Coming Trends of Radiation Effects on Transition Metal Hydrates, Complexes and Environmentally Benign Substances- A Review

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ABSTRACT

A review is present on recent work on the influence of radiation effect on transition metal hydrates, complexes and environmentally benign substances. On the basis of the result radiation induced changes of materials in various physico-chemical properties can be exploited. Radiation is one of the most novel means for chemical damage. Surface morphological changes were also seen due to radiation damage.

Keywords: Radiation, spectral, thermal, particle size, antimicrobial.

INTRODUCTION

The interaction of radiations depends on mass, electrical charge, energy, and on the composition of the surrounding materials. Gamma rays belong to ionizing radiation are the most energetic form of such electromagnetic radiation. Therefore, they are more penetrating than other types of radiation such as alpha and beta rays. Gamma radiation can be useful for the alteration of physical, chemical and biochemical properties of materials. Solid state irradiation leads to lattice defect and chemical damage. Collective information on the effect of radiation and chemical damage has a greatest interest in interdisciplinary sciences. However due to practical difficulty such kind of combined data are scare. The present investigation focuses the effect of irradiation leading to defect production which inturn leads to the changes on physico-chemical and pharmacokinetic properties of the substances.

Generation sources and units

$^{60}$Co and $^{137}$Cs are the most suitable gamma radiation sources for processing because of the relatively high energy of their gamma rays and fairly long half-life. Currently, all
Radiation processing facilities employ $^{60}$Co as the gamma radiation source. Natural as well as artificial radioactive isotopes have been used as generator of radiation products. Measurement in radiation treatment is based on the amount of energy deposited in the material being treated and is referred to as the absorbed dose. Ionizing radiation doses may be quoted as gray (Gy), kilogram (kGy), rad, kilorad (krad) or megarad (Mrad) of which Gray is the international unit.

**Radiation induced decomposition of crystalline solids.**

In crystalline solids the interaction of ionization radiation is very complex and is usually described on the basis of mainly two factors, primary interactions and secondary interactions. In most cases only the stable final products are actually observed. Depending on the crystalline nature, different solids behave differently under irradiation. Radiation induced decomposition has been studied in many crystalline salts having oxy anions, numerous organic compounds, polymers and a few transition metal complexes. Studies concerning radiation effects of different substances over the past decades are shown in (Figure 1). Radiation effects can also be studied through PXRD, spectral, surface morphological and thermal techniques are briefly reviewed.

**Studies of radiation effects on different substances**

![Image](image.png)

*Figure 1 shows radiation effects of transition materials over the past decades.*

**Powder X-ray diffraction studies of irradiated materials**

PXRD method is a well-known tool to study the phase transformation and also for microstructural characterization for most of the inorganic materials after heavy ion irradiation. Powder X-ray diffraction pattern of crystalline solids are considerably affected by irradiation. The effect of gamma irradiation on PXRD of inorganic complexes is studied in many researches. M.S.Refat *et al.* studied Ca(II), Mg(II), Sr(II) and Ba(II) aspirinate complexes with a dose of 80Gy. The average grain size of the samples was estimated with the help of the Scherrer equation. A definite line broadening of the PXRD peaks is an indication that the synthesized materials are in the nano meter range. I.S.Sumithra *et al.* reported the PXRD of diaquamalonatomanganese(II) shows structural changes after irradiation and orthorhombic geometry was found to be retained after irradiation.
Gamma irradiated Ni (II) tetraphenylporphyrin thin films shows the formation of amorphous nanostructure. ZnO film showed decreased in grain size while that of SHI irradiated ZnO thin film showed increase in grain size. Effect of gamma irradiation on PXRD of SiO$_2$ xerogel doped with Fe$_2$O$_3$ has been reported. Slight decrease in the intensities of the XRD peaks after irradiation reveals that gamma irradiation in the applied dose (60 kGy) creates only minor dislocations in the crystal lattice.

Studies on PXRD of effect of gamma-irradiation on the surface and catalytic properties of Co$_3$O$_4$ doped with NiO were investigated. The result revealed that gamma irradiation upto 0.8 MGy caused a measurable decrease in crystalline size and increase in degree of ordering. Irradiation brought a significant decrease in the particle size of Co$_3$O$_4$ phase and subsequent increase in surface area. The effect of 120 MeV Ag$^{9+}$ ion irradiation on the structural properties of NaSr$_{1-x}$BO$_3$: xSm$^{3+}$ ($x = 0.5-2.5$ mol%) phosphor, has been reported. The as-prepared as well as irradiated samples were characterized by PXRD techniques. After irradiation, the structure of the phosphor did not change except that the loss of crystallinity which may be due to the fragmentation caused by the SHI.

Effect of irradiation on PXRD pattern of inorganic complexes and salts, organic compounds, antibiotics, polymers, natural products, technologically important materials, etc. have been studied. X-ray diffraction pattern of crystalline solids are considerably affected by irradiation. The observed general effects include changes in lattice parameters, crystallinity and intensity of peaks. Particle size may be changed by irradiation. In certain systems no significant changes are observed.

SPECTROSCOPIC STUDIES

Radiation induced transformations in materials can be studied by spectroscopic techniques. The various spectroscopic techniques include FTIR, UV Visible, Photoluminescence, etc.

1. Infrared spectral studies

Fourier transform infrared analysis (FTIR) has been one of the most powerful techniques applied to monitor the structural as well as chemical changes that occur in materials upon irradiation. The IR peaks are characterized by the vibrational frequency, shape and intensity. The reported investigations suggested that these characteristics are considerably affected by irradiation.

Various bands present in IR spectrum are corresponding to the characteristics functional group and bonds present in a substance. The functional groups have absorption which is characteristics not only in position but also in intensity. Moreover the shape of IR band provides information regarding molecular environment and morphology of the substance. Hence FTIR is widely used for studying the irradiated materials. Vibrational spectra can be readily used to identify the presence of defect groups or radiation-induced defects.

Moreover any shift in peak position in a spectrum directly refers to a change in bond strength or bond angle. Weakening and strengthening of a bond shifts the wave number of the
corresponding absorption peak to lower and higher values, respectively. Absence of a particular molecular bond relates to scission or break in the particular bonding structure. Variation in intensity of particular peak in a spectrum correlates to the proportion of that functional group present in the material. Change in intensity of IR peaks of irradiated materials has been observed in almost all the cases.

Infrared spectra of irradiated metal complexes, inorganic compounds, glasses, organic compounds and polymers have been investigated. The observed effects due to irradiation include shift in peak position, variation in intensity and shape of spectral bands. Appearance of new bands is observed in some cases. In most cases neither appearance of new bands nor disappearance of existing bands were observed in the irradiated samples. Cases in which no significant changes recorded have also been reported.

2. Electronic spectral studies

UV–Vis spectra are important item for most chemical characterization to get important information about the structural aspects of complexes. The effect of γ-rays have been studied on aqueous solutions of Copper(II) Complexes containing (substituted salicylic acid and benzoin semicarbazone) has been reported. Results indicated that copper (II) was reduced to copper (I) and a charge transfer between metal ion and ligands in some complexes were noticed. Some complexes have been completely decomposed while others did not affect by the radiolysis.

Effect of gamma irradiation on electronic spectra of some inorganic complexes and salts, organic compounds, polymers and glasses have been studied. Shifting and broadening of peaks is observed as a result of gamma irradiation in most of the cases. Variation in intensity of peaks is brought about by irradiation.

3. Photoluminescence

Luminescence spectroscopy provides detailed information of emitting state distortions as well as an understanding of competing non-radiative processes. Furthermore, luminescence techniques provide a means to probe the nature of the ground state in much more detail than afforded from vibrational spectroscopic methods. The change in fundamental spectroscopic parameters can be related to changes in molecular structure and bonding properties.

The photoluminescence spectrum (PL) is obtained by the selection of a single excitation wavelength, followed by the spectroscopic scanning of multiple emission wavelengths. The micro-structural changes occurring due to gamma irradiation are identified by the peaks and bands in the PL spectroscopy. Effect of gamma radiation on photoluminescence Properties of Copper (II)-picolinate Complex was studied. Quenching of photoluminescence was observed upon γ-irradiation. The single crystal of tris(thiourea)zinc sulphate (Zn[CS(NH$_2$)$_2$]SO$_4$) was irradiated by 150 MeV Au$^{9+}$ swift heavy ions and analyzed in comparison with pure crystal for crystalline perfection and optical properties. The defects induced by heavy ions act as the color centers and resulted in enhancement of photoluminescence emission intensity.
The effect of gamma irradiation on photoluminescence of diaquamalonatomanganese (II) was investigated. PL intensity is found to be increased and the band positions are found to be slightly shifted upon irradiation. Effect of irradiation on photoluminescence spectra of inorganic complexes and salts, organic compounds, technologically important materials, glasses and polymers have been studied under different sources of irradiation. In most cases the PL intensity was found to be changed. Broadening and shifting of existing bands and appearance of additional bands were also observed. Research output in the field of irradiation effects on spectral studies of transition metals as shown in (Figure 2).

Surface morphological studies by AFM

AFM measurements provide information regarding shape, height and diameter of nanostructures, roughness, particle size, pore size, etc. The Roughness value obtained from this study is accounted by different parameters such as average roughness (Ra), root-mean-square surface roughness (Rq) and Rmax. Hillocks, cones, craters, nodules etc are commonly encountered in AFM images. Formation of the hillocks results mostly from a physical reorganization of the molecules. It is well known that solid state irradiation of molecular crystals leads to crystal defects and chemical damage. The extended lattice defects and displacements thus generated are likely to facilitate the collective movement of molecules leading to the formation of large number of hillocks.

The formation of protrusions has been explained in terms of radiation damage and the thermal spike model. Due to the radiation damage the crater areas contain numerous dangling bonds which can favour accumulation of water molecules or hydroxyl groups that leads to the appearance of artificial centrally located protrusions in craters or complete conversion of craters into hillocks in the AFM images.
Development of local stress or strain is likely in irradiated solids. In this situation additional hillock formation occurs which corresponds to the onset of surface roughening. The increase in roughness may also be due to conformational changes induced by gamma irradiation. Thus larger the number of hillocks and protrusions higher will be the roughness while a reduction implies smoothening.

The effect of irradiation on surface morphology of various substances like technologically important materials, polymers and natural products has been studied by AFM. Different sources of irradiation were used. Defect formation, change in surface roughness, pore size, grain size and particle shape were reported. In some cases there were no significant changes in surface morphology.

**Antimicrobial studies of gamma irradiated compounds**

Some recent studies have suggested that gamma irradiation is effective for improving certain beneficial biological properties of materials. A search of the available literature revealed that antimicrobial properties of synthetic as well as natural materials are affected by irradiation. The reported investigations indicate that the biological activities of natural as well as synthetic substances are sensitive to radiation treatment.

**Thermo-gravimetric studies**

An abundant literature is available on the effect of gamma irradiation on thermal decomposition kinetics of crystalline solids containing oxy anions while the same in transition metal complexes are limited. Literature survey revealed that thermal process is enhanced upon irradiation in most cases with a few exceptions where the reverse is true. It is established that pre-treatment with energetic radiation can accelerate the thermal decomposition of solids.

Effect of gamma irradiation on thermal decomposition kinetics of various acetates has been studied by isothermal and non-isothermal methods. Results of isothermal studies in acetates of uranium, thallium, palladium, cobalt, samarium, gadolinium and erbium revealed that irradiation enhances decomposition in all cases except in that of cobalt and gadolinium where it was found to be retarded. Nair et al. studied the effect of gamma irradiation on the thermal decomposition of bromates of barium, calcium, strontium, sodium, potassium, magnesium, zinc, and cadmium. Kinetic analysis revealed that irradiation enhances the decomposition and the effect increases with the irradiation dose. The activation energy is decreased upon irradiation. The mechanism for the thermal decomposition was also established.

Nair et al studied the effect of gamma irradiation on thermal decomposition of nitrates of lead, strontium and barium. Non-isothermal data were analysed by Coats-Redfern, Freeman-Carroll and Horowitz-Metzger methods and the reaction mechanism was established for each stage. Similarly lanthanum nitrate and cadmium nitrate were also studied. Effect of gamma irradiation on thermal decomposition of various ionic oxalates has been investigated. Effect of gamma irradiation on isothermal decomposition kinetics of malonato, succinato and crotonato complexes of cobalt was studied. In cobalt (II) malonato complex the activation energy for the dehydration stage decreased upon irradiation while that
for the decomposition stage remained the same. The kinetics of decomposition is controlled by first order mechanism while the dehydration is controlled by phase boundary mechanism. In succinate complex irradiation enhanced both the decomposition and dehydration reactions without modifying their mechanisms. The activation energy decreased with increased dose. In crotonato complex irradiation enhances the decomposition without modifying its mechanism.

The effects of pre-irradiation on the isothermal decomposition kinetics of hexamine cobalt (II) chloride have been investigated. It was observed that pre-treatment reduced the length of the induction period and increased the rate of decomposition without modification of the mechanism of decomposition, which has been shown to proceed by a nucleation and growth process. The activation energy reduced from 46.8 to 20.2 kJmol\(^{-1}\) upon irradiation.

The thermal decomposition of gamma-irradiated complexes of mandel hydroxamic acid with Co(II), Mn(II), Ba(II), and Cd(II), were studied under isothermal condition. The effect of gamma-irradiation on the kinetic parameters of thermal decomposition is discussed. Radiation accelerated the dehydration steps in the case of Co (II), and Mn (II), complexes but did not modify the mechanism. Effect of gamma-irradiation on non-isothermal decomposition of tris(1,2-diaminoethane) Cobalt(II) Sulphate and tris(1,2-diaminoethane)nickel(II)sulphate have been studied. Kinetic parameters E, Z and ΔS were evaluated by Coats-Redfern, Freeman-Carroll and Horowitz-Metzger equations. Results showed that irradiation enhanced thermal decomposition, lowering thermal as well as kinetic parameters. Mechanism of decomposition for each stage has been established. In the former case irradiation modifies the mechanism of the first stage of decomposition from R\(_2\) to R\(_3\) while in the later both unirradiated and irradiated samples follow the R\(_3\) function. Isothermal decomposition of unirradiated and gamma irradiated zirconium acetyl acetone using 1000 kGy absorbed dose was carried out in static air. Both model free and model fitting approaches were applied for the determination of the kinetic and thermodynamic parameters. It was found that \(\gamma\)-irradiation has almost no significant effect on the thermal behaviour up to the absorbed dose of 10\(^3\) kGy.

Thermogravimetric analysis was conducted to a series of natural rubber/recycled ethylene-propylene-diene rubber blends irradiated with electron beam. The obtained TG profiles and the calculated kinetic parameters indicated that introducing electron beam irradiation into the blends enhanced the thermal stability of the blends irrespective of pre-vulcanising time or irradiation dose. Gamma irradiation effects on the thermal decomposition behaviour of piperacillin were also studied. A degradation mechanism was suggested. Effects of gamma radiation on the thermal properties of poly(L-lactic acid)/ethylene-co-vinyl acetate blends with various blend ratios were investigated. The TGA showed that the irradiated blends were less thermally stable than the unirradiated blends, at higher temperatures the opposite situation was seen. Effects of gamma radiation on thermal decomposition of various inorganic salts are extensively studied while the same in metal complexes are scanty. Similar studies have been reported in some organic compounds and polymers. It is established that pre-treatment with energetic radiation effect the thermal decomposition kinetics. Generally irradiation enhances thermal decomposition thereby lowering thermal as well as kinetic parameters. In isothermal
decomposition studies it was observed that pre-treatment reduces the length of the induction period and increases the rate of decomposition with or without modifying the mechanism of decomposition. Exceptions are also reported in which irradiation retard the thermal process.

In the present investigation tries to study the irradiation effects and radiation damage using various physicochemical properties on inorganic salts, metal complexes, polymers and alloys, etc.7, 96-100.

CONCLUSIONS

The observed general effects of powder X-ray diffraction studies include changes in lattice parameters, crystallinity and intensity of peaks. Particle size may be changed by irradiation. In certain systems no significant changes are observed. Infrared spectra of most of the irradiated materials shows shift in peak position, variation in intensity and shape of spectral bands. In the electronic spectral studies shows shifting, broadening and variation in intensity of peaks is observed as a result of gamma irradiation. In most cases the PL intensity was found to be changed. Broadening and shifting of existing bands and appearance of additional bands were also observed. AFM studies revealed that irradiation is capable of changing the surface defect, roughness, size and shape of particles. The biological activities of natural as well as synthetic substances are sensitive to radiation treatment. Generally irradiation enhances thermal decomposition thereby lowering thermal as well as kinetic parameters.

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