Cairo University

EXCITED STATE INTERACTIONS OF URANYL ION

Thesis Submitted By

AMR ABD EL-NABY IBRAHIM ESSAWY
B.Sc.(Chemistry) 2000

To

CHEMISTRY DEPARTEMENT FACULTY OF SCIENCE CAIRO
UNIVERSITY (FAYOUM BRANCH)

In
PARTIAL FULFILLMENT OF THE REQUIREMENT

For

M.Sc. DEGREE IN CHEMISTRY

Thesis Advisors

Prof. Dr. M. S. A. Abdel-Mottaleb
Professor of Chemistry, Director of the Photoenergy Center

Dr. S. M. El-Medani
Assistant Professor of inorganic chemistry, Faculty of Science at
Fayoum

2003

English Summary

Summary

During the past decads the actinide elements have been attracted intense experimental and theoretical interest. The reasons for this are of course, that they are radioactive, chemically toxic and of great importance for the nuclear power industry.

The uranyl ion is the most important species in the aqueous chemistry of uranium where it has several attractive features:-

1) It has an absorption band in the visible range (413nm) and absorbs strongly in the near UV.
2) Highly stable, readily soluble and mobile.
3) Its excited state has a long life time (1 l|xs in water).
4) It is a strong excited state electron acceptor.
5) Forms many complexes.

From all these aspects, this study includes the excited state interactions of uranyl ion as a potent oxidant that helps in the oxidation of several organic compounds which inturn effords a methods for the removal of pollutants that may present in air and water.

The objective of this work is to study the influence of the different advanced oxidation technologies on the removal of 3,5- dinitro salicylic acid (DNS) and salicylic acid (SA) [as an examples of aromatic compounds that have dangerous effects and a relatively high degree of solubility in water] by using UV-Visible photolysis then comparing the effeciency of photolysis by using different techniques such as

homogeneous (H_20_2), heterogeneous (Ti02) photocatalysis, and the new • ♦ * 9 i. trend involving excited state uranyl ion (UO2).

This thesis consists of three chapters:

Chapter 1 deals with a general introduction of the subject. In **chapter 2,** the experimental procedures and instrumentations used are presented.

We have used the following spectroscopic methods for following up the light-induced interactions:-

- UV-Visible absorption spectroscopy.
- Fluorescence spectroscopy.

Moreover, TOC analysis was performed to confirm the suggested degradation mechanism. Methods used for data treatments and handling such as chemical kinetics and determination of the apparent formation constant are included.

In **chapter 3,** we reported the results obtained as follows:- ***a-***

Spectroscopic characteristics.

Both of absorption and Fluorescence spectra of uranyl nitrate, DNS, and SA were recorded where a relatively characteristic absorption peaks are obtained at 413, 358, 295nm, respectively. Both of uranyl nitrate and SA show characteristic fluorescence spectra, unlike DNS where it has been found to be non-luminescent.

Also the influence of different concentrations of uranyl nitrate on the absorption and fluorescence spectra of SA and on the absorption spectrum of DNS, and the addition of these compounds on the absorption and fluoresence spectra of uranyl ion where it has been noticed that imder this conditions there is no ability for complex formation between uranyl ion and DNS while a ground state complexation between uranyl ion and SA have been established. These observations are confirmed by fluorescence quenching studies that refer to a pure dynamic collisional quenching in case of uranyl ion and DNS. But the quenching of fluorescence spectrum of uranyl ion via addition of different concentrations of SA is obeyed to Stern-Volmer equation at concentrations of SA (quencher) ranges from (0.1-20)X10"^{5}M, but at higher concentrations of SA than 20X10"^{5}M, the quenching of fluorescence intensity could be attributed to complex formation between uranyl ion and such high concentrations of SA.

b- Photostability of DNS and SA.

It was found that DNS and SA have a high degree of photostability and direct photolysis has not been found effective in their degradation.

c- Light- Induced interactions in presence of uranyl ion. Upon irradiation of a mixture contains uranyl nitrate and DNS in constant concentration and in different media (aqueous, in presence of HCIO4 and in presence of NaOH solutions), a remarkable change in the absorption spectrum of the mixture DNS and uranyl ion was observed due to photodegradation of DNS. It was found that the photodegradation reactions obey first order kinetics and the photodegradation rate of DNS in presence of traces of NaOH solution was faster by one order of magnitude than that performed without adding NaOH solution. These results could be due to the formation of the less stable sodium salt of the phenoxyl radical of the DNS and/or the more reactive Na02* and O2*" species.

Also the addition of H2O2 to a mixture contains uranyl ion and DNS in the presence of HCIO4, leads to the photodegradation of DNS much rapidly if it is compared with the photodegradation of DNS (in aqueous medium, in presence of HCIO4, and in presence of NaOH).

Unlike DNS, it was found that, irradiation of a mixture contains uranyl ion and SA in constant concentrations (in the form of complex) under the same previous media increase the absorption peak of the formed {UO2 - SA} complex at 363nm refering to a photoinduced complexation process where the value of K_{app} of the formed photo-induced complex obeys a Benesi-Hildebrand equation where the intervals of irradiation is the factor of increasing complex formation. Also it was found that K_{app} has the maximum value in presence of perchloric acid (i.e. in presence of excess [H*"]), while the minimum value of K_{app} was in presence of H2O2 due to the formation of OH* radicals (very efficient oxidizing species) that lead to degradation of the formed complex. The following could be concluded:-

1) uranyl ion is more efficient catalyst than H_20_2 in the photodegradation of DNS.
2) The interaction between uranyl ion and SA is occured via a photo-induced process involves the phototransformation of SA from the free form to the complexed form.
3) The photodegradation of SA takes place markedly in the presence of $H20_2$ as a homogeneous oxidizing agent.
4) Addition of micelles in the reaction medium decreases the efficiency of the photodegradation of DNS and SA due to the retardation of the oxidizing effeicency of the used catalyst (i.e. uranyl ion in case of DNS and H2O2 in case of SA).

d- Photocatalytic degradation in heterogeneous media. A high degree of light response for DNS and SA have been observed in presence of aqueous solution of colloidal Ti02 nano-particles where the photodegradation of SA occurs by a faster rate if its compared with DNS. This could be attributed to the inductive effect of the two nitro groups which inturn increase the stability of DNS molecules as a result of increasing its electronic resonance.

e- Total organic carbon (TOC) analysis.

It was found that when measuring the amount of total organic carbon for a mixture of aqeous DNS and uranyl nitrate before and after illumination, a noticeable decrease in the amount of TOC is observed. These results suggest that complete degradation of DNS by $*U0_2^{2+}$ ion takes place. These is in complete agreements with the findings of phenolic compounds (similar compounds), where complete mineralization is achieved by the photolysis of DNS.