Preparation of a New Anion Exchanger by Pre-irradiation Grafting Technique and Its Adsorptive Removal of Rhenium(VII) as an Analogue of 99Tc (Postprint)

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Date: 2023-06-18T00:00:00+00:00

Abstract

A new anion exchanger with pyridine groups was prepared by grafting of 2-vinyl pyridine onto polypropylene (PP) nonwoven fabrics by pre-irradiation grafting technique, followed by quaternization of pyridine rings in grafted chains in reaction with bromoethane. The results showed that the grafting yield increased with the monomer concentration and conversion ratio of quaternization increased with the time. The grafted and quaternized fabrics were characterized by FT-IR, DSC, SEM and ICP. The possibility of adsorption of perrhenate (ReO4-), a nonradioactive analogue to pertechnetate (99TcO4-), from aqueous solution by anion exchanger was investigated. The experiments performed at pH= 0.1-6 showed that pH=2.2 was the optimal acidity for ReO4- adsorption, and an adsorption equilibrium was achieved in 30 min. The reaction enthalpy was -12.55 kJ/mol, indicating that the adsorption process is exothermic. XPS tests indicated that the ReO4- uptake was a typical ion exchange between Cl- on anion exchanger and ReO4-.

Full Text

Preamble

NUCLEAR SCIENCE AND TECHNIQUES 26, S10302 (2015)

Preparation of a New Anion Exchanger by Pre-irradiation Grafting Technique and Its Adsorptive Removal of Rhenium(VII) as Analogue to ^{99}Tc

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(Received May 7, 2014; accepted in revised form July 7, 2014; published online December 20, 2014)

Abstract: A new anion exchanger with pyridine groups was prepared by grafting 2-vinyl pyridine onto polypropylene (PP) nonwoven fabrics using a pre-irradiation grafting technique, followed by quaternization of the pyridine rings in the grafted chains via reaction with bromoethane. The results showed that the grafting yield increased with monomer concentration, and the conversion ratio of quaternization increased with reaction time. The grafted and quaternized fabrics were characterized by FT-IR, DSC, SEM, and ICP. The adsorption of perrhenate (ReO_4^-) from aqueous solution by the anion exchanger was investigated. Experiments performed at pH = 0.1-6 demonstrated that pH 2.2 was optimal for ReO_4^- adsorption, with equilibrium achieved within 30 min. The reaction enthalpy was -12.55 kJ/mol, indicating an exothermic adsorption process. XPS tests indicated that ReO_4^- uptake occurred via typical ion exchange between Cl^- on the anion exchanger and ReO_4^-, a nonradioactive analogue to pertechnetate ($^{99}TcO_4^-$).

Keywords: 2-vinyl pyridine, pre-irradiation grafting, anion exchanger, perrhenate
DOI: 10.13538/j.1001-8042/nst.26.S10302

Introduction

Rhenium (Re), one of the rarest metals with an abundance of just 10^{-7}% in the Earth’ s crust, has been widely used in chemical engineering, metallurgy, aerospace, and national defense. Located in group VIIB of the periodic table together with technetium (Tc), rhenium serves as a good chemical analogue of technetium due to their similar electronic configuration, stereochemistry, and thermodynamic properties. Technetium-99 (^{99}Tc) is a β-emitter fission product with a half-life of 2×10^5 years and a high fission yield (6.3% of ^{235}U) [?]. Removal of ^{99}Tc from spent nuclear fuel is important because of its long lifetime, toxicity, and high mobility in the environment. In the literature, rhenium is typically chosen as an alternative element for radioactive ^{99}Tc to avoid handling high radioactivity. This study aimed to provide experimental data for ^{99}Tc separation.

For bulk separation of rhenium, liquid-liquid extraction is normally applied [?, ?]. However, this process generates large amounts of secondary waste that is difficult to treat and dispose of [?]. Therefore, new materials and methods have been developed to protect the environment and improve rhenium removal efficiency [?]. Adsorptive separation using an extractant-impregnated resin (EIR) has been reported as a promising method to achieve high selectivity for both low and high concentration solutions, as it combines the advantages of ion exchange and extraction [?, ?]. The main disadvantage of these extractant materials, however, is their low stability due to extractant leakage from the support, which results in gradual loss of separation capacity and reduced lifetime [?]. Additionally, due to the absence or weak attractive tendency between the extractants and solid support, the impregnation process is often inadequate. These drawbacks restrict the application of EIR in hydrometallurgy and other industries.

Kim et al. demonstrated that ReO_4^-, which is often used as a pertechnetate analogue, is efficiently absorbed by natural organic polymer chitosan containing amino groups \cite{9–11}. Liang et al. showed that adsorption of pertechnetate by Forager sponge could be attributed to the presence of amino groups [?]. Therefore, based on our previous research and literature data, it is possible to use amino-functionalized copolymers for perrhenate sorption [?, ?]. In this article, we report our work to develop an advanced ion exchanger of high stability with compact equipment for separation of perrhenate. A new anion exchanger with quaternary ammonium functional groups was prepared by grafting 2-vinyl pyridine (2-VP) onto polypropylene (PP) nonwoven fabrics using a pre-irradiation technique and subsequent quaternization of the graft copolymers by reaction with bromoethane. This material was successfully used for removal of perrhenate in our research.

II. Experimental

A. Materials

PP nonwoven fabrics composed of Φ 10–20 μm fibers (Shanghai Rundong Nonwoven Co., Ltd, China) were washed with acetone and vacuum-dried at 50 °C. 2-vinyl pyridine was obtained from Shanghai Yuanqiang Chemical Reagent Co., Ltd, China. $KReO_4$, from Tianjin No.3 Chemistry Reagent Factory, was spectroscopically pure. N,N-dimethylformamide (DMF), bromoethane, and other chemicals were of analytical-reagent grade and used as received.

B. Equipment

The PP nonwoven fabrics were irradiated by 2 MeV electron beams at the Shanghai Applied Radiation Institute, School of Environmental and Chemical Engineering, Shanghai University. The virgin, grafted, and quaternized nonwoven fabrics were characterized by FT-IR spectroscopy (IR Affinity-1, Shimadzu), differential scanning calorimetry (DSC, 200PC, Netzsch), and scanning electron microscopy (SEM, JSM-6700, JEOL). Metal ion concentrations were measured by an inductively coupled plasma atomic emission spectrometer (ICPS-7510, Shimadzu). Solution pH was determined by a pH meter (PHB-4, Shanghai Leici Instrument Scientific Co. Ltd.).

C. Preparation of Anion Exchanger

Figure 1 [Figure 1: see original paper] shows the synthesis process of the anion exchanger prepared by radiation-induced grafting of 2-VP onto PP nonwoven fabrics and quaternization of the grafted nonwoven fabrics by reaction with bromoethane.

The PP fabrics were sealed in polyethylene bags containing high-purity nitrogen and irradiated with 2 MeV electron beams, which scanned an area of 120 cm (length) × 7 cm (width). The total absorbed dose was 100 kGy for all samples. For grafting, a Pyrex tube containing DMF solvent and 2-VP monomer was bubbled with nitrogen for 15 min. The pre-irradiated fabrics were immersed in the Pyrex tube, which was sealed after 5 min of N_2 bubbling and placed in a water bath at constant temperature. The grafted fabrics were washed several times with a mixture of ethanol and water (1:1) to remove unreacted monomer and homopolymer on the fabric surface, then vacuum-dried at 60 °C to constant weight.

The grafting yield was calculated by:

$$\text{Grafting yield} = \frac{W_g - W_0}{W_0} \times 100\%$$

where W_g and W_0 are the weights of PP-g-VP fabrics and the virgin PP, respectively.

The grafted samples were reacted with bromoethane in ethanol solution at 65 °C for several hours, then washed several times with deionized water. The conversion ratio was calculated by:

$$\text{Conversion ratio} = \frac{W_a - W_g}{W_g - W_0} \times \frac{M_1}{M_2} \times 100\%$$

where W_a is the weight of the quaternized PP-g-VP, M_1 is the molecular weight of 2-VP, and M_2 is the molecular weight of bromoethane.

D. Adsorption Experiments

The anion exchanger pre-equilibrated with 1 M HCl solution was immersed in the feed Re(VII) solution adjusted to the desired pH. The mixture was stirred throughout the experiment at appropriate temperature and initial ion concentration. The anion exchanger was then removed and the rhenium concentration was measured by ICP. The adsorption amount (Q) and distribution ratio (D) were calculated using Eqs. (3) and (4), respectively:

$$Q = \frac{(C_0 - C) \cdot V}{W}$$

$$D = \frac{Q}{C}$$

where Q is the amount of Re(VII) adsorbed on the anion exchanger (mg/g); C_0 and C are the concentrations of Re(VII) before and after adsorption (ppm), respectively; W is the mass of the anion exchanger (g); and V is the volume of the metal ion solution (L).

E. Characterization of the Samples

1. DSC Analysis Changes in crystallinity and thermal behavior induced by grafting and quaternization were evaluated by DSC. The samples were loaded into the system at 20 °C, and the experiment was run from 20-200 °C in N_2 atmosphere at a heating rate of 20 °C/min. The fusion heat values were obtained from the area under the thermogram curves.

2. X-ray Photoelectron Spectroscopy X-ray photoelectron spectroscopy (AXIS UltraDLD, Shimadzu-Kratos, Japan) was applied to determine the interactions between the organic functional groups in anion exchangers and the adsorbed ReO_4^-. The XPS spectra were obtained using a monochromatic Mg Kα ray energy source (1253.6 eV) at 15 kV and 10 mA. The residual pressure in the analysis chamber was 5×10^{-8} Pa. The samples were scanned from 0 to 1200 eV in 80-eV steps. The elements C, O, N, and Re were measured at 282-294 eV, 528-536 eV, 396-404 eV, and 43-51 eV, respectively. The spectra were deconvoluted using a curve-fitting program with Shirley background subtraction and a Gaussian (0)-Lorentzian (100%) ratio.

3. SEM Surface morphology of the virgin PP and grafted PP was captured with SEM. The dried samples were mounted on specimen studs and sputter-coated with a thin gold film to prevent charging. Topographical images in SEM were formed from backscattered primary or low-energy secondary electrons.

4. FT-IR FT-IR analysis of the PP, PP-g-VP, and quaternized PP-g-VP was performed by FT-IR spectroscopy. The spectra were measured in transmission mode in the range of 1200 cm^{-1} to 1800 cm^{-1}.

III. Results and Discussion

A. Effect of Reaction Time on Grafting Yield at Different Monomer Concentrations

Figure 2 [Figure 2: see original paper] shows that the grafting yield increases rapidly with reaction time up to 180 min, after which it tends to level off, while it consistently increases with monomer concentration. Grafting depends largely on the availability of monomers to the radical sites in the nonwoven fabrics. Higher monomer concentration means greater availability of 2-VP in the fabrics; however, with excessively long reaction times, some radicals become inactivated and monomers tend to homopolymerize, which affects the diffusion rate of monomers and consequently decreases the grafting rate, leading to a slow increase in grafting yield.

B. Effect of Quaternization Time on Conversion Ratio

The conversion ratio during quaternization at 65 °C as a function of quaternization time is shown in Fig. 3 [Figure 3: see original paper]. It increases with time up to 48 h, after which it begins to level off.

C. Samples Characterization

Structural changes of the nonwoven fabrics grafted with 2-VP and quaternized with bromoethane were analyzed by FT-IR. Fig. 4 [Figure 4: see original paper] shows FT-IR spectra of the virgin PP (a), quaternized PP-g-VP (b), and PP-g-VP (c). The absorption peaks at 1592 and 1558 cm^{-1} in spectrum (c) are attributed to stretching vibrations of C–N in grafted 2-VP, and the peaks at 1434 and 1475 cm^{-1} are due to stretching of C–C in the pyridine ring. After quaternization, a new peak at 1630 cm^{-1} is observed in spectrum (b), indicating that the nitrogen atom in the pyridine ring is positively charged. Moreover, the peaks at 1592 and 1558 cm^{-1} related to C–N groups become weaker. These observations confirm the introduction of quaternary amine groups onto the graft chains of PP-g-VP.

Figure 5 [Figure 5: see original paper] shows DSC curves of the virgin PP (a), 26.9% PP-g-VP (b), 47.6% PP-g-VP (c), and quaternized PP-g-VP (d). Although the shape of the thermograms remains almost identical for all samples, the peak intensity decreases with increasing grafting yield. The fusion heat (ΔH) values, obtained from the areas under the thermogram curves, were 70.15, 63.75, 50.32, and 24.88 J/g for curves (a), (b), (c), and (d), respectively. Additionally, both ΔH and melting point (T) decrease with increasing grafting yield. Grafting occurred by incorporation of amorphous polyvinyl pyridine chains in the non-crystalline region of the PP nonwoven fabrics. The grafted polyvinyl pyridine chains thereby exerted a dilution effect on the inherent crystallinity of the PP fabrics. Crystallinity of the grafted fabric decreased with increasing grafting yield, hence the decreased ΔH . For grafted or quaternized samples, the melting point is lower than that of the virgin fabrics because the presence of graft chains hinders the formation of large crystallites, which typically melt at lower temperatures than larger ones.

Surface morphology of the virgin PP (a) and 51.2% PP-g-VP (b) is shown in Fig. 6 [Figure 6: see original paper]. The fibers became thicker after grafting, and the fabric surface became rougher due to growth of the graft chains.

D. Adsorption Ability

1. Effect of pH on Adsorption The pH effects on Re(VII) adsorption are shown in Fig. 7 [Figure 7: see original paper]. It can be seen that Re(VII) is poorly adsorbed on the anion exchanger at lower pH (pH < 0.5), and the adsorption amount increases sharply with pH up to 2.2, after which it begins to decrease. This result explains the phenomenon of decreasing adsorption amount with increasing hydrochloric acid concentration through competitive adsorption between ReO_4^- and Cl^- on the anion exchanger. At low pH (pH < 0.5), the high Cl^- concentration creates significant competitive effects with ReO_4^- for the quaternary amine groups on the anion exchanger, reducing electrostatic attraction to ReO_4^-. At high pH (pH > 2.2), conditions are not conducive to protonation of tertiary amines that did not react with bromoethane during quaternization, resulting in fewer exchangeable groups on the anion exchanger and consequently decreased adsorption.

2. Effect of Anion Exchanger Concentration on Adsorption Efficiency Figure 8 [Figure 8: see original paper] shows the relationship between anion exchanger concentration in solution and adsorption efficiency. The adsorption efficiency increases with anion exchanger concentration and levels off at approximately 98.1%. The optimum anion exchanger concentration is 8 mg/mL for a constant initial Re(VII) concentration of 320 ppm.

3. Calculation of Adsorption Rate Constant Using constant anion exchanger concentration, the concentration of Re(VII) ions in solution was determined at different times. As shown in Fig. 9 [Figure 9: see original paper], adsorption of Re(VII) ions reached equilibrium within 30 min. The results can be described by the adsorption equation [?]:

$$-\ln(1 - Q/Q_e) = kt + c$$

where Q_e is the adsorption amount of Re(VII) ions at equilibrium, t is the adsorption time, k is the adsorption rate constant, and c is a constant. The results can be converted into the plot $-\ln(1 - Q/Q_e)$ vs. t as shown in the insert of Fig. 9 [Figure 9: see original paper]. The linear relationship indicates that liquid film diffusion controls the rate of the adsorption process [?]. The adsorption rate constant of Re(VII) ions calculated from the slope is 3.81×10^{-3} s^{-1}.

4. Effect of Temperature on Adsorption Amount The temperature effect on Re(VII) ion adsorption was studied at 20-50 °C. The data of $\log D$ vs. $1000/T$ are plotted in Fig. 10 [Figure 10: see original paper], where D was obtained by calculating the experimental data with Eq. (4). Using the slope of Fig. 10 and the Van' t Hoff equation, $\partial(\log D)/\partial(1/T) = -\Delta H/(2.303R)$, the adsorption enthalpy of Re(VII) ions was determined to be $\Delta H = -12.55$ kJ/mol, indicating that the adsorption process is exothermic.

5. Effect of Initial Concentration on Adsorption Amount By changing the initial concentration of Re(VII) ions at constant pH and adsorption temperature, a series of equilibrium concentrations (C_e) were obtained, and the corresponding equilibrium adsorption amounts (Q_e) were determined. When adsorption reached saturation, the Freundlich equation $\ln Q = (\ln C_e)/n + \ln K$ was used to clarify the adsorption mechanism. The plot of $\ln Q_e$ vs. $\ln C_e$ (Fig. 11 [Figure 11: see original paper]) shows a linear relationship, indicating that the adsorption behavior of the exchanger fits the Freundlich equation. The slope ($1/n$) is 0.487, and $1/n < 0.5$ means that the adsorptivity of the anion exchanger for Re(VII) is a facile process.

6. Reusability of Anion Exchanger To evaluate reusability, adsorption-desorption cycles were repeated three times. The adsorbed Re(VII) ions were easily desorbed by 3 mol/L hydrochloric acid solution at room temperature for 1 h under stirring. The adsorption amounts of the anion exchanger in the 1st, 2nd, and 3rd cycles were 123.8, 120.7, and 117.0 mg/g, respectively, showing a slight decrease with an adsorption capacity loss of about 2.5–5.5% over three cycles. These results indicate that the anion exchanger exhibits good reusability.

7. XPS Analysis of Re(VII) Adsorption Samples of anion exchangers before and after ReO_4^- adsorption were evaluated by XPS to study binding energy shifts of different atoms. Binding energies of C, O, and N in the anion exchanger, and C, O, N, and Re in the anion exchanger after binding ReO_4^- are shown in Fig. 12 [Figure 12: see original paper]. The N1s peak before ReO_4^- adsorption was at 399.1 eV, and after adsorption it was at 398.7 eV, with virtually no change observed, indicating that rhenium uptake occurs through typical ion exchange between Cl^- on the anion exchanger and ReO_4^-. The new peak at 45.43 eV in Fig. 12(b) is assigned to Re 4f in ReO_4^-, confirming that Re(VII) is adsorbed onto the anion exchanger.

IV. Conclusion

A new type of anion exchanger with quaternary ammonium functional groups was prepared by grafting 2-VP onto PP nonwoven fabrics using a pre-irradiation technique, followed by quaternization of the graft copolymers through reaction with bromoethane. The results show that grafting yield increases with monomer concentration, and the conversion ratio of quaternization increases with time. FT-IR and DSC characterizations of the grafted and quaternized fabrics confirm that the expected functional groups are anchored onto the PP nonwoven fabrics.

The anion exchanger exhibits maximum rhenium ion adsorption at pH 2.2. The adsorption process is exothermic, so rhenium ion adsorption can be carried out at low temperatures. The adsorption behavior of the anion exchanger for

Re(VII) can be described by the Freundlich equation. XPS tests indicate that rhenium uptake occurs via typical ion exchange driven by electrostatic attraction. The adsorption rate constant is 3.81×10^{-3} s^{-1}. The adsorbed rhenium ions can be easily desorbed by 3 M HCl, and the anion exchanger demonstrates good reusability, with only a slight decrease in adsorption capacity after three adsorption-desorption cycles.

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Note: Figure translations are in progress. See original paper for figures.