

Conversion of Waste Bottles' PET to a Hydrogel Adsorbent via PET Aminolysis

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ABSTRACT. To ensure sustainable use of natural resources and circulation of materials, efficient methods of waste plastic conversion into value chemicals and scenarios for utilization of the latter are increasingly demanded. Here, we propose a method of waste PET bottles conversion to cross-linked hydrogels through PET aminolysis using tri- and tetraamines as a method of plastic waste valorization. Water-soluble oligomeric products of PET aminolysis were cross-linked in water using diglycidyl ether to get mechanically stable hydrogels that show typical polyelectrolyte behavior for polycation. PET-derived hydrogels abundant with amino groups and aromatic moieties were tested as adsorbents for an anionic dye such as Congo Red, and their absorption capacity towards dye was found to be *ca.* 500 mg/g. Beside demonstrated here application of PET-derived hydrogels for water cleaning from an industrial dye, utilization of such hydrogel materials in fields of environment, agriculture, separation, etc. are also anticipated.

INTRODUCTION

Billions of tons of plastics are estimated to be produced to date [1] and due to progressive accumulation of waste plastic during past decades, [2] the problem of its utilization has drawn considerable attention. Landfill and incineration that are commonly used for treatment of waste plastic considerably contribute

to CO₂ emissions and are thus associated with major environmental problems. [3] Pollution of marine environment by microplastics caused by its slow degradation is another global environmental issue. [4] To assure “green” and sustainable use of fossil resources, robust methods of waste plastic conversion to useful materials are increasingly demanded, yet possible chemical technologies are still limited by basic synthetic processes.

Poly(ethylene terephthalate) (PET), the fourth largest produced polymer in the world, [5] is a thermoplastic polymer which is widely used for production of soft drink bottles, food packaging, textile fibers, [6], etc. Depolymerization of PET is an essential synthetic step to prepare low-molecular-weight intermediates that can be further converted to materials. [7] Such chemical recycling of PET is usually performed by glycolysis, methanolysis, and hydrolysis reactions. [8-11] Aminolysis is another approach to PET chemical recycling, which has been intensively investigated these years. [12-21] Primary products of PET aminolysis are bis(2-hydroxy ethylene) terephthalamide (BHETA), [12-14] bis(2-aminoethyl) terephthalamide (BAET), [15] α,ω -aminoligo(ethylene terephthalamide) (AOET) [15] and N,N'-dimethylterephthalamide. [16] These monomeric or oligomeric primary products were used to synthesize secondary products such as benzoxazine resins, [17] unsaturated polyester resins, [18] novel polyurethanes, [19, 20] non-ionic polymeric surfactants, [21] etc. Preparation of further more functional materials, especially the hydrophilic ones, from PET-derived chemicals is still a challenge.

Conversion of primary products of PET depolymerization to hydrogels, to the best of our knowledge, has not been studied and here we developed an approach of preparing PET-derived water-based hydrogel by chemical cross-linking of PET aminolysis products. Hydrogels are three-dimensional hydrophilic polymer networks containing a large amount of water. Hydrogels are broadly applied in pharmaceuticals, agriculture, biotechnology, biosensor, oil recovery, environmental cleaning, and other fields. [22, 23] In particular, water pollution caused by industrial dyes is still an environmental problem that requires water treatment technologies, among which adsorption techniques show a good promise due to high efficiency [24] and nearly quantitative uptake of dye molecules from wastewater while leaving no harmful residues.

[25] Application of hydrogels as adsorbents for dye removal has been actively developed, [26] owing to hydrogels' hydrophilicity, controllable swelling, modifiability, and high absorption capacity.

Herein, a hydrogel material was prepared by a complete conversion of PET bottle plastic to intermediate water-soluble building blocks by aminolysis followed by chemical cross-linking with ethylene glycol diglycidyl ether (EGDE). Subsequently, absorption of Congo Red dye by PET-derived hydrogel was studied and its absorption mechanism was clarified. While the present study demonstrates one possible sustainable route of waste PET conversion to a hydrogel adsorbent, optimization of PET to hydrogel conversion process and chemical design will help increasing the conversion efficiency and target-specific adsorption capacity in such systems.

EXPERIMENTAL SECTION

Materials

PET was obtained directly from waste soft drink bottles. Bottles were washed with Milli-Q water, dried at 70 °C for 1 h in oven, and cut into chips no larger than 1 cm × 0.5 cm.

Diethylenetriamine (DETA), triethylenetetramine (TETA), Congo Red (CR) were purchased from Kishida Chemical Co., Ltd. (Japan). Ethylene glycol diglycidyl ether (EGDE) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Dimethyl sulfoxide (DMSO) and Zinc Acetate were purchased from Fujifilm Wako Pure Chemical Corporation (Japan). 1% Methylene Blue solution (MB), 99.9% dimethyl sulfoxide-d₆ (DMSO-d₆) and acetone were purchased from Kanto Chemical Co., Inc. (Japan). Ethanol was purchased from Nacalai Tesque, Inc. (Japan). Milli-Q water purified by Purelab Chorus 1 Life Science apparatus was used in all experiments.

Methods

UV-Vis spectroscopy. UV-vis spectra of Congo Red and Methylene Blue were recorded on a Jasco V-630 spectrophotometer (Japan) in 100 μL quartz microcells with an optical path 1 cm at room temperature.

FT-IR spectroscopy. Fourier transform infrared spectra of PET aminolysis products and hydrogel were recorded on a FT-IR spectrometer FT-IR-460 (Jasco, Japan) at room temperature. Freeze-dried 13-PD hydrogels were thoroughly mixed with KBr and compressed to form a thin disc, which was next scanned in a wavenumber range between 4000 cm^{-1} and 400 cm^{-1} .

NMR spectroscopy. DMSO- d_6 solutions (0.55 mL) of PET aminolysis products (*ca.* 3 mg) were transferred into an NMR tube and ^1H NMR spectrum was measured on a JNM-ECA500 instrument (JEOL, Japan). Chemical shifts of ^1H NMR were recorded in parts per million (ppm, δ) relative to the solvent resonance as an internal standard (DMSO- d_6 : $\delta = 2.50$ ppm).

Mass spectrometry. ESI (positive) mass spectrometry was performed with a Compact spectrometer (Bruker Diagnostics, USA).

Scanning Electron Microscopy (SEM). SEM observations of freeze-dried hydrogels were pre-frozen at $-20\text{ }^\circ\text{C}$, freeze-dried overnight, coated with a thin carbon film, and observed by JSM-6610 microscope (JEOL, Japan) at an acceleration voltage 10-15 kV.

Sample preparation

PET aminolysis. The PET aminolysis reaction was carried out at PET/DETA and PET/TETA ratios from 1:1 to 1:3 (w/w). 1 g of PET chips, the required amount of DETA/TETA and 0.01 g of zinc acetate were added in a 20 ml round bottom flask with stirrer and reflux condenser. The aminolysis reaction was carried out at $190\pm 5\text{ }^\circ\text{C}$ until all the PET chips were dissolved. All the aminolysis reactions were completed within 30 min and obtained products were stored in glass bottles at room temperature and used for cross-linking reaction without further purification. The solubility of products in different solvents was determined by adding 1% of aminated PET products to different solvents.

Preparation of PET-derived hydrogels. 0.2 g of PET aminolysis product was added to 2 mL Milli-Q water, heated to $100\text{ }^\circ\text{C}$ for 1 min at 200 rpm stirring and maintained at $50\text{ }^\circ\text{C}$ for 1 min. Then, the required amount of EDGE was added at $50\text{ }^\circ\text{C}$ and 250 rpm stirring. After 20 ± 5 min, when the solution became

viscous, the stirring was stopped and the reaction mixture was incubated at 50 °C for 10 min and at room temperature overnight. The hydrogel was washed 5 times with 500 mL Milli-Q water during 24 hours and stored in Milli-Q water. Dry samples of PET-derived hydrogels were prepared by lyophilizing using an Eylea FDU-1200 freeze-drier (Japan).

Hydrogels' swelling ratios were calculated using the following equation:

$$Q = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad (1)$$

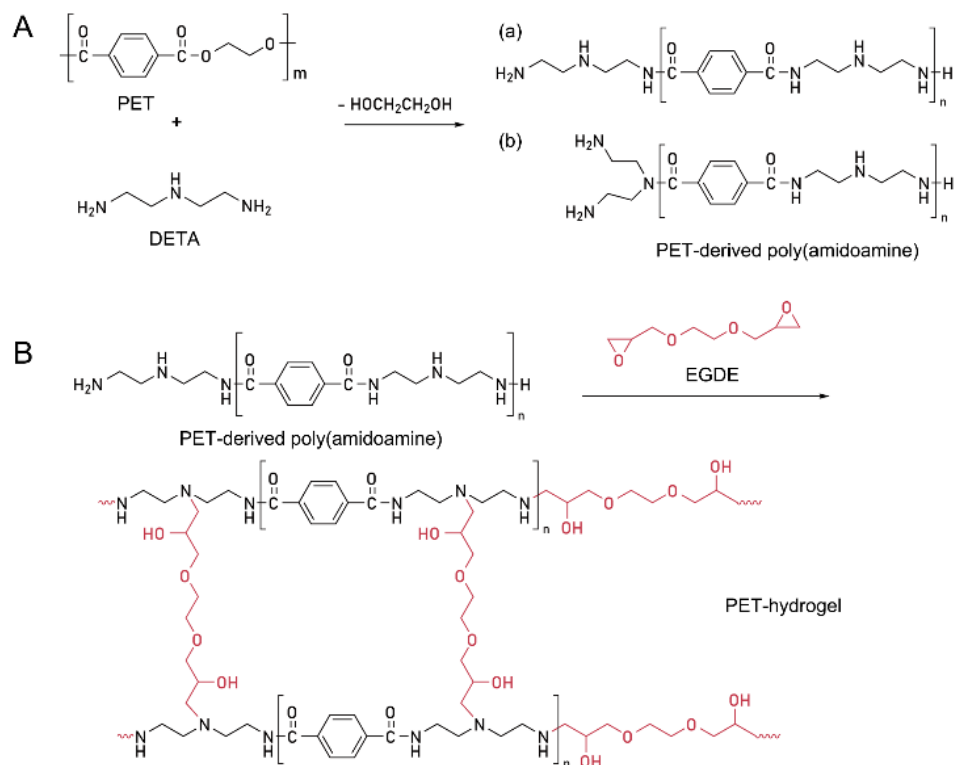
in which m_{wet} and m_{dry} are weights of swollen and lyophilized hydrogel, respectively.

Congo Red absorption by PET-derived hydrogel. A piece of PET-derived hydrogel was placed into Congo Red solution with different concentration and the decrease of Congo Red concentration in the solution above hydrogel was measured by UV-vis spectroscopy. Details of Congo Red absorption data analysis are given in **Supporting Information**.

RESULTS AND DISCUSSION

Preparation of water-soluble oligomers via PET aminolysis. Preparation of a hydrogel from PET requires its conversion to suitable water-soluble polymeric or oligomeric building blocks. Such building block can be obtained by depolymerization of PET by either glycolysis [27, 28] or aminolysis [29, 30] giving mono- or oligomeric water-soluble products. While both aminolysis and glycolysis reactions were considered for preparation of cross-linkable precursors in this study, solubility of PET glycolysis products was not sufficient (**Supporting Information, Table S1**) to carry out cross-linking reaction. PET aminolysis products were more suitable as precursors for hydrogel synthesis not only due to their higher water solubility, but also due to higher reactivity of amino groups in the cross-linking reaction used for hydrogel preparation.

PET plastic was depolymerized in the reaction with either diethylenetriamine (DETA) or triethylenetetramine (TETA) (**Scheme 1A**) based on protocols reported previously. [31, 32] Reaction of each polyamine with PET results in cleavage of ester bonds of PET and formation of one of two types of possible amides (**Scheme 1A**). [32] Due to higher reactivity of primary amines in the ester bond cleavage, the amide (a) is the main reaction product. Aminolysis reactions were carried out at different m(PET)/m(amine) ratios from 1:1 to 1:3 and the corresponding products of PET aminolysis with DETA and TETA are abbreviated hereafter as 11PD, 12PD, 13PD and 11PT, 12PT, 13PT, respectively. Reaction of PET with either amine at the above ratios upon heating (190 °C) resulted in a complete dissolution of plastic material within 30 min. Upon cooling, aminolysis products of PET appeared as white or yellow opaque pastes (**Supporting Information, Figure S1**).



Scheme 1. (A) Aminolysis of PET using DETA. (B) Cross-linking of PET aminolysis product by EGDE.

Good water solubility of PET aminolysis products is a critical prerequisite to the hydrogel preparation; therefore, solubility characteristics of aminated PET oligomers in different solvents were examined (**Table 1**). PET aminolysis products showed a good solubility in polar solvents such as water, DMSO, or ethanol, while all types of aminolysis products were insoluble in acetone. Furthermore, their solubility depended on the amount of amine in the aminolysis reaction. Depolymerization products obtained at PET:TETA = 1:1 or PET:DETA = 1:1 ratios were insoluble in water, while at PET: amine ratios 1:2 or 1:3 the aminolysis products were readily soluble in a boiling water. The enhanced solubility of the products obtained at higher amine ratios is apparently due to increase in the hydrophilicity of PET-derived products. Among studied systems, PET reaction with DETA at 1:3 ratio yielded 13PD product having the best water solubility. To determine the chemical structure of 13PD product, it was characterized using NMR and FTIR spectroscopies, and mass spectrometry (**Figure 1**).

Table 1. Solubility of PET aminolysis products at 1% concentration in different solvents.

	H ₂ O	DMSO	Ethanol	Acetone
PET:DETA (1:1)	-	±	-	-
PET:DETA (1:2)	±	+	±	-
PET:DETA (1:3)	±	+	±	-
PET:TETA (1:1)	-	±	-	-
PET:TETA (1:2)	±	+	+	-
PET:TETA (1:3)	±	+	+	-

+, soluble; ±, soluble on heating at 100 °C; -, insoluble.

¹H NMR spectrum of 13PD is shown in **Figure 1A**. Disappearance of the singlet at 8.16 ppm corresponding to the protons of PET aromatic ring and the triplet at 4.82 ppm corresponding to methylene group (-CH₂-) adjacent to ester bond [33, 34] indicated the complete depolymerization of PET during aminolysis. New peaks at 3.35 - 3.32 ppm were assigned to methylene groups adjacent to amide bonds (e, f).

The presence of multiple peaks was mainly due to formation of different types of amides with primary and secondary amines of DETA. In addition, the peaks at 7.88 and 7.89 ppm were assigned to the protons of aromatic rings of the aminated PET (g). FTIR analysis was used to obtain further information about the structure of 13PD (**Figure 1B, a**). The characteristic absorption peak of PET ester group at 1725 cm^{-1} [35] almost disappeared, which was in agreement with ^1H NMR data. The peak at 3302 cm^{-1} was assigned to N-H stretching [12, 15] and peaks at 2928 cm^{-1} and 2850 cm^{-1} were assigned to asymmetric and symmetric vibrations of the $-\text{CH}_2-$ groups, respectively. [36] The peaks observed at 1632 cm^{-1} and 1548 cm^{-1} were assigned to N-H bending vibrations of primary and secondary amines. [15, 37]

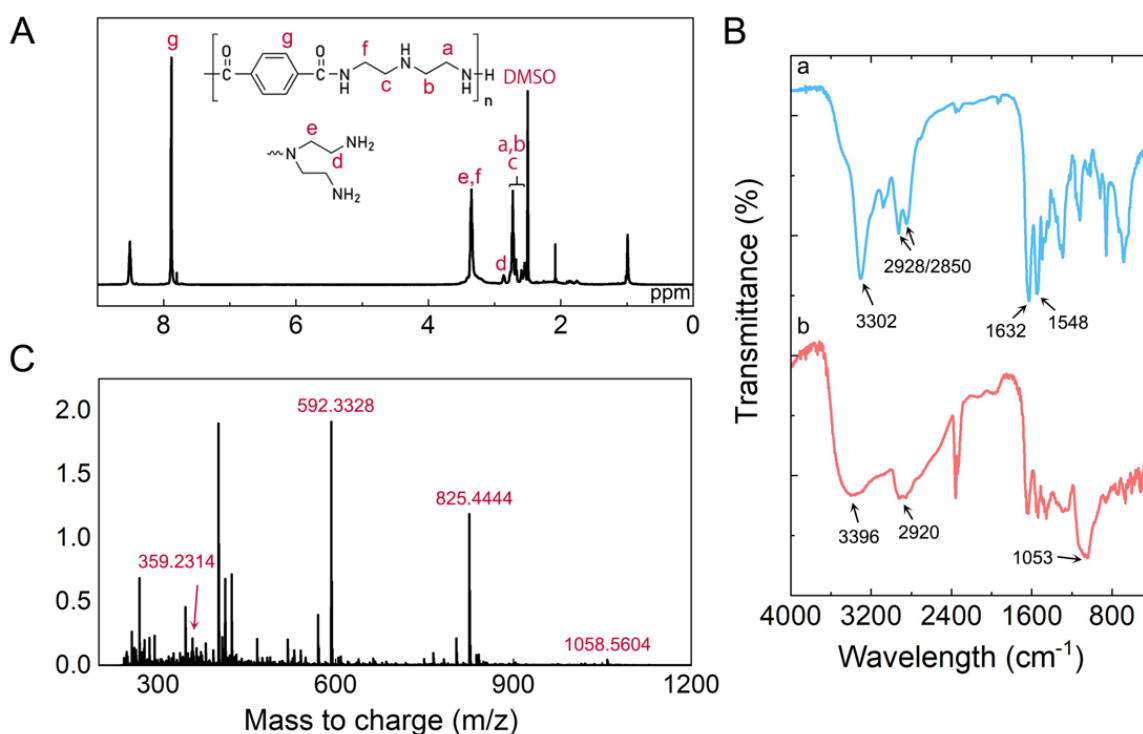


Figure 1. (A) ^1H NMR spectra of 13PD aminolysis product. (B) FT-IR spectra of (a) 13PD and (b) freeze-dried 13PD-hydrogel. (C) Mass spectrum (ESI, positive) of 13PD.

Earlier studies found that depolymerization of PET in the presence of an excess of amine followed by formation of copolymers between terephthalic acid and amines. [15, 17, 32] The NMR and FTIR analysis also made clear formation of amide bonds between terephthalic residues and amines used in the aminolysis reaction. Polymerization degree of oligomers in 13PD was analyzed by mass spectrometry analysis

(**Figure 1 (C)**). The identified molecules and their molecular weight are summarized in **Table 2**. The main components in 13PD reaction mixture were a dimer ($n=2$), which was indicated by the appearance of the peak at m/z 592.3 ionized by Na^+ and a trimer ($n=3$) corresponding to the peak at m/z 825.4. The dimer contains two monomeric units of terephthalic acid and three monomeric units of DETA, while the trimer is formed by three terephthalic acid residues and four units of DETA.

The presence of a monomer and a tetramer were also confirmed by the appearance of peaks at m/z 359.2 ($n=1$), and m/z 1058.5 ($n=4$) ionized by Na^+ . Formation of water-soluble oligomeric building blocks suggests a possibility of further material design. In the present study, we utilized 13PD products to prepare a hydrogel adsorbent.

Table 2. Molecular formulas and calculated molecular masses of the main compounds in 13PD product.

n	n-mer ¹⁾	Molecular formula	Calculated molecular mass
1	Monomer	$\text{C}_{16}\text{H}_{28}\text{N}_6\text{O}_2$	336.4
2	Dimer	$\text{C}_{28}\text{H}_{43}\text{N}_9\text{O}_4$	569.7
3	Trimer	$\text{C}_{40}\text{H}_{58}\text{N}_{12}\text{O}_6$	802.9
4	Tetramer	$\text{C}_{52}\text{H}_{73}\text{N}_{15}\text{O}_8$	1036.2

¹⁾ n-mer is formed by n molecules of terephthalic acid and (n+1) molecules of DETA

Chemical cross-linking of PET-derived aminated products. Products of PET decomposition are rich in amino groups that can be readily cross-linked by a suitable epoxide reagent, e.g. ethylene glycol diglycidyl ether (EGDE) (**Scheme 1B**, **Figure 2A**). The role of EGDE in hydrogel formation process is not only cross-linking, but also chain extension (**Figure 2A**). Interaction of EGDE with terminate primary amines of oligomeric building blocks assures formation of sufficiently long polymeric chain that are necessary to impart the cross-linked polymeric network with a mechanical strength.

Products of PET aminolysis by DETA and TETA at $m(\text{PET})/m(\text{amine})$ ratios 1:2 and 1:3 had a good solubility in a hot water (**Table 1**) and were used to prepare hydrogels. The cross-linking reaction was

carried out by pre-heating of PET aminolysis products in a hot (100 °C) water and then crosslinking by EGDE at 50 °C. In all studied systems hydrogels were successfully formed. A clear transparent hydrogel was formed by cross-linking of 13PD. Due to limited solubility of TETA aminolysis products in boiling water, the reaction mixtures were turbid at the time of cross-linking, and 12PD-hydrogel and 12PT-hydrogel (**Figure 2B**) showed a semi-transparent or apparently opaque state, respectively. 13PT hydrogel appeared transparent, but also incorporated a small fraction of insoluble precipitate in its matrix. Minimum concentration of EGDE necessary to induce gelation of 13PD was the highest (**Figure 3A**). Smaller amounts of EGDE were necessary to induce gelation of other samples containing a fraction of water-insoluble, and thus non-cross-linkable material.

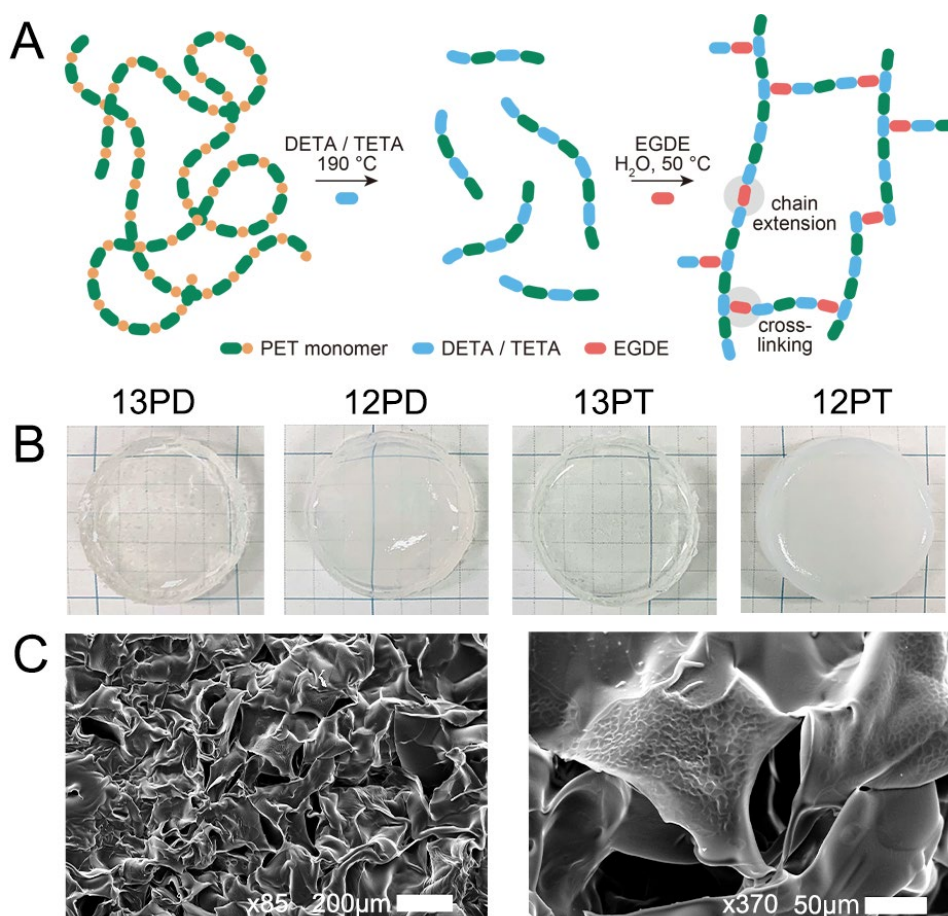


Figure 2. (A) Schematic representation of PET-derived hydrogel formation by cross-linking of oligomeric products of PET aminolysis. (B) Photographic images of 13PD, 12PD, 13PT, and 12PT hydrogels as prepared. (C) Typical SEM images of the 13PD-hydrogel after freeze-drying.

The swelling ratios of four kinds of PET-hydrogels are shown in (Figure 3A). 13PD-hydrogel showed the highest swelling ratio (~70) among all prepared hydrogels. Lower swelling degrees of 12PD, 12PT, and 13PT hydrogels are ascribed to the presence of insoluble phase that, upon cross-linking, limits conformational mobility of hydrogel polymeric network.

FT-IR spectra of freeze-dried 13PD-hydrogel (Figure 1B, b) showed characteristic peaks of EGDE moieties indicating successful cross-linking: $\text{-CH}_2\text{-}$ peak between 2855 and 2934 cm^{-1} , [37] a strong -C-O-C- stretching peak at 1053 cm^{-1} , [37, 38] and a broad peak corresponding to N-H group and O-H groups between 3500 and 3200 cm^{-1} . [37, 39] SEM image of the 13PD-hydrogel after freeze-drying (Figure 2C) shows irregular porous morphology composed of microfilms.

Abundant amino groups of PET-derived hydrogel determine its electrostatic behavior as a polycation that becomes apparent from the pH dependent swelling behavior (Figure 3B). Decrease in the solution pH results in a notable increase of hydrogel's swelling ratio due to NH_2 groups protonation leading to repulsive interactions between NH_3^+ . Unexpected decrease of swelling ratio at $\text{pH} = 2.8$ might be due to partial hydrolysis of amide bonds of the hydrogel.

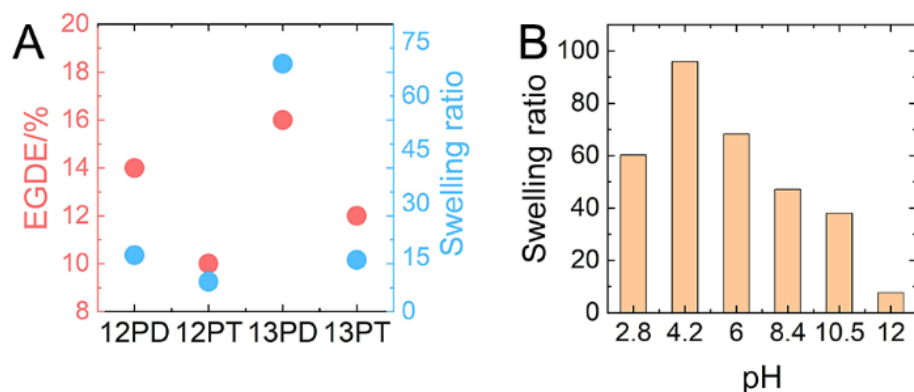


Figure 3. (A) Minimal concentrations of EGDE necessary to prepare hydrogels and their swelling ratios. (B) Dependence of 13PD-hydrogel swelling ratio on solution pH.

Absorptive removal of Congo Red dye by PET-derived hydrogel. Hydrogels are widely used in applications that involve absorption and separation processes. In order to demonstrate a potential application of PET-derived hydrogels, we tested their absorption properties towards typical anionic (Congo Red (CR))

and cationic (Methylene Blue (MB)) dyes using UV-vis spectroscopy (**Figure 4A,B**). In contrast to high removal rates of the anionic CR, no notable changes in the concentration of cationic MB were measured (**Figure 4A,B**), indicating the electrostatic mechanism of dye absorption by the cationic hydrogel matrix. The adsorptive property of four kinds of PET-hydrogels were compared under the same conditions (**Figure 4C**). 13PD hydrogel showed higher removal rates and ~40% higher absorption capacity than other hydrogels that might be caused by a presence of water-insoluble domains in 12PD, 12PT, and 13PT hydrogels explained earlier.

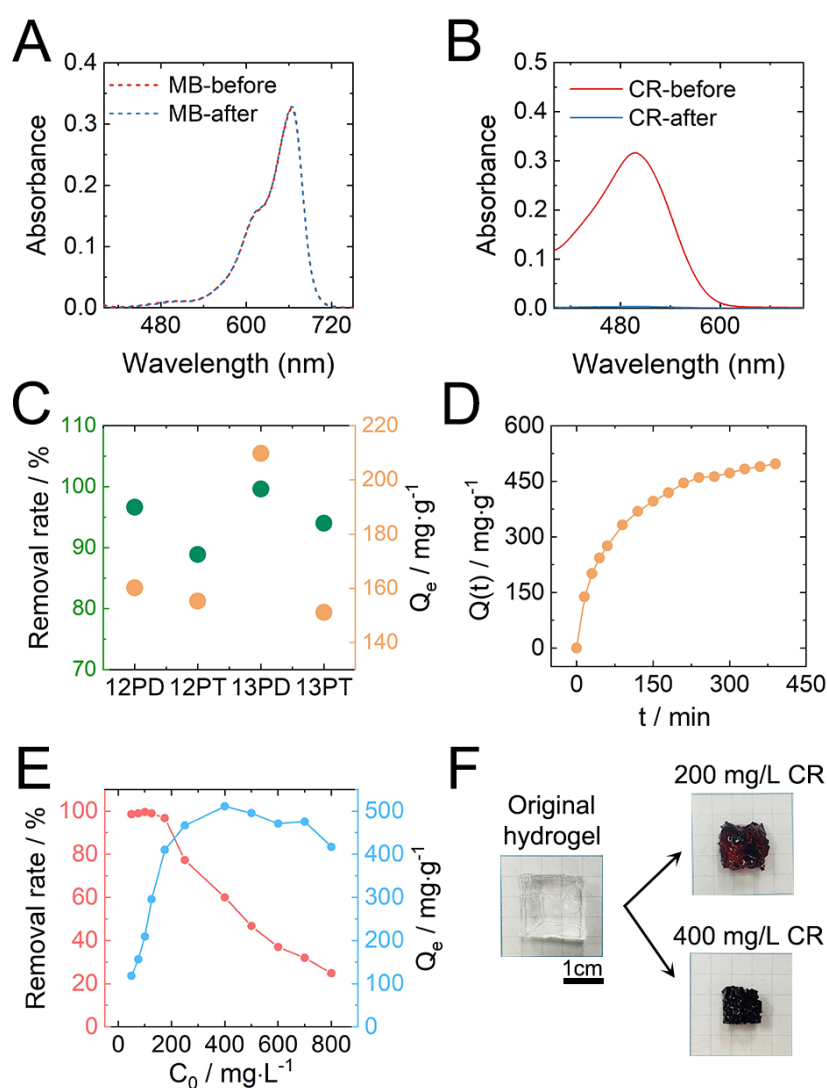


Figure 4. (A-B) UV-vis spectra of MB (A) and CR (B) before and after absorption by 2 mg 13PD-hydrogel from 200 mg/L solutions. (C) CR removal rates and absorption capacities of PET-hydrogels. 2

mg PET-hydrogel was used for absorption of CR from 100 mg/L solution at pH 9. (D) Kinetics of CR absorption by 3.8 mg 13PD-hydrogel from 100 mg/L CR solution. (E) Removal rates and absorption capacities of CR by 2 mg 13PD-hydrogel. (F) Photographic images of 13PD-hydrogel before and after absorption of CR from 200 mg/L and 400 mg/L CR solutions.

In order to understand the absorption mechanism of CR by 13PD-hydrogel, kinetics data **Figure 4D** were fit to pseudo-first, pseudo-second, and intraparticle diffusion models (**Figure 5A-C**) [40, 41] and corresponding fitting parameters are summarized in **Table 3**. Correlation coefficients (R^2) of pseudo-first and pseudo-second kinetic models were higher than R^2 of intraparticle diffusion model. For a more accurate comparison of pseudo-first and pseudo-second kinetic models, residual sum of squares (RSS) analysis was applied. Pseudo-second kinetic model had smaller RSS than pseudo-first model (**Table 3**) indicating a better fit. Therefore, the absorption process of CR by PET-hydrogel was finally assigned to the chemisorption.[42]

Table 3. Kinetics parameters of three models for CR absorption on 13PD-hydrogel

Pseudo-first order				Pseudo-second order				Intraparticle diffusion		
Q_e (cal) (mg/g)	K_1 (min^{-1})	R^2	RSS	Q_e (cal) (mg/g)	K_2 ($\text{g}/\text{mg}\cdot\text{min}$)	R^2	RSS	C (mg/g)	K_p ($\text{mg}/\text{g}\cdot\text{min}^{0.5}$)	R^2
387.6	0.0079	0.9949	0.066	568.1	2.96×10^{-5}	0.9983	0.00107	100	21	0.9492

Figure 4E shows the effect of the initial CR concentration. With the increase of CR concentration, removal rate decreased, on the contrary, absorption capacity increased. **Figure 4F** showed the sharp of 13PD-hydrogel before and after absorption. With an increase of CR concentration, the shrinkage of 13PD-hydrogel increase, due to the continuous interaction of positive charge from hydrogel and negative charge from CR.

Table 4. Isotherm parameters of three models for CR absorption on 13PD-hydrogel

Langmuir	Freundlich	Temkin
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$Q_{m(cal)}^{1)}$ (mg/g)	$K_L^{1)}$ (L/mg)	$R_L^{1)}$	R^2	$K_F^{1)}$ (mg/g)	$n^{1)}$	R^2	$K_T^{1)}$ (L/g)	$b_1^{1)}$ (J/mol)	R^2
489	0.8	0.04	0.9984	227	7	0.6573	66	52	0.8043

¹⁾Parameters were calculated using non-linear fitting curves

To further analyze the distribution of adsorbate molecules on adsorbent surfaces during absorption, the Langmuir, Freundlich, and Temkin isotherm models were used to fit experimental data **Figure 5D-F**. [24, 42, 43] Calculated parameters of each fitting model are listed in **Table 4**. The Langmuir isotherm model was more relevant than other two isotherm models ($R^2 > 0.99$). The value of R_L reflects the essential property of the Langmuir isotherm model to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The obtained $R_L=0.04$ indicated the favorable character of CR absorption. The maximum absorption CR capacity of 13PD-hydrogel was calculated as 489 mg/g. The above results suggest that the absorption of CR by 13PD-hydrogel processes a monolayer absorption and occurs on the homogeneous surface with binding sites.

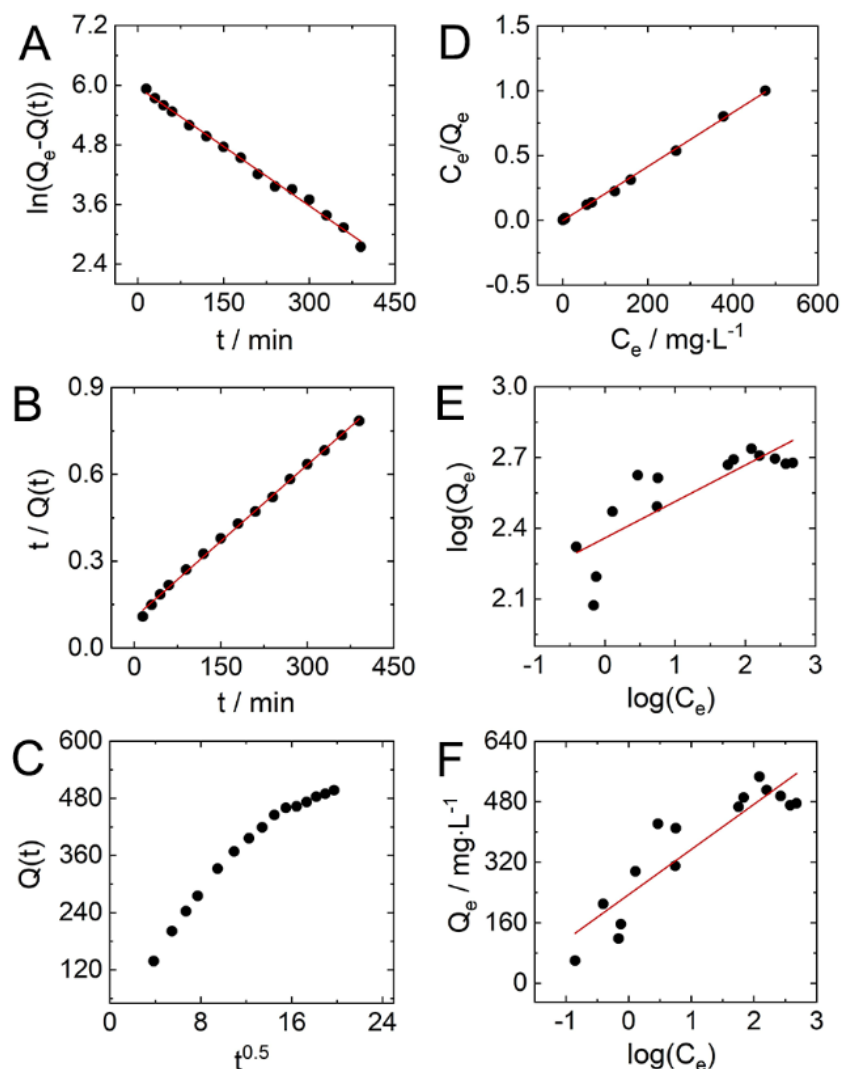


Figure 5. (A-C) Absorption kinetics data linear fit by (A) pseudo-first, (B) pseudo-second, and (C) intraparticle diffusion kinetic models for CR absorption by 13PD-hydrogel. (D-F) Absorption data linear fit by (D) Langmuir, (E) Freundlich, and (F) Temkin isotherm models for CR absorption by 13PD-hydrogel.

CONCLUSIONS

In this study, PET-derived hydrogels were successfully prepared through two-step conversion of PET via aminolysis and cross-linking of water-soluble PET-derived poly(amidoamine) and ethylene glycol diglycidyl ether (EGDE). To the best of our knowledge, this is the first example of PET waste conversion to the hydrogel type of material that may help to significantly broaden the scope of possible applications

of PET waste. All the reactions were performed either without solvent or in water assuring the “greenness” of the proposed conversion process. The transformation of petrochemicals-derived polymer to a water-based hydrogel is novel, promising scenario of plastic waste conversion to a hydrophilic, environmentally friendly functional materials. While in this study we demonstrated one possible application of PET-derived hydrogel as an adsorbent for removal of an industrial dye, its application in other fields that require water-based materials is anticipated and will be likely addressed in the near future.

SUPPORTING INFORMATION

Details of Congo Red absorption data analysis, photographic images of PET aminolysis products; solubility data of PET glycolysis products.

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