Radiation Physics and Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Application of full-factorial design in the synthesis of polypropylene-g-poly(glycidyl methacrylate) functional material for metal ion adsorption

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ARTICLE INFO

Keywords:
Full factorial design
Poly(glycidyl methacrylate)
Electron beam grafting
Radiation
Metal ion adsorbent

ABSTRACT

The graft polymerization of glycidyl methacrylate onto electron beam pre-irradiated polypropylene (PP) nonwoven fabric was optimized using a 4^3 full factorial design analysis. The analysis yielded a polynomial equation that relates the linear, quadratic and interaction effects of the independent parameters to degree of grafting (Dg). The linear terms (i.e. absorbed dose, reaction time and monomer concentration), quadratic terms of time and concentration, and interaction term between absorbed dose and time were determined as significant independent parameters based from analysis of variance (ANOVA). The optimum grafting time and absorbed dose to achieve 150% Dg at 5% monomer concentration were 3.5 h and 39.8 kGy, respectively. The pristine PP, polypropylene-g-poly(glycidyl methacrylate) (PP-g-PGMA) and functionalized grafted materials were characterized using ATR-FTIR spectroscopy, thermogravimetric analysis and scanning electron microscopy. The affinities of the synthesized adsorbents towards the target metal ions at pH 4 were established to be in the following order: Cr(VI) > > Pb(II) ~ Cd(II) for the amine functionalized PP-g-PGMA; and Pb(II) > Cd(II) > Cr(VI) for the carboxylic acid functionalized PP-g-PGMA.

1. Introduction

In many countries in the Asia and Pacific Region, including the Philippines, industrial wastes in the form of toxic metals, organic compounds, dyes and microorganisms are significant sources of water pollution. These wastes have detrimental health and environmental effects, therefore treatment of waste and process waters containing significant amount of these materials is of utmost importance. The general separation of heavy metals from aqueous wastes is normally carried out using chemical precipitation techniques, usually transforming them into their hydroxide form. However, hydroxide precipitation alone is not sufficient to decrease the heavy metal concentration and meet the limit indicated in the regulation. Moreover, the large amount of waste sludge formed from the precipitation process is also another source of problem in the treatment process. In this regard, membrane and ion exchange techniques are normally used to bring down the concentration to the allowable limits. Previous studies showed that radiation grafted polymers were capable of reducing heavy metal ion concentrations to ppb level (Sokker et al., 2009; Wojnarovits et al., 2010; Madrid et al., 2013); sufficient to meet the criteria set by the Philippines' environmental agency regulation.

Radiation-induced graft polymerization can impart desired functional groups on otherwise unreactive trunk polymers (e.g. polyethylene, PE, and polypropylene, PP) without the use of chemical initiators. Initiation of graft polymerization using electron beam or gamma irradiation is more desirable than chemical initiation because it does not leave chemical initiator residues in the synthesized material and the polymerization can be performed at ambient conditions. The process is generally simple, easy to control and can be applied to trunk polymer materials of various sizes and forms (e.g. powder, fibers, films, etc). The use of PE or PP nonwoven fabrics allows the application of higher feed flow rate which increases the amount of waste water that can be processed per unit time, leading to lower treatment cost and higher productivity (Jyo et al., 2001; Sekine et al., 2010). These synthetic NWFs have desirable features that make them suitable as trunk materials in synthesis of adsorbents for waste water treatment. These features include chemical inertness, high mechanical strength, low resistance to liquid flow and high surface area leading to high adsorbent loading (Nasef and Guven, 2012). Also, carrying out grafting with the monomer in emulsion state is an environmental merit because the grafting mixture contains more than 90% water, hence avoiding the use of too much organic solvent that are normally utilized in typical grafting processes.

The application of design of experiments provides a wider analysis of how the different factors affect a target parameter, instead of the traditional one-variable-at-a-time experiments, which were used by

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http://dx.doi.org/10.1016/j.radphyschem.2017.01.047
Received 14 September 2016; Received in revised form 3 January 2017; Accepted 14 January 2017

majority of researchers. Experimental design techniques, such as full factorial design, central composite design and Box-Behnken design are useful tools in the characterization of various industrial and analytical processes by studying the effects and interactions of variables affecting them. Nowadays, factorial designs have proved their applicability and are widely utilized in the statistical planning of experiments to obtain empirical models relating process factors to process response. The factorial design method determines which independent parameters have significant effect on the response variable as well as how the effect of one independent parameter varies according to the level of other factors (Passos et al., 2006). In the field of radiation-induced graft polymerization, only few studies that utilized design of experiments were reported (Arayapranee and Rempel, 2004; Nasef et al., 2012).

This paper reports the optimization of reaction parameters on the electron beam-induced grafting of glycidyl methacrylate onto PP using a 4^3 full factorial design analysis. The PP-g-PGMA was functionalized to prepare amine and carboxylic type adsorbents, and the Cr(VI), Pb(II) and Cd(II) adsorption capabilities of the functionalized materials were measured.

2. Materials and methods

2.1. Materials

The polypropylene nonwoven fabric (PP NWF) that was provided by Agriculture & Supplies Corp. (Philippines) was used as trunk polymer. Glycidyl methacrylate monomer (GMA, ≥99.7%, Aldrich), polyoxyethylene sorbitan monolaurate (Tween 20), ethylenediamine (EDA, ≥99%, Sigma-Aldrich), iminodiacetic acid (IDA, >98%, Aldrich), potassium dichromate ($K_2Cr_2O_7$, ≥99.9%, Vetec), lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$, >99.5%, Techno Pharmachem), cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$, >98%, Sigma-Aldrich), dimethylsulfoxide (DMSO, RCI Labscan), isopropanol (IPA, >99.8%, RCI Labscan) and methanol (>99.9%, RCI Labscan) were all used as received.

2.2. Irradiation of PP NWF

PP samples (2 cm×2 cm) were placed in polyethylene resealable bags. Prior to irradiation, the air inside the polyethylene bags was displaced with nitrogen gas. The samples were irradiated to the desired dose using electron beam (2.5 MeV energy and 6.5 mA current) at room temperature.

2.3. Grafting of GMA onto PP and functionalization reactions

Factorial design allows the simultaneous study of the effects that several parameters may have on an optimization of a particular process. In a full-factorial design, responses are measured at all combinations of the experimental parameter levels. A four-level full-factorial model was utilized in this study. The degree of grafting (Dg) was chosen as the response parameter and the absorbed dose, reaction time and monomer concentration were selected as the factors/independent parameters. Each factor was studied on four levels (i.e. 4^3 full factorial design) and the values of the levels for each factor were predetermined based from previous experiments (Table 1).

The GMA monomer was mixed with Tween 20 and water to prepare emulsions containing different monomer concentrations (e.g. 3%, 5%, 7% and 9% (wt/wt) GMA) at 5:1 monomer to surfactant weight ratio. The monomer mixture was homogenized at a rate of 4800 rpm for 15 min and then deoxygenated by nitrogen bubbling for 1 h. The irradiated PP was transferred in a glass ampoule and the air inside the ampoule was immediately evacuated using a vacuum line. Afterwards, the deoxygenated GMA emulsion was drawn into the glass ampoule. The grafting reaction was carried out in a thermostatic water bath at 40 °C for 1–4 h. The polypropylene-g-poly(glycidyl methacrylate) (PP-g-PGMA) samples were repeatedly washed with methanol to remove non-reacted monomers, then dried *in vacuo* overnight at 40 °C.

Table 1
Factors and levels for the optimization experiment using 5:1 monomer-to-surfactant weight ratio.

Experimental Factors	Level 1	Level 2	Level 3	Level 4
Absorbed dose, kGy	10	20	30	40
Reaction time, h	1	2	3	4
GMA Concentration, %(wt/wt)	3	5	7	9

The degree of grafting (Dg) was determined gravimetrically using Eq. (1):

$$Dg = \frac{W_g - W_i}{W_i} x \quad 100 \tag{1}$$

where w_i and w_g are the weights of the PP before and after grafting, respectively. Five samples were grafted for each combination of grafting parameters and the average Dg was reported.

Amine functional groups were introduced to the PP-g-PGMA by ring-opening reaction of the epoxy groups with EDA. PP-g-PGMA samples with approximately 150% Dg were added to a glass ampoule containing 100 g solution of EDA in isopropanol. Amination of grafted samples was carried out for 15–180 min in a thermostatic water bath at 60 °C. The amine functionalized PP-g-PGMA was repeatedly washed with methanol and then dried in a vacuum oven. The amine functional group density was calculated using Eq. (2):

$$amine\ group\ density\ (mmol/gram - adsorbent) = \left(\frac{w_f - w_g}{w_f}\right) x \frac{1000}{MW} \tag{2}$$

where w_g and w_f are the weights of PP-g-PGMA before and after functionalization, respectively, and MW is the molar mass of EDA. Three samples were functionalized and the average amine group density was reported.

Besides amine group, carboxylic acid is another functional group capable of adsorbing metal ions via chelation or ion exchange. PP-g-PGMA samples with approximately 150% Dg were reacted with 100 mL of 0.4 M IDA solution to impart carboxylic functional groups on the olefinic trunk material. The reaction was carried out in a thermostatic water bath at 80 °C for 24 h. The carboxylated PP-g-PGMA was stirred in water for 4 h at room temperature, and then washed repeatedly with methanol. After drying *in vacuo*, the IDA functional group density was calculated using Eq. (2). Three grafted samples were functionalized and the average IDA group density was reported.

2.4. Response fitting

The 4^3 full factorial design required 64 experiments. The average of five runs of the independent parameters in correlation with the responses was recorded. The experimental design and analysis of data were performed using commercial statistical software Design Expert Version 9 (Stat-Ease, Inc., Minneapolis, MN). The software was used to fit the responses to a quadratic polynomial regression equation that relates the linear, quadratic and interaction effects of the independent parameters to Dg. The software was also used to produce 3D-surface and 2D-contour plots and to perform ANOVA and optimization using the desirability function.

2.5. Batch adsorption

Metal ion solutions (5–1000 ppm initial concentration) were prepared by dissolving the metal salts in deionized water. A weighed piece of the functionalized PP-g-PGMA was added to each 50-mL metal ion solution. The batch adsorption studies were conducted in a continuously stirring batch process at room temperature. After 24 h, the