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Utilization of modification polyester non-woven as an affordable sorbent for oil removal

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ABSTRACT

A novel reusable sorbent (PET-g-LA) based on lauryl acrylate (LA) monomer and polyester (PET) non-woven matrix was developed by ultraviolet irradiation method, which fully took the advantages of both PET non-woven and acrylate resins to overcome each shortcoming when used alone in oil recovery. The optimum grafting degree was obtained with a monomer concentration of 10% and an iniferter concentration of 1.25%. The PET-g-LA showed a maximum sorption capacity of 17.38 g/g for diesel, while the sorption capacity of the original PET was only 6.89 g/g. In addition, the sorption capacity of PET-g-LA with a grafting degree of 25.22% was maintained above 85% of its initial sorption capacity after being regenerated 10 times, which showed a high performance as an economically competitive and environmentally friendly sorbent for the removal of oil from water body.

Keywords: Polyester non-woven; Lauryl acrylate; Graft polymerization; Sorption capacity; Reusability

1. Introduction

Oil is a rather stable compound in water, and its hydrolysis half-life is estimated to be about several decades. Nowadays, with frequent and massive oil spill accidents, ocean ecology and the natural environment are becoming seriously damaged. Even a minor-scale oil spill accident contributes to an undesirable taste and odor to drinking water, which causes irreversible environmental problems [1,2].

Treatment of oil spills before effluent disposal remains a challenge to environmental scientists and technologists. Therefore, it is important to establish and develop new techniques for oil removal from the spilled sites in order to apply appropriate procedure to clean up. Among all the existing techniques used for combating oil spills, quick recovery by sorbent is one of the most important countermeasures in oil-spill response [3–5]. The use of sorbent for oil removal is attractive principally due to its ability to transform spilled oil in the liquid phase into solid or semi-solid phase. Once this change is achieved, the recovery of the spilled oil is not difficult [6–8].

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The preferable sorbent materials are those that, besides being inexpensive and readily available, demonstrate fast oil sorption rate, high oil sorption capacity, low water pickup, high oil retention capacity during transfer, and high recovery of the sorbed oil with simple methods and good reusability. Various sorbents have been studied for this purpose at present, most of the commercially available oil sorbents are synthetic products such as high-sorption acrylate resin, which were prepared by radical suspension copolymerization of acrylate monomer, giving them good flexibility, sorption properties, and retention performance [9–11]. However, their small specific areas, long adsorption equilibrium times (6–8 h), difficult recycling characteristics, and certain aspects of their morphologies have become obstacles for the further application of acrylate resins, and they are usually burnt after one use.

Recently, an estimate of about 800 million tonnes polyester (PET) products are discarded as industrial wastes in China and the PET waste can be obtained as a low-cost material and made into non-woven by traditional spinning methods. It is well established that PET non-woven has a quicker saturation-sorption rate and an excellent sorption selectivity when being applied on oil-over-water baths. The flimsy characteristic of non-woven polypropylene has restricted its applications, especially influenced its oil sorption capability. However, due to the PET monofilament's excellent physical performance, the non-woven PET has high sorption efficiency. On the other hand, the sorbed oil recovery can be recovered through simple squeezing. However, the PET is not always ideal, though the PET non-woven are of considerable importance for quick cleaning up, but the inadequate sorption capacity, low retention performance, high hydroscopicity, and poor reusability may limit their application after several sorption–regeneration cycles. Furthermore, the density of PET is 1.38 g/cm^3 on average, which is higher than water and will not float in water, which limit their application in spill treatment and might cause secondary pollution.

Nowadays, much attention has been paid to the technique of graft polymerization on polymeric matrixes to prepare polymeric sorbent, the technique usually can enhance sorption efficiency of the sorbents [11]. In this research, the direct radiation grafting technique was used to graft lauryl acrylate (LA) monomer onto PET non-woven matrixes. The PET non-woven used in this article is a familiar material in industry, and made from recycled plastic bottles. It is much less expensive than polypropylene. The optimum grafting conditions at which the grafting process proceeds extensively and homogeneously were investigated. The sorption properties of PET matrix increased significantly as a result of graft modification, which exhibited a fast sorption rate, high sorption capacity, good retention characteristic, and excellent reusability. It presents the advantages of simple operation, easy to maintain and low cost, which makes its use very economical and thus a green process with potential use in a real spillage treatment plant [8].

2. Experimental

2.1. Materials

The PET non-woven was offered by Tianjin Polytechnic University (Tianjin, China). LA (purity ≥ 99%) was purchased from Zibo Haipeng Fine Chemical Co., Ltd. (Shandong, China). Diesel was obtained from the Sheng Da Chemical Reagent Co., Ltd. (Tianjin, China), whose properties were presented in Table 1. Photosensitizer benzophenone (BP, purity ≥ 98%) was obtained from Tianyi Chemical Reagent Institute Co., Ltd. (Tianjin, China). All of the other chemicals including isopropanol and ethanol were of analytical grade and purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All reagents and solvents were used as received.

2.2. Preparation of PET-g-LA

The procedure for the preparation of PET-g-LA is as follows:

(1) Pretreatment: The PET was firstly immersed into the ultra-pure water for 24 h to remove the impurities. After drying in the oven, they were in a Pyrex polyethylene bag with the thickness of 2 mm was used as a matrix for the grafting reaction.

(2) Grafting step: The pretreated PET samples were then put into the monomer of LA grafting solution for the grafting reaction by ultraviolet (UV) irradiation. Isopropanol/water solution (if there is no special explanation, the proportion of isopropanol/water is 1:4) as solvent was added first, followed by predetermined concentration of LA monomer, and the oxygen was purged by bubbling nitrogen for 5 min. After grafting, the achieved PET-g-LA samples were extracted with ethanol. UV radiation with a wavelength of 312 nm was adopted to initiate the graft polymerization.

Table 1
Properties of diesel

Oil type	Density (g/cm^3)	Viscosity (cP)	Content of water (w%)	Weight losing (%)	
				After 24 h (w%)	After 48 h (w%)
Diesel	0.843	4.50	≤0.05	0.21	0.34

The grafting degree (DG) was calculated by the following equation:

$$\text{DG}\,(\%) = [(W_1 - W_0)/W_0] \times 100\% \quad (1)$$

where W_0 and W_1 are the weights of PET non-woven before and after graft polymerization, respectively. All the results were the average of five parallel experiments [11,12,17].

The grafting conditions are shown in Table 2.

2.3. Characterization of PET-g-LA

The surface morphology was analyzed using scanning electron microscope (QUANTA 200, FEI). The contact angle measurements were performed on Cam 100 optical angel meter (YH-168A instruments Ltd, Japan). The measurement was repeated five times and the mean value was calculated. A SANS CMT-4503 tensile tester (MTS systems Co., Ltd, China) was used to measure mechanical properties of the studied modification fibers. Tensile measurement was performed using a strain gage extensometer (gauge length: 20 mm) tested up to breaking at the crosshead speed of 7.5 mm = min (measurements were repeated ten times to calculate the mean value). All tests were carried out at 25℃, 65% RH.

2.4. Sorption test of PET-g-LA

The sorption experiment was aimed at investigating the sorption capacity of PET-g-LA for oil spilled on water under a certain condition. 10 mL of the test diesel oil was poured onto 80 mL of water in a series of glass beakers. After attaining a steady state condition (30 min), 0.5 g sorbent (original PET or PET-g-LA) was evenly spread over the entire oil liquid surface in each beaker. The sample were removed after continuous sorption for 5 s, and placed on the top of a filter allowing drainage for 5 min before weighing. All tests were carried out at room temperature. The above measurements were repeated for five times [8].

The oil-sorption capacity of PET-g-LA (W, g/g) was calculated as follows:

$$W(\%) = (G_1 - G_0)\,/\,G_0 \times 100\% \quad (2)$$

where G_0 and G_1 represent the weights of the dried sorbent sample and the sample sorbed oil, respectively.

2.5. Retention capacity and reusability of PET-g-LA

In order to investigate the oil retention capacity of original PET or PET-g-LA, the sorbent after weighing was hung on a digital balance, whereupon the sorbed oil began to drip from the sorbents [6–8]. The sorbent samples were recorded after 1–60 min. The dynamic retention capacity was also evaluated as follows:

$$\text{Dynamic retention capacity} = W_{t=i}\,/\,W_{t=1} \times 100\% \quad (3)$$

where $W_{t=1}$ is the weight of oil bath (g) at 1 min dripping, $W_{t=i}$ is the weight of oil bath (g) at t min dripping, $i = 2, 3, 4, \ldots$.

The reusability efficiencies of the original PET or PET-g-LA were determined after repeated sorption–regeneration cycles. Ten cycles of the sorption process were performed for each sample. Between each cycle, the material was squeezed and weighed again. The weight of the squeezed material was used as the initial weight of the sorbent in each subsequent sorption cycle [6–8].

Table 2
The recipe for preparation of PET-g-LA

	LA concentration (v/v)	Irradiation time (min)	Iniferter concentration (wt.%)
Typical recipe	10	30	1.25
Parameters	1–20	0–30	0.25–1.75

3. Results and discussion

3.1. Graft polymerization and characterization of PET-g-LA

The degree of LA grafting on PET non-woven at different monomer concentration as a function of irradiation time is given in Fig. 1. It could be seen that the degree of grafting increases with increasing irradiation time. As UV irradiation time increased, there were more active sites excited on the PET matrix and much more monomers accessible to the surface radicals, resulted in the increase of grafting degree [11–13]. However, with the irradiation time prolonged, the consumption of initiator and monomer lead to an asymptotic saturation of the grafting degree. Thus, the irradiation time was set as 30 min in the following experiments. The grafting degree of PET non-woven increased nearly proportional with an increase in the monomer concentration up to 10% and then declined. This trend is believed to be related to higher concentrations of monomer available to react with the active sites on irradiated PET matrix, so that a higher grafting degree was achieved with the increase in monomer concentration. Furthermore, the grafting degree inclined to level off at higher concentration which can be due to the homopolymerization of LA monomer [9]. In fact, the grafting is controlled by a cumulative effect of the monomer diffusion within the polymer matrix, termination of the growing polymer chains, and the deactivation of the primary radicals. If the surface of PET matrix was covered with the homopolymer, the diffusion of monomer into the inner area was hindered, resulting in the decrease of grafting degree with the sequent increase of monomer concentration [12–14].

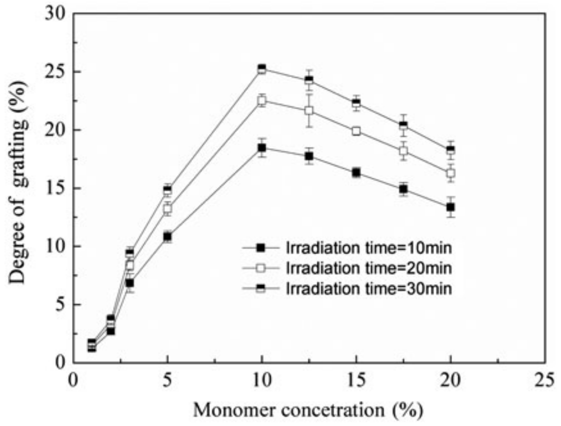

Fig. 1. The relationship between the monomer concentration and grafting degree, following different irradiation time.

Fig. 2 shows the effect of iniferter concentration on the degree of grafting. In this case, iniferter acts not only as an initiator but also as a terminator. This trend can be attributed to the iniferter as it decomposes to give two different radicals with very different properties, one is able to initiate polymerization and the other is stable but capable of terminating the growing polymer chains by recombination. With the increasing of iniferter concentration in the region of low concentration (≤1.25 wt.%), the radicals which derived from the alkyl group have a very high activity and can initiate polymerization simultaneously, the grafting degree of PET non-woven increased from 0 to 25.22% with the iniferter concentration continuously increasing from 0 to 1.25%. However, when the iniferter concentration is over the concentration of 1.25%, the other radicals derived from the sulfur centered is a much less activity, which does not react with monomers and would terminate the graft polymerization reaction, the grafting degree of LA decreased. From the above mentioned results, it could be concluded that the use of an iniferter concentration of 1.25% in this case has somehow a maximum accelerative effect on the grafting onto PET matrix [13–16].

In order to further determine the morphology of the surface characteristics of original PET matrix after graft modification, SEM observation were conducted. A considerable difference between original PET and PET-g-LA is observed in SEM observation. Fig. 3(A) and (B) suggested that a heterogeneous grafting layer structure was formed on the PET matrix surface randomly after graft polymerization, making the smooth surface of original PET became rougher obviously.

As shown in Fig. 4, the contact angle of the PET matrix increased with the subsequent increase of the

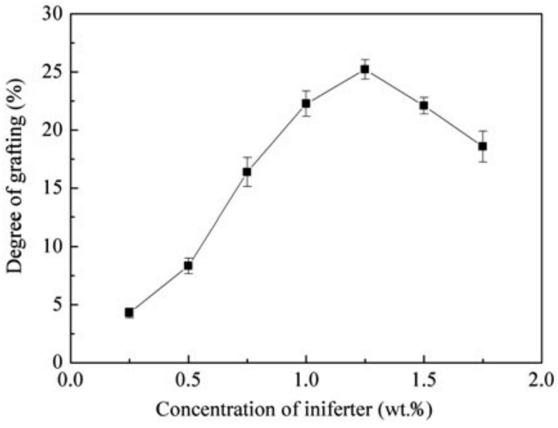

Fig. 2. The relationship between the iniferter concentration and grafting degree.

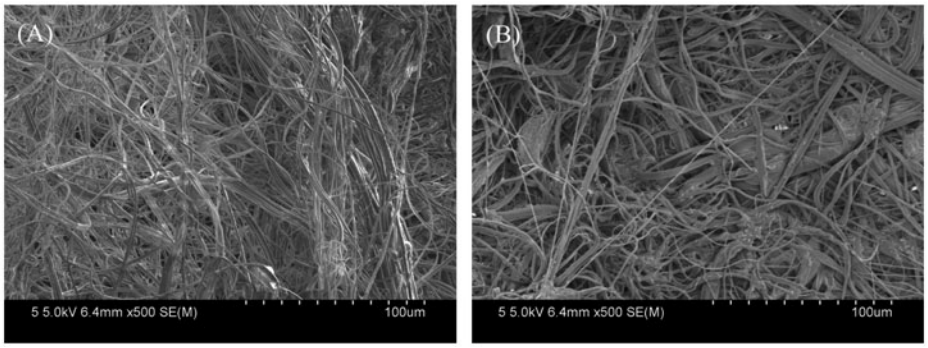

Fig. 3. SEM micrographs of (A) original PET non-woven and (B) PET-g-LA.

grafting degree. Water contact angle of PET-g-LA exhibited an increase from 65.50 to 122.38° with the grafting degree increasing from 0 to 15.54%, which indicated that the hydrophobicity of original PET matrix surface was greatly improved after graft polymerization. It could therefore be hypothesized that the enhancement in hydrophobicity greatly improved the affinity between PET-g-LA and spilled oil.

3.2. *Sorption capacity of PET-g-LA*

As shown in Figs. 5 and 6, when being applied on oil-over-water baths, the PET-g-LA exhibited a quick saturation-sorption rate for the oils over the water; almost all the spilled oil could be removed in 5 s and only an invisible oil slick on water is left, which indicated the PET-g-LA still reserved the fast sorption rate of original PET and exhibited a high selectivity of oil over water. Furthermore, its ability to float on the water surface after sorption was important preconditions for an efficient oil sorbent [18,19].

In addition, it showed that the oil-sorption capacity was increased with the increasing of the grafting degree. It is well known that acrylate is a versatile monomer with unique chemistry, and the acrylate monomers with a long-chain ester group have a good

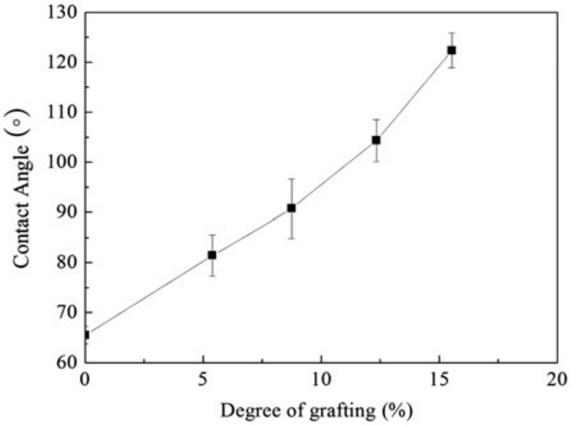

Fig. 4. Water contact angle of original PET and PET-g-LA with different grafting degree.

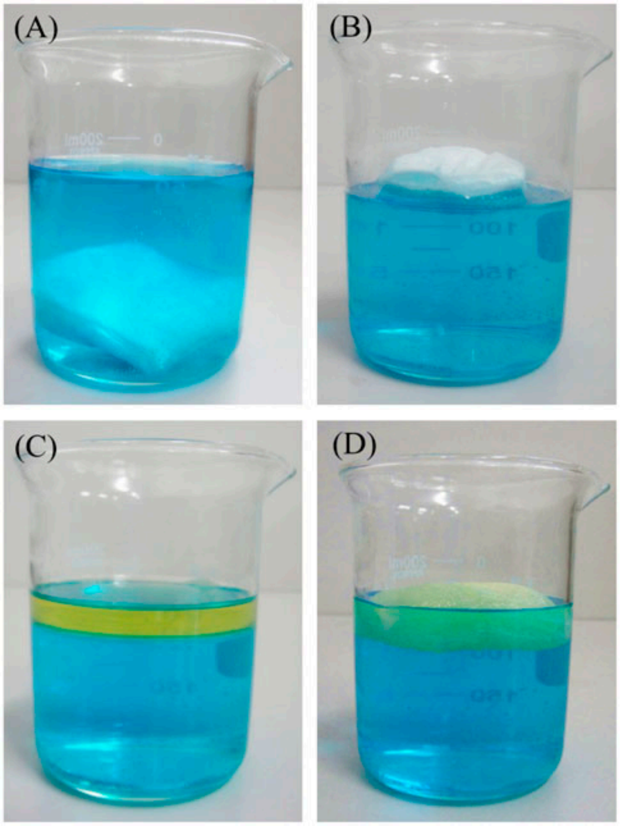

Fig. 5. Cleanup of diesel oil film on water by the obtained PET-g-LA sorbent. (A) original PET; (B) PET-g-LA; (C) before Cleanup; (D) cleanup by PET-g-LA after 5 s.

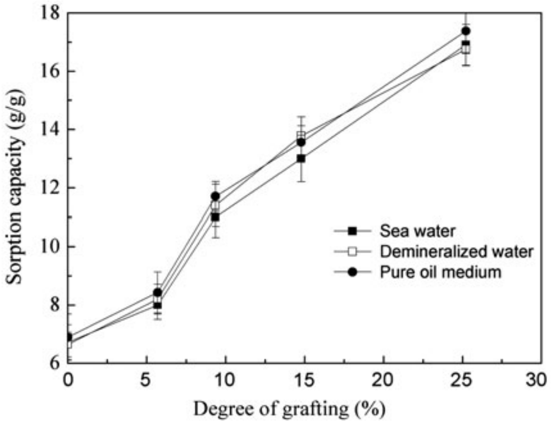

Fig. 6. The sorption capacity of PET-g-LA for water with different grafting degree.

affinity to oil. When contact with grafted PET, oil was first coating with the Van der Walls forces and hydrophobic interactions between oil and PET-g-LA grafted surface. When the grafting degree of PET-g-LA was 25.22%, the oil-sorption capacity reached a maximum value of 17.38 g/g which was 2.52 times as that of the original PET, which indicates that the sorption performance of original PET non-woven was significantly improved.

3.3. Retention characteristic of PET-g-LA

The oil retention capacity during field application, transfer, and handling operation is an important parameter for PET-based sorbent evaluation. The dynamic oil retention was measured by allowing the oil to drip from the sorbent for a specified duration. As shown in Fig. 7, the amount of oil retained on original PET was about 28–36%, while those of PET-g-LA was more than 54–72%. The enhanced hydrophobicity improved the compatibility between the PET non-woven and the oil, which may increase the interaction between them. Subsequently, it stabilized the liquid bridges between non-woven individual fibers and oil, and more oil was retained within the modification PET. When the grafting degree increased to a certain value, the capillary pressure would become the predominant force that hold up the oil within PET-g-LA. Therefore, the oil retention capacity of the original PET was improved after graft polymerization and prevented the leak of oil in practice [20,21].

3.4. Reusability of PET-g-LA

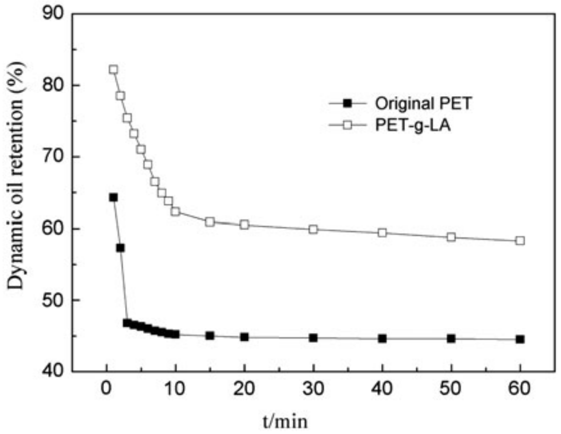

Fig. 7. The percentage of dynamic oil retention of original PET and PET-g-LA with a grafting degree of 20.55% for diesel.

As shown in Fig. 8, the reusability of original PET was very poor. The oil-sorption capacity of original PET was maintained only about 39.4% for diesel. The poor of physical properties and irreversible deformation of the original PET matrix was believed to be one of the main factors. When the original PET was regenerated by squeeze, the structures were destroyed and lost its puffiness, the interfiber pores may not be achieved immediately when the sorbents were subsequently soaked into aqueous solution. In addition, the residual oil trapped in the interfiber pores was also contributed to the decrease of sorption capacity [22,23].

Compared to the original PET, it can be seen that the reusability of PET-g-LA was improved significantly after graft modification. The PET-g-LA after

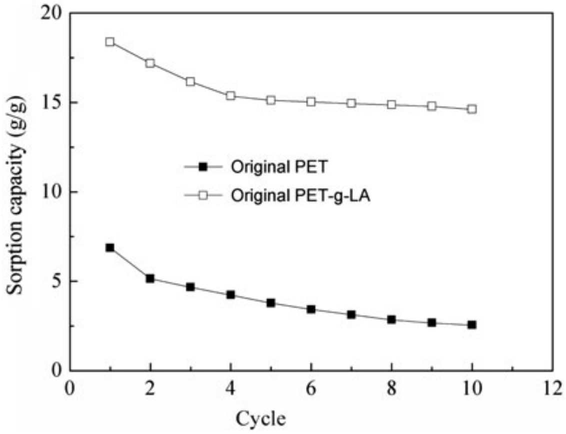

Fig. 8. Reusability of original PET and PET-g-LA with a grafting degree of 20.55% during 10th sorption cycles for diesel.

being regenerated 10 times was still able to maintain its initial sorption capacity about 80% for diesel oil. This trend may be resulted from the following two aspects: (a) a litter energy was absorbed by PET matrix by UV irradiation; (b) LA grafted onto the surface of PET helped the original PET substrate maintained its elasticity and capillary, which can be of large help to the tensile strength of the PET. As a result, the physical properties did not change significantly in spill cleanup, thus prolonging the lifetime of PET-g-LA.

4. Conclusions

In this study, we investigated the utilization of modification PET waste as a low-cost sorbent for the removal of oil from water. The novel polymeric of PET-g-LA obtained after modifying PET matrix using UV irradiation method. The grafting degree could be controlled by adjusting the irradiation time and the monomer concentration. The achieved PET-g-LA retained the advantages of both PET and acrylate resin to overcome the shortcomings of each used alone, which exhibited a quicker sorption rate, higher sorption capacity, good retention behavior, and excellent reusability, which made it feasible for the treatment of large-scale oil spilling.

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References

[1] E. Khan, W. Virojnagud, T. Ratpukdi, Use of biomass sorbents for oil removal from gas station runoff, Chemosphere 57 (2004) 681–689.
[2] X.Y. Song, Enhanced treatment of polluted surface water from yellow river (China) with biooxidation as pretreatment: Pilot scale studies, Desalin. Water Treat. 9 (2009) 59–65.
[3] T.T. Lim, X.F. Huang, Evaluation of kapok (Ceiba pentandra (L.) Gaertn.) as a natural hollow hydrophobic–oleophilic fibrous sorbent for oil spill cleanup, Chemosphere 66 (2007) 955–963.
[4] J. He, K. Yang, M. Dougherty, C. Li, Y. Wan, Removal of manganese from surface water with oxidants in supplement to natural manganese sand in Sinopec Shanghai Ltd, Desalin. Water Treat. 11 (2009) 245–257.
[5] R.R. Huang, J. Hoinkis, Q. Hu, F. Koch, Treatment of dyeing wastewater by hollow fiber membrane biological reactor, Desalin. Water Treat. 11 (2009) 288–293.
[6] Q.F. Wei, A.F. Fotheringham, Evaluation of nonwoven polypropylene oil sorbents in marine oil-spill recovery, Mar. Pollut. Bull. 46 (2003) 780–783.
[7] E.H. Ali, H.A. Shawky, M.H. El-Sayed, H. Ibrahim, Radiation synthesis of functionalized polypropylene fibers and their application in the treatment of some water resources in western desert of Egypt, Sep. Purif. Technol. 63 (2008) 69–76.
[8] C. Lin, Y.J. Hong, A.H. Hu, Using a composite material containing waste tire powder and polypropylene fiber cut end to recover spilled oil, Waste Manage. 30 (2010) 263–267.
[9] F. Yuan, J.F. Wei, K.Y. Zhao, Synthesis of butyl acrylate grafted polypropylene fibre and its applications on oil adsorption in floating water, E-Polymers 89 (2009) 1–8.
[10] N.K. Xu, C.F. Xiao, Y. Feng, Study on absorptive property and structure of resin copolymerized by butyl methacrylate with hydroxyethyl methacrylate, Polym. Plast. Technol. Eng. 48 (2009) 716–722.
[11] K. Hidetaka, K. Uezu, S. Tsuneda, K. Saito, M. Tamada, T. Sugo, Recovery of Sb(V) using a functional-ligand-containing porous hollow-fiber membrane prepared by radiation induced graft polymerization, Hydrometallurgy 81 (2006) 190–196.
[12] D. Berenyi, Atomic physics today, Radiat. Phys. Chem. 76 (2007) 367–369.
[13] P.A. Kavaklı, N. Seko, M. Tamada, Radiation-induced graft polymerization of glycidyl methacrylate onto PE/PP nonwoven fabric and its modification toward enhanced amidoximation, J. Appl. Polym. Sci. 105 (2007) 1551–1558.
[14] P.Y. Qin, B.B. Han, C.X. Chen, S. Takuji, J.D. Li, B.H. Sun, Poly (phthalazinone ether sulfone ketone) properties and their effect on the membrane morphology and performance, Desalin. Water Treat. 11 (2009) 157–166.
[15] J.P. Wang, Y.Z. Chen, X.W. Ge, H.Q. Yu, Gamma radiation-induced grafting of a cationic monomer onto chitosan as a flocculant, Chemosphere 66 (2007) 1752–1757.
[16] X.L. Ma, Y.L. Su, Q. Sun, Y.Q. Wang, Z.Y. Jiang, Enhancing the antifouling property of polyethersulfone ultrafiltration membranes through surface adsorption-crosslinking of poly(vinyl alcohol), J. Membr. Sci. 300 (2007) 71–78.
[17] S.A. Gürsel, H.B. Youcef, A. Wokaun, Influence of reaction parameters on grafting of styrene into poly (ethylene-alt-tetrafluoroethylene) films, Nucl. Instrum. Methods Phys. Res., Sect. B 265 (2007) 198–203.
[18] H.M. Choi, R.M. Cloud, Natural sorbents in oil spill cleanup, Environ. Sci. Technol. 26 (1992) 772–776.
[19] G. Deschamps, H. Caruel, M.E. Borredon, C. Bonnin, C. Vignoles, Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents, Environ. Sci. Technol. 37 (2003) 1013–1015.

[20] M.M. Radetić, D.M. Jocić, P.M. Jovančić, Z.L. Petrović, H.F. Thomas, Recycled wool-based nonwoven material as an oil sorbent, Environ. Sci. Technol. 37 (2003) 1008–1012.

[21] V. Rajaković-Ognjanović, G. Aleksić, Governing factors for motor oil removal from water with different sorption materials, J. Hazard. Mater. 154 (2008) 558–563.

[22] X.F. Sun, C. Hu, J.H. Qu, Adsorption and removal of arsenite on ordered mesoporous Fe-modified ZrO_2, Desalin. Water Treat. 8 (2009) 139–145.

[23] J.L. Xie, Q. Wei, B.H. Su, B.S. Qian, Q.Y. Ling, C.S. Zhao, Preparation and characterization of sandwich-structure polyethersulfone membrane with pH sensitivity, Desalin. Water Treat. 8 (2009) 163–170.