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Upcycling of polypropylene waste by surface modification using radiation-induced grafting

Muhammad Inaam ul Hassan, Shaista Taimur, Tariq Yasin*

Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences (PIEAS), P.O. Nilore, Islamabad, Pakistan

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ABSTRACT

In this work, upcycling of polypropylene waste into amidoxime functionalized polypropylene adsorbent was studied using radiation-induced grafting technique. Polypropylene waste (PPw) was resulted from accelerated thermal ageing of polypropylene (PP). Bulk grafting of acrylonitrile (AN) onto PPw was achieved by simultaneous radiation grafting method using gamma rays. Degree of grafting of AN on PPw is affected by absorbed dose and dose rate. The acrylonitrile groups of grafted PPw were chemically converted into amidoxime functionality. Both the acrylonitrile-grafted PP waste and its amidoxime product were investigated by FTIR, XRD, SEM-EDX and TGA techniques. The prepared amidoxime adsorbent with amidoxime group density of 8.06 mmol/g was used for removal of copper ions from aqueous solutions. The effects of various physicochemical conditions such as: solution pH, adsorbent content, initial metal ion concentration and time on adsorption were studied to maximize adsorption of metal ion. Pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to study the kinetics of adsorption. Maximum Langmuir adsorption capacity of 208.3 mg/g at pH 5.0 with optimum contact time of 120 min was observed. Utilization of PP waste and its comparable adsorption capacity with existing radiation grafted polymer-based adsorbents provide a new, cheap and cost effective system.

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1. Introduction

Plastic waste is perceived as one of the major environmental problems these days as most of the plastic products are not biodegradable. The worldwide generation of plastics has now reached to 311 million tons/year [1]. Polypropylene (PP) is an extensively used polymer in the production of plastic products because of its good processibility and mechanical properties [2]. However, most of the PP products are degraded by oxygen, heat, light, humidity, etc., thus, affecting the optical, physical, chemical and mechanical properties and may experience reduced service life [3]. With growing demand of PP disposable products in modern society, its percentage in waste has risen. Conventionally, polymeric wastes are either disposed in landfill or incinerated [4] but these practices are also damaging to the environment. Most of PP products are produced without fillers, hence, making them good candidate for recycling. Recycled PP products also undergo faster degradation and contribute to plastic pollution. Transformations of PP into composites or laminates, pyrolysis into monomers and melt blown nonwovens and conversion into graphene flakes have also

been tried [5–8]. Exploration of new economically feasible technology to make this waste reusable is of great importance.

Contamination of water with heavy metals is another serious concern for environmentalists these days. Rapid industrial growth has caused pronounced increase in consumption of heavy metals like Cu, Cr, Mn, Pb, Ni, Hg, Zn and Cd [9]. Being non biodegradable in nature, these may accumulate in living organisms, thus, affect the biosphere and pose serious threat to human health. Excessive intake of heavy metals like copper can even cause death in human beings [10]. Significant amounts of these metals have been detected in the industrial effluents despite strict discharge regulations in many countries. Among various technologies available to uptake heavy metal ions from industrial wastes, adsorption is one of the most simple and common methods [11]. Many natural as well as synthetic materials have been employed for adsorptive removal of heavy metals. Polymeric adsorbents are a good choice because of their design flexibility, easy regeneration and good mechanical properties, nevertheless, prove to be costly when treating large volumes of the industrial wastes [12]. Therefore, research on the development of new low-cost polymeric adsorbents that can efficiently remove heavy metals from industrial effluents has gained much impetus.

The objective of the present study is to simultaneously address the two crucial aspects of pollution as described above. The

study exploits radiation-induced graft polymerization (RIG) as an ecofriendly tool to upcycle PP waste into a cost-effective adsorbent having good capacity for removal of heavy metals. RIG polymerization is a greener technology which incorporates special functional groups in polymers, hence, eliminating the use of chemicals, initiators and extra heat energy required to initiate free radicals for polymerization [13]. Various kinds of synthetic and natural polymers have been radiation-grafted with different monomers for various applications, especially, separation and preconcentration of heavy metals [14–17]. Some of previously reported works demonstrate many radiation grafted amidoxime-based polymers forming stable complexes with metal ions [18,19]. Generally, pristine polymers are used but very few studies have been conducted on radiation grafting of polymeric waste [20,21].

The present work aims to utilize simulated PPw powder to explore the optimum conditions for radiation grafting of acrylonitrile onto this easily available cheaper substrate. Simultaneous irradiation method has been used for bulk grafting of acrylonitrile (AN) on PPw by gamma rays. The effect of irradiation conditions like absorbed dose (kGy) and dose rate (kGy/h) on grafting has also been investigated. The nitrile grafted PPw particles have been subsequently converted into amidoxime form and used for the removal studies of copper ions from aqueous solutions.

2. Materials and methods

2.1. Materials and chemicals

Injection-molded specimens of Topilene (J842), a block co-polymer of polypropylene, made by Hyosung, South Korea, were used for generation of simulated PP waste. Acrylonitrile monomer of purity more than 99.0% (Daejung Chemicals, Korea) was employed without furthur purification. All the other chemicals such as hydroxylamine hydrochloride, acetone, dimethyl formamide (DMF), methanol, anhydrous sodium carbonate, sodium hydroxide and hydrochloric acid were of analytical grade. Nitrogen gas of (99.999% purity) was utilized for providing inert atmosphere. Desired concentration of copper solution was prepared from copper sulphate (Sigma Aldrich, 99.9% purity) by dissolving the appropriate quantity in deionized water (type-I) produced from Millipore Simplicity UV water purification system.

2.2. Preparation of PP waste

The injection-molded sheets of polypropylene were irradiated by Co–60 gamma rays at 100 kGy absorbed dose at dose rate of 1.1 kGy/h and furthur oven-aged at 60 °C for 200 h. This ageing corresponded to 10 years of indoor ageing of pristine polypropylene (PPP) as it has been reported earlier [21]. The resultant PPw was ground to obtain fine powder of 120 mesh. PPw powder was washed with ethanol several times and then vacuum-dried at 60 °C.

2.3. Radiation grafting of PP waste

Precisely-weighed identical quantities (5.0 g) of dried PPw were immersed in 20 mL of acrylonitrile monomer (dearated by bubbling N$_2$ gas) contained in separate Pyrex$^{®}$ bottles with screw caps. The reactant mixture of the bottle was again dearated for 10 min by bubbling N$_2$ gas prior to gamma ray irradiation. A self-shielding Cobalt–60 gamma irradiation chamber (24 kCi) was used for irradiating these vials. The absorbed dose was varied from 2.5 to 10.0 kGy to monitor the grafting yield. The effect of dose rate on grafting was also studied by using three different dose rates (5.4–6.6 kGy/h) culminating in the dose of 10.0 kGy. The grafted PPw (PPw-g-AN) was made free of homopolymer and unreacted monomer by extraction with DMF for 16 h followed by washing with acetone.

It was then dried under vacuum at 50 °C till constant weight was achieved. The degree of grafting (**D.G.**) of PPw-g-AN was computed by solving Eq. (1).

$$\textbf{D.G.}\,(\%) = \frac{w_g - w_o}{w_o} \times 100 \tag{1}$$

Where, $\textbf{w}_o$ stands for the weights of the ungrafted PPw and $\textbf{w}_g$ represents weight of completely-dried grafted powder.

2.4. Conversion into amidoximated adsorbent

PPw-g-AN was refluxed at 80 °C with hydroxylamine hydrochloride (10% w/v) solution of 1:1 mixture of methanol and water maintained at pH 7.0 + 0.1 with anhydrous sodium carbonate [22,23]. After 06 h, the product was filtered and washed with methanol and deionized water repeatedly to remove unreacted hydroxylamine. The amidoximated product was designated as PPw-g-AO and vacuum-dried at 60 °C to constant weight. The conversion% of cyano groups (CN) to amidoximated groups (AO) and amidoxime group density (D$_{AO}$) was calculated by Eqs. (2) and (3) respectively as reported elsewhere [23,24].

$$Conversion\,of\,CN\,to\,AO\,(\%) = \frac{(w_{AO} - w_g)}{(w_g - w_o)} \times \frac{53}{33} \times 100 \tag{2}$$

$$D_{AO}\left(\frac{mmol}{g}\right) = \frac{(w_{AO} - w_g)}{w_g \times 33} \times 1000 \tag{3}$$

Where w_{AO} is the dry weight of the PPw-g-AO. The value 33 is the molecular mass of hydroxylamine produced *in situ* at pH = 7.0 from hydroxylamine hydrochloride and 53 is the molecular mass of each grafted AN unit.

2.5. Characterization study

2.5.1. FTIR analysis
Presence of different functional groups in PPP, ungrafted, AN grafted and amidoximated PPw was characterized by FTIR-ATR spectrophotometer (Nicolet 6700, Thermo Electron Corporation). The samples were vacuum-dried at 50 °C before being scanned at the resolution of 6 cm^{-1} from 4000 to 500 cm^{-1}. Fifty scans per sample were recorded to achieve high signal to noise ratio. Oxidation index of the PPw was also determined from FTIR spectrum by using Eq. (4).

$$Oxidation\,Index = A_c/A_e \tag{4}$$

Where A_c represents area of peak in FTIR spectrum of PPw from 1850 to 1650 cm^{-1} and A_e is the area of peak from 1420 to 1315 cm^{-1} [25].

2.5.2. X-ray diffraction analysis
X-ray diffraction (XRD) analysis was performed by using Panalytical Xpert Pro X-ray diffractometer at room temperature to find out the variation in crystalline nature of PPw during grafting and amidoximation. The X-ray beam was nickel filtered copper Kα (λ¼ 1.540 Å) radiation operated at 40 kV and 30 mA. Continuous scan was obtained from 2θ value from 10 to 80° at the rate of 1.0/min.

2.5.3. Thermogravimetric analysis
The degradation process and thermal stability of PPP, PPw, PPw-g-AN and PPw-g-AO were evaluated through TGA experiments using Mettler-Toledo TGA/DSC1 thermogravimetric analyzer. Sample mass of 10 mg was subjected to temperature range from ambient to 800 °C under nitrogen atmosphere at the heating rate of 10 °C/min.