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Natural Dyes in Cyanide and Anion Sensing

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Cyanide is one of anions of concern due to its high toxicity. It causes death at a low dosage (2.6 mM) and the allowable level should be lower than 1.9 mmolar according to World health Organization (WHO). Cyanide contamination in the environment comes from many sources as metallurgy, gold mining, cyanide fishing, manufacturing acrylonitriles and related polymers, and natural sources. Cyanide also is present in some foods and food products such as cassava, bitter almonds, apple seeds, and some beans. The wide spread of cyanide in these food is of concern and the levels should be monitored and evaluated. In addition cyanide, may leak and get into water bodies or soil accidentally or intentionally, therefore, developing an easy, simple method for its detection is a priority. Many methods have been developed for detection of cyanide and anions such as titrations, distillations, GC-ECD, and spectrophotometrically. Colorimetric methods have been developed which are easy and simple that can give qualitative results visually and quantitatively using absorption or fluorescence spectroscopy. We have tuned into using dyes and natural dyes that are none toxic and available to use as visual (colorimetric) using both absorption and fluorescence techniques. Curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione] is obtained from dry rhizomes of Curcuma longa, as the main yellow pigment used as spices, cosmetic and traditional medicine. It has been reported that curcumin also has many pharmacological functions like antioxygenation, antibiosis and antitumor. Despite the fact that extensive colorimetric and related photophysical studies of curcumin has been extensively studied, less study has done on its potentiality in application as a colorimetric and naked eye sensor of biologically and environmentally important anions like fluoride, acetate and phosphate. Some studies reported interaction of curcumin with cyclodextrin based on changes in basicity in acetonitrile which showed its importance in supramolecular chemistry. We herein describe a simple and efficient visible colorimeric cyanide and fluoride ions detection using commercially available curcumin as a receptor. The method could allow application in detection of curcumin, fluoride and cyanide, important chemical and biological species The choice of curcumin as a sensor for anion was mainly based on the fact that curcumin is a phenol and therefore exist in a equilibrium between its

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protonated and deprotonated forms in relatively basic media. It also contains a carbonyl group succeptable to nucleophilic addition, this will make it have two anion receptors., hydroxyl for hydrogen bonding to associate with basic anions. The carbonyl is areceptor for nucleophilc anions such as cyanide. Due to this reason curcumin can interact differently with different anions and enhance its selectivity based on the sovent choice. It will behave as a chemodosimeter. Acetonitrile, a polar aprotic solvent is is a good media for the analysis, it does not compete with anion in the recognition sites of curcumin. Variation in color changes of curcumin in acetonitrile was done by addition of aliquots of various anions as tetrabutylammonium salts. Addition of fluoride and cyanide ions induced color change from yellow, purple, blue to deep blue with intensity at every level dependent on the fluoride ion concentration. Acetate ion changed the color of solution to light purple, while dihydrogen phosphate induced only a tinge of color enhancement. Chloride, bromide and perchlorate were found to show no effect on the solution of curcumin. In an aquaeous acetonitrile solution the effect was observed only for cyanide only with a clear color change from yellow to red. While other anions had no significant effect. This indicates that the mechanism of interaction is based on nucleophilic addition in the case of cyanide in aqueous media and hydrogen bonding in nonpeotoc solvents. The stoichiometry was determinned to be 1:1 for cyanide and 1:2 for fluoride. The binding constants and detection limits were calculated form the UV-vis absorption titrations. In this presentation the method, structures of dye and complexes, the titration curves, color changes, binding constants and aplication will be discussed.

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