عن المبيدات الفوسفاتية. ويظهر المتراكب تفاعل لافت مع مبيد الكروتوكسيفوس، حيث أن الطيف الومضي للمتراكب تزيد بزيادة تركيز الكروتوكسيفوس. وتم احتساب الحد من الكشف = ١.٨٦ مكرومول/لتر و الحد من الكميات = ٦.١٩ مكرومول/لتر. وقد تم حساب كلاً من ثابت التفاعل بين المتراكب والمبيد باستخدام معادلة بنيزي-هيلدبراند (Kb) وحساب عوامل الديناميكا الحرارية ΔH, ΔS, ΔG باستخدام معادلة فانت-هوف للتفاعل متراكب الأوروبيوم مع الكروتوكسيفوس في الإيثانول لتحديد طبيعة التفاعل. وأخيراً تم دراسة اثر تداخل من مختلف الأنيوناتوالكاتيونات ويعض المبيدات والتي قد تتواجد في البيئة على تقدير الكروتوكسيفوس بإستخدام متراكب الأوروبيوم في الإيثانول.