Preparation of Polymeric Adsorbents by Radiation-Induced Graft Polymerization

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Abstract
Adsorption methods using specified adsorbents are economically feasible and environmentally friendly for capturing useful and harmful ions and molecules. Our group has thus far prepared various qualities and forms of polymeric adsorbents by radiation-induced graft polymerization. Here, the preparation schemes for novel adsorbents capable of collecting catechin and palladium ions, and of removing cesium ions and urea are described along with their performance.

Key Words: Adsorbent, Radiation-induced graft polymerization, Nylon fiber, Porous polyethylene hollow-fiber membrane

1. Radiation-induced graft polymerization to modify existing polymeric materials

Radiation-induced graft polymerization involves irradiation with electron beams or gamma rays onto a polymeric substrate and radical polymerization of vinyl monomers. The irradiation produces radicals in the polymeric substrate, and subsequent polymerization starts from the radicals and proceeds until termination occurs. The grafted polymer branches are referred to as graft chains.

One end of a graft chain is fixed in the substrate and the other end is free; therefore, the graft chain can extend or shrink in accordance with internal and external factors. The internal factors include the type and density of functional groups on graft chains, whereas the external factors include the type of solvent surrounding the graft chains and ambient conditions such as pH and temperature. For example, the introduction of charged groups such as the sulfonic acid (-SO₃H) and trimethylammonium chloride (-N(CH₃)₃Cl) groups onto the graft chains causes the extension of the graft chains because of mutual electrostatic repulsion among the charged groups. The charged graft chains will also shrink in a high-ionic-strength solution.

Radiation-induced graft polymerization techniques are divided into two types in terms of the timing of irradiation: preirradiation and simultaneous grafting. In preirradiation grafting, the irradiation is performed before contact with a vinyl monomer, whereas in simultaneous grafting, the irradiation is performed in the presence of both the substrate and vinyl monomer. Preirradiation grafting is advantageous in that the irradiation process is separated from the graft polymerization process: the irradiation is outsourced to private companies and the radicals produced can be stored below the glass-transition temperature of the polymeric substrate. Additionally, the preirradiation may suppress the formation of homopolymers.

Adjusting the radiation energy of electron beams or gamma rays changes the depth at which radicals are produced in the substrate. To prepare high-performance adsorbents, high capacities for target ions such as noble or heavy metal ions are essential; therefore, the production of radicals over the entire substrate is required to form graft chains containing high-density functional groups such as ion-exchange or chelate-forming groups. Thus, radiation-induced graft polymerization is applicable to bulk modification of a substrate as well as surface modification.

The first industrial use of radiation-induced graft polymerization was demonstrated by Dr. Takanobu Sugo of the former Japan Atomic Energy Research Institute. He developed the diaphragm of a button-shaped silver oxide (Ag₂O) battery by preirradiation grafting¹. A roll of high-density polyethylene (HDPE) film is discharged for electron-beam irradiation. Subsequently, the irradiated HDPE film is immersed in acrylic acid (AAc, CH₂=CHCOOH) solution. Finally, the AAc-grafted film is washed and dried and then rolled up. This diaphragm has been manufactured by Yuasa Battery Co., which is now called GS Yuasa Corporation.

The great potential of radiation-induced graft polymerization was demonstrated in a large-scale project of the collection of uranium from seawater by Dr. T. Sugo¹. As shown in Fig. 1, acrylonitrile (CH₂=CHCN) and methacrylic acid (CH=CHCOOH) were cогrafted onto an irradiated non-woven fabric made of polyethylene/polypropylene, after which some of the cyano groups produced were converted to...
into amidoxime (AO) groups through their reaction with hydroxylamine (NH₂OH). The AO groups selectively collected uranyl tricarbonate ions (UO₂(CO₃)₃⁴⁻) in seawater. The AO nonwoven fabric was assembled into a stack, 29 cm long, 16 cm wide, and 0.2 mm thick, with spacer nets. The adsorption cage, 16 m² in cross-sectional area and 16 cm in height, packed with 144 stacks was submerged in the Pacific Ocean 7 km offshore from Sekine-Hama in Aomori Prefecture, Japan (Fig. 2). In total, about 1 kg of uranium in terms of yellow cake was collected from seawater from the autumn of 1999 to the autumn of 2001.

In this review, the preparation schemes for novel adsorbents by radiation-induced graft polymerization are described along with their performance for target ions or molecules.

2. Selection of vinyl monomers and functional groups

Graft polymerization starts from radicals produced by irradiation of electron beams or gamma rays onto a substrate. Functional groups introduced into graft chains are selected in accordance with targets. The use of a vinyl monomer originally containing functional groups enables the preparation of the adsorbent only by graft polymerization. Some vinyl monomers containing hydrophilic or ion-exchange groups are commercially available; however, vinyl monomers containing specific groups and ligands may not be commercialized. Glycidyl methacrylate (GMA) is a vinyl monomer that enables the easy introduction of various moieties into graft chains because the epoxy groups produced...
readily react with reagents containing amino, imino, thiol, and hydroxyl groups. Therefore, GMA is a useful precursor for the modification of substrates.

Here, we present two approaches using the following vinyl monomers. N-vinylpyrrolidone (NVP) as a hydrophilic vinyl monomer was grafted onto a nylon fiber to capture catechin in green tea extract. GMA as a precursor vinyl monomer was graft-polymerized onto a porous hollow-fiber membrane and grafted poly-GMA chains subsequently reacted with adenine to bind palladium complex ions in a hydrochloric acid medium.

1) Catechin

Catechin is a component of green tea extracted with hot water. In the current manufacturing process for green tea beverages, catechin may be bound to poly-NVP powder to adjust the concentration of catechin, which has a bitter taste. Catechin-bound powder is disposed of because it is tedious to handle. To repeatedly use the adsorbent to bind catechin, we graft-polymerized NVP onto a nylon fiber (Fig. 3). The catechin bound to the NVP-grafted fiber could be quantitatively eluted with 0.1 M NaOH aqueous solution.

2) Palladium

In 1965, Rosenberg found that palladium compounds suppress the proliferation of *Escherichia coli*. He elucidated a mechanism in which palladium compounds form a complex structure with the nucleic acids constituting the DNA of *E. coli*. As a result, the anticancer drug Cisplatin TM was developed.

On the basis of this chemical principle, we introduced the purine adenine, one of the four constituent bases in DNA, into the epoxy groups of a GMA-grafted porous hollow-fiber membrane for palladium collection (Fig. 4). The palladium anion PdCl\(_4\)\(^{2-}\) dissolved in a hydrochloric acid medium was collected when a palladium solution was allowed to permeate across the adenine-immobilized porous hollow-fiber membrane. In this permeation mode, ideal adsorption characteristics with negligible diffusional mass-transfer resistance was achievable.

### 3. Selection of substrates of various qualities and forms

One of the merits of radiation-induced graft polymerization is its applicability to substrates of various qualities and forms. However, the quality can be compromised because of degradation of the substrate and the reactivity of the vinyl monomer. For example, the irradiated polypropylene degrades with time. The irradiated polyimide incorporates radicals into its aromatic rings to stabilize the radicals. The polymeric substrates that have been thus far adopted as substrates for radiation-induced graft polymerization are polyethylene and nylon. Adsorbents made of porous polyethylene hollow-fiber membrane and nylon fiber are described as follows.

1) Porous hollow-fiber membrane

A microfiltration (MF) membrane with a pore size of about 0.1 to 1 \(\mu\)m can remove microorganisms and colloids. An MF membrane of hollow-fiber or flat-sheet form has been used in household cleaners of tap water and also in membrane bioreactors for sewage treatment.

We adopted a porous hollow-fiber membrane made of polyethylene, manufactured by Asahi Kasei Co., as a substrate. This hollow fiber has inner and outer diameters of 2 and 3 mm, respectively, with an average pore size of 0.34 \(\mu\)m and a porosity of 71%. GMA was graft-polymerized onto an electron-beam-irradiated porous hollow-fiber membrane, after which the epoxy groups were converted into diethylamino (DEA) groups (-N\(\left(C_2H_5\right)\_2\)) (Fig. 5). The DEA groups were introduced uniformly across the membrane into the graft chain appended by radiation-induced graft polymerization. The resultant porous hollow-fiber membrane was referred to as a DEA hollow fiber.

The DEA hollow fiber functions as an anion exchanger for...
proteins. When a protein is dissolved in a buffered solution, the pH of which is higher than the isoelectric point (pl) of the protein, the net charge of the protein is negative. A protein solution was forced to permeate through the pores of the DEA hollow fiber from the inside of the hollow fiber to the outside, and then the protein was captured by the DEA-group-containing graft chains. Moreover, proteins were adsorbed in multilayers by the graft chains extending from the pore surface of the DEA hollow fiber.

A bovine serum albumin (BSA) solution was allowed to permeate through the pores of the DEA hollow fiber. The effluent penetrating the outside surface of the hollow fiber was continuously collected. The breakthrough (BT) curve, that is, the relationship between the BSA concentration in the effluent and the accumulated effluent volume, is shown in Fig. 6. The BT curves overlapped irrespective of the flow rate of the BSA solution. This finding means that the higher the flow rate of the protein solution, the higher the overall adsorption rate of the protein onto the hollow fiber. Ideal adsorption characteristics of a porous adsorbent modified by radiation-induced graft polymerization were demonstrated.

2) Fiber

At TEPCO (Tokyo Electric Power Company) Fukushima Daiichi Nuclear Power Plant (NPP), groundwater flows from the hillside to the seaside; therefore, groundwater came in contact with the melted core and was thereby contaminated with radionuclides. To reduce the volume of contaminated water, groundwater was pumped up before it flowed into the damaged reactor buildings, and a frozen soil shield was constructed around the reactor buildings. The groundwater contained radioactive strontium ions derived from the emissions caused by the NPP accident.

Wound cartridge filters consisting of chelate-forming fibers have been used to remove radioactive and nonradioactive strontium ions from the groundwater pumped-up from subdrains. The preparation of the chelate-forming fibers consisted of three steps as follows (Fig. 7): (1) gamma ray irradiation of bobbins with inner and outer diameters of 3 and 15 cm, respectively, a height of 15 cm and a weight of about 1 kg; (2) graft polymerization of GMA; and (3) conversion of epoxy groups into iminodiacetate groups (N(CH₂COOH)₂). Gamma ray irradiation of the bobbins is suitable for the mass-production of fibrous adsorbents because the radicals are produced uniformly throughout the bobbins.

4. Advanced application of graft chains

The above-described adsorbents contain functional groups such as ion-exchange and chelate-forming groups along a graft chain. However, when the target ions have extremely low concentrations in the presence of concentrated foreign ions or when target molecules are small or electrically neutral, conventional functional moieties are poor candidates for collecting the targets. For example, radioactive cesium ions in seawater and urea in ultrapure water (UPW) are difficult to remove. Inorganic compounds and enzymes work effectively in the specific collection of the targets or the specific reactions with the targets, respectively. We entangled inorganic compounds and enzymes with graft chains to generate a novel adsorption or reaction field. In these cases,
the graft chains play a supporting role in the process.

In the following, the impregnation of insoluble cobalt ferrocyanide and the immobilization of urease in the polymer chains grafted onto a nylon fiber are described. Insoluble cobalt ferrocyanide specifically collects cesium ions via ion exchange. Urease specifically hydrolyzes urea through an affinity interaction.

1) Precipitate formation in graft chains

Because of the NPP accident, seawater in front of the seawater-intake area of Reactors No. 1 to 4 at TEPCO Fukushima Daiichi NPP was contaminated with radionuclides such as radioactive cesium ions. Naturally occurring or nonradioactive cesium ions dissolve in seawater at a concentration of 0.3 mg-Cs/m$^3$. No adsorbent can distinguish radioactive Cs ions from nonradioactive Cs ions; therefore, any adsorbent adsorbs nonradioactive Cs ions as well as radioactive Cs ions. Additionally, sodium and potassium ions at much higher concentrations coexist with cesium ions in seawater; therefore, specificity or high selectivity for Cs ions is a crucial requisite for the adsorbents.

Metal ferrocyanides, in which copper, cobalt, nickel, or iron is a representative metal, have been reported to exhibit a high affinity for cesium ions. The jungle-gym-like crystal structure of metal ferrocyanides incorporates cesium ions in place of potassium ions via ion exchange. Mixing a potassium ferrocyanide ($K_4[Fe(CN)]_6$) and a cobalt chloride ($CoCl_2$) aqueous solution forms a precipitate of fine particles having a size of about 50 nm; however, the use of this precipitate as an adsorbent is not practical.

Watari and Izawa in 1965 impregnated insoluble copper ferrocyanide onto commercially available anion-exchange resin beads by the reaction of ferrocyanide ions adsorbed by the anion-exchange groups with cupric ions for the removal of radioactive cesium ions. We impregnated insoluble cobalt ferrocyanide onto an anion-exchange fiber prepared by radiation-induced graft polymerization of GMA and the subsequent addition of tetraethylene diamine (TEDA), as shown in Fig. 8. The resultant insoluble-cobalt-ferrocyanide-impregnated fiber is referred to as a CoFC fiber.

Braids composed of the CoFC fiber were immersed in the harbor of the NPP to remove cesium ions from seawater in December 2014. Thereafter, the braids were installed at drainage areas, rainwater boxes, and trenches of the NPP (Fig. 9).

2) Enzyme immobilization in graft chains

Ultrapure water (UPW) used in a semiconductor factory has been produced from river water. Urea is detected at an extremely low concentration in UPW even at the final step of the UPW production process. Urea is derived from fertilizers used at upstream farms and from feces and urine excreted at upstream stock farms. Urea is difficult to remove because of its relatively small size and electrical neutrality.

The enzymatic hydrolysis of urea using urease is effective in removing urea from UPW. Urea is hydrolyzed to form carbon dioxide and ammonium ions in seawater. These products are removed with ion exchangers. We immobilized urease onto anion-exchange fibers (Fig. 10): urease was adsorbed onto the anion-exchange graft chain and subsequently crosslinked with other ureases using transglutami-
nase as a crosslinker. A quantitative hydrolysis of urea was demonstrated even at a space velocity of 300 h⁻¹ of a urea solution flowing through a fiber-packed bed.

5. Summary

Our group has prepared various adsorbents for targets involving 40 elements that range from hydrogen (as a proton) to uranium (as the uranyl tricarbonate ion). Radiation-induced graft polymerization is advantageous over other modifications of existing polymeric materials in that adsorbents are designed by selecting quality, form, and functional group suitable for applications. However, the economic feasibility of this process may be restricted because of the cost of irradiation with electron beams or gamma rays.

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References

4) B. Rosenberg, Platinum coordination complexes in cancer chemotherapy, Naturewissenschaften, 60, 399-406 (1973)

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