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Effect of gamma irradiation on the ion exchange capacity of polyaniline

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HIGHLIGHTS

- Effect of γ-irradiation upto 3.6 MGy (cumulative dose) on polyaniline was studied.
- Elemental composition of PAni gets modified on irradiation.
- FT-IR analysis indicated that PAni is fairly stable towards gamma irradiation.
- Chloride–PAni is more stable towards γ-irradiation, compared to base-PAni.
- Ion exchange capacities indicated better radiation stability of PAni than that of Dowex 1 × 8.

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ABSTRACT

Polyaniline (PAni) was synthesized by a chemical oxidation of aniline, using ammonium persulphate in 1 M HCl and was investigated for radiation stability. The chloride salt as well as the base form of PAni (in air, water and HCl media) was subjected to gamma radiation using a ^{60}Co source. Radiation induced effect on the stability of PAni was evaluated by the data obtained from elemental analysis and Fourier Transform Infrared (FT-IR) spectroscopy. Anion exchange capacities of PAni before and after gamma irradiation were determined by the neutron activation analysis technique from the measured chloride activity. The ion exchange capacity decreased with increase in the absorbed dose. Chloride form of PAni was more stable towards gamma-radiation compared to the base form.

1. Introduction

Polyaniline (PAni), one of the well-known conducting polymers, has been extensively studied by researchers during the last two decades, because of its high electrical conductivity, reversible redox properties, environmental stability and ease of preparation (Chiang and Mac Diarmid, 1986; Epstein and Mac Diarmid, 1995; Mac Diarmid and Epstein, 1989; Mac Diarmid et al., 1985; Travers et al., 1985). PAni is an oxidation product of aniline, and can be synthesized electrochemically as a film and through the thermo-chemical route in powder form. The chemical route of synthesis involves the oxidation of aniline by ammonium peroxydisulfate or potassium dichromate in HCl/H_2SO_4 medium (Cao et al., 1989).

PAni has been shown to possess ion exchange properties (Syed and Dinesan, 1991, 1990). It has been used for the separation of noble metals Pt, Pd, Ir, and Au (Kumar et al., 1993) and mercury from aqueous solution (Ansari and Raofie, 2006; Ghorbani et al., 2011; Remya Devi et al., 2006). Excellent chemical stability of PAni in both stongly acidic and alkaline media has been reported (Brozova et al., 2008).

Synthetic organic ion exchangers are extensively used in the nuclear industry for processing highly radioactive solutions. The radiation stability of the ion exchanger is the key factor for its use in radioactive environment. Ionizing radiations (alpha, beta, gamma and X-ray) alter the properties of organic ion exchanger significantly (Pillay, 1986; Smith and Groh, 1961). Effects of gamma radiation on commercially available organic ion exchangers had been reported by Remya Devi et al. (2010).

Objective of the present work is to study the effects of gamma irradiation on the anion exchange capacity of PAni for its possible use in radioactive environment. Effects of ionizing radiation on the electrical properties of PAni are available in literature (Bhadra and Khastgir, 2007; Kane et al., 2010; Sevil et al., 2003; Sonkawade et al., 2010). To the best of our knowledge, the impact of ionizing radiation on the ion exchange properties of PAni has not been reported till date. The range of cumulative gamma radiation dose for this study has been chosen as 1.2–3.6 MGy, anticipating the highest/most severe radiation damage to PAni, during most of the practical ion exchange applications in radioactive environments. Radiation induced effect on the stability of PAni was evaluated by

Abbreviations: PAni, Polyaniline; NAA, Neutron Activation Analysis; meq g^{-1}, milli-equivalents per gram (unit for expressing ion exchange capacity)

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the data obtained from elemental analysis and Fourier Transform Infrared (FT-IR) spectroscopy.

2. Experimental

2.1. Reagents

Aniline (S. D. fine-chem Ltd.) was distilled under atmospheric pressure at elevated temperature (boiling point = 184 °C) and stored in dark glass bottle, prior to use. Ammonium persulphate (Merck, purity: 98.5%), hydrochloric acid (Merck, 11.3 M) and all other reagents were used without further purification. All aqueous solutions were prepared using de-ionized water (Conductivity = 0.05 μs cm^{-1}).

2.2. Synthesis of PAni

PAni was synthesized by the method we used earlier (Kumar et al., 1993; Remya Devi et al., 2006) and a brief description is given here. Aniline (0.55 mol) was dissolved in 1500 mL of 1 M HCl and cooled to 5 °C in an ice bath. Ammonium persulphate (0.55 mol) was added to the above solution with constant stirring, using a mechanical stirrer and the stirring was continued for ~2 h while maintaining the reaction mixture temperature below 5 °C. The reaction mixture was left undisturbed for 24 h and was filtered through a Buchner funnel to separate the precipitate. The precipitate, thus obtained, was washed with excess of 1 M HCl. Finally, the precipitate was washed with acetonitrile and vacuum dried for ~16 h. PAni powder thus obtained was designated as chloride–PAni. Base form of PAni was prepared by equilibrating it with 1 M NH_4OH, followed by washing with deionized water. This was assigned the name base–PAni. Chloride–PAni and base–PAni are thus the salt and neutral forms of PAni respectively.

2.3. Gamma-ray irradiation

Gamma chamber GC-5000 (supplied by M/s BRIT, India) with ^{60}Co gamma radiation source stationed at Radiation Technology Development Division, BARC, Mumbai, India was used for irradiating the PAni samples. The source has a dose rate of 5 kGy h^{-1}, as measured by Fricke dosimetry. Approximately 1 g each of PAni samples (accurately weighed) were subjected to gamma irradiation, in stoppered glass vials (capacity = 50 mL). Base–PAni powder was irradiated in, air as well as water. Chloride–PAni was irradiated in air, water and 1 M HCl media. Volume of the media viz. water and 1 M HCl in each of the irradiation vials was 40 mL. All PAni samples were subjected to cumulative doses of 1.2 MGy, 2.4 MGy and 3.6 MGy.

2.4. FT-IR measurements

Infrared experiments have been performed on unirradiated and irradiated PAni samples, using FT-IR in transmission mode under vacuum. For infrared measurements, PAni sample powders were dispersed in CsI matrix (0.5% w/w) and pelletized. The spectra were recorded using a Bruker Vertex 80V FT-IR Spectrometer in the spectral range 400–4000 cm^{-1}. The spectrometer was equipped with Globar source, KBr beamsplitter and DTGS (MIR) detector. A total of 100 scans at a resolution of 2 cm^{-1} were co-added to get the desired spectra. Background spectrum, recorded under similar conditions, using bare CsI pellet was divided in each case to obtain the transmission spectrum, denuded from instrumental and environmental profiles. The spectra were analyzed using ORIGIN and OPUS (Opus, 2006). All experiments were performed at room temperature.

2.5. Elemental analysis

Carbon, hydrogen and nitrogen in PAni were determined, using a CARLO-ERBA elemental analyzer (Model no. 1106). All the samples were air-dried and desiccated before elemental analysis. Chlorine in PAni was determined by the neutron activation analysis (NAA) technique (Butler and Marsh, 1972). About 5–10 mg of accurately weighed PAni samples alongwith chlorine standards (100 μL of NaCl solution, containing 1 mg of chlorine mL^{-1}) were irradiated for 1 min, in the Pneumatic Carrier Facility of Dhruva reactor (BARC, Mumbai, India). The gamma spectra of the irradiated samples were acquired using HPGe detector (30% relative efficiency, Canberra), coupled to a 16k-channel analyzer. Total chlorine in PAni samples was determined by the relative method of NAA, using ^{38}Cl isotope($t_{1/2}$ = 37.25 min.; gamma energies: 1642.43 and 2167.54 keV) (http:nds.iaea dt. 17th June, 2013).

2.6. Determination of ion exchange capacity

Ion exchange capacities of PAni samples (as ionizable chlorine), were also determined by the NAA technique. Ionizable chlorine in PAni was calculated from the difference between the total chlorine and the non-ionizable (covalently bound) chlorine. In order to determine the total chlorine, PAni samples were converted to chloride form by equilibration with 1 M HCl for 4 h. Excess HCl was washed with deionized water. The chloride–PAni samples were air-dried and total chlorine in PAni samples was determined by the NAA technique (Section 2.5). For determining the non-ionizable chlorine, PAni samples were equilibrated with 1 M NH_4OH, washed with deionized water, air-dried and chlorine was determined as described above. Ion exchange capacities (milli-equivalents of chloride per gram of PAni) were obtained by subtracting the non-ionizable chlorine values from the total chlorine.

3. Results and discussion

The term polyaniline refers to a class of polymers, the base form of which is shown in Fig. 1a (Mac Diarmid and Epstein, 1989). The various oxidation states of PAni are characterized by the ratio of imine to amine nitrogen atoms.

When subjected to high energy radiation, properties of organic polymers may get modified significantly. Extent of these changes

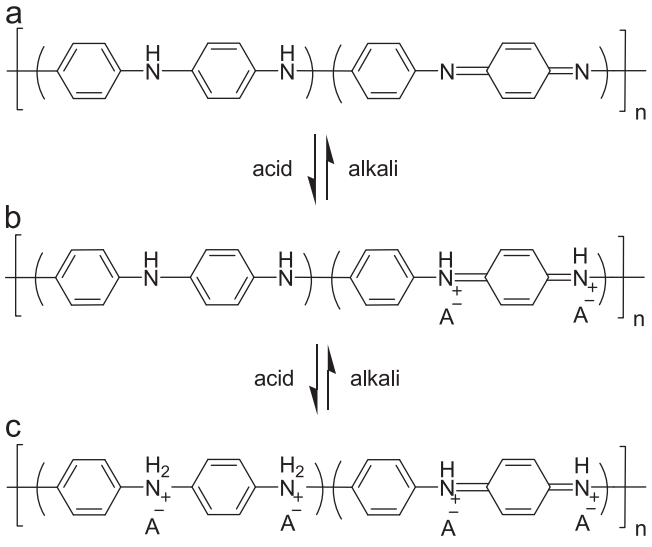

Fig. 1. Structure of emeraldine form of PAni during protonation and deprotonation.