



## Development of low cost adsorbent from recycled polyethylene terephthalate for treatment of acephate contaminated water

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Keeping in view, the need for low cost and effective method for treatment of water, herein an attempt is made to depolymerize polyethylene terephthalate (PET) to aromatic amide terephthalic dihydrazide (TDH). TDH is further used as a precursor for synthesis of co-polymer along with glutaraldehyde. The synthesized co-polymer was well characterized using FTIR and Raman spectroscopy, elemental and thermal analysis. The co-polymer was thermally stable and showed good storage stability as well. The co-polymer has been further used as low-cost and non-conventional adsorbent for organophosphate pesticide (acephate) removal from waste water. Various parameters are used for adsorption studies like adsorbent dose, contact time and pesticide concentration. Hence, the synthetic co-polymer can be used as a good alternative for treatment of contaminated water.

Keywords: Polyimine, PET, TDH, adsorption, organophosphorous, pesticide, water treatment.

### Introduction

PET is widely accepted commercial polyester. The large amount of PET products used each year has posed a potential problem, which involves the disposal of these products, especially packaging stuffs. PET is widely used in packaging applications, which become waste after a very short term use<sup>1-3</sup>. This is especially true in case of PET bottles. These bottles increase plastic wastes that cause environment pollution in the form of their disposal<sup>4,5</sup>.

Both chemical and mechanical methods are used for recycling of PET wastes. Fiber products (low grade) are usually generated from mechanical recycling method. Depolymerisation processes such as hydrolysis, glycolysis, aminolysis, and methanolysis are used in chemical method of recycling<sup>6-10</sup>. Moreover PET depolymerization may also be carried out by organo catalysts with surplus quantity of ethylene. Herein this research, an attempt was made to generate a potentially applicable compound TDH from PET waste by easy and facile chemical method i.e. aminolysis<sup>11</sup>. This compound was further used as a monomer for the synthesis of co-polymer based upon Schiff's reaction. Here, a difunctional aldehyde was condensed with difunctional amine. The low cost industrial chemical, TDH (difunctional amine) were reacted with glutaraldehyde (difunctional aldehyde) to form

the synthetic co-polymer via nucleophilic addition elimination reaction<sup>12,13</sup>. In recent years, due to agrochemicals application in crop farms and in forest lands a very serious environmental issue has developed which give rise to contamination over surface and ground water by pesticides. The contamination of surface and ground water is also due to surface runoff, wind erosion, leaching and different applications<sup>14-17</sup>.

Pesticides have various harmful effects in human life due to their toxic effects, mutagenic symptoms and also carcinogenic properties<sup>18</sup>. These pesticides have harmful effects on environment and also on human health which have lead to rigid legislation on drinking quality of water in most of the countries<sup>19,20</sup>. The removal of pesticides from ground and surface water is a major environmental concern. Photocatalytic degradation is one of the method which is convenient for removal of pesticides from water<sup>21,22</sup> and there are other procedures as well: ultrasound combined with photo-Fenton treatment<sup>23</sup>, advanced oxidation processes<sup>24</sup>, aerobic degradation<sup>25</sup>, electro dialysis membranes<sup>26</sup>, ozonation<sup>27</sup>, and adsorption<sup>28-30</sup>. An economic equilibrium separation process is adsorption which is effective method for various applications such as decontamination. The technique is regarded as superior to other techniques in terms of flexibility, simpli-

city of design, initial cost, ease of operation, and recyclability. In this present work, the synthesized co-polymers have been used as low-cost and non-conventional adsorbent for removal of organophosphate pesticide from waste water.

*Materials and method:*

*Chemicals:*

The post consumed plastic water bottles have been collected and used after pretreatment. Hydrazine monohydrate (90%) and glutaraldehyde (25%) were procured from Fisher Scientific, Central Drug House. Methanol and dimethylsulfoxide (DMSO) were procured from Fisher Scientific.  $\gamma$ -Butyrolactone (99%) was procured from Loba Chemie. Pesticide TATA ASATAF acephate (75%) from TATA was purchased from the local market.

*Instrument:*

Systronic double beam spectrophotometer T2201 was used for UV-Visible spectroscopy with bandwidth 2 nm (200–800 nm). FTIR spectra of compounds were recorded on Agilent FTIR Specrometer (ATR module of from Cary 630 FTIR, Agilent Technologies). Differential scanning calorimetry (DSC) was recorded on DSC7020 thermal analysis system Hitachi. Elemental analysis was performed using Elementar Vario EL III CHN Elemental Analyser. Thermogravimetric analysis (TGA/DTA) was performed at 20°C/min in nitrogen atmosphere using Perkin-Elmer, Diamond TG/DTA. Raman spectrum of the compound was recorded on indigenously designed Raman spectrometer, RI Instrument and Innovation, India.

*Method:*

*Pretreatment of PET waste:*

The post consumed water bottles have been collected from vicinity and PET flakes were prepared by cutting these bottles. These PET flakes were washed with boiling water and methanol and then dried in oven at about 80°C for 5 h.

*Synthesis of TDH from PET waste:*

The pretreated PET flakes was treated with hydrazine monohydrate in the ratio 1:10 (w/v) in a sealed reaction flask with continuous stirring at ambient temperature and pressure conditions. The aminolysed product was collected after 24 h and treated with distilled water. The precipitate was dried in oven. A potentially applicable precursor aromatic amide (TDH) was synthesized from PET by aminolysis chemical degradation.

*Synthesis of co-polymer:*

The monomer units used for the synthesis of co-polymer were TDH and glutaraldehyde in the stoichiometric ratio [1:1], [1:2] and [1:4]. TDH solution [0.94 g (5 mmol) in 30 mL DMSO] was added to 20 mL glutaraldehyde [0.50 mL (5 mmol) in 20 mL DMSO] and the reaction mixture was heated at 45°C for 3 h. The white color reaction mixture was obtained. The reaction mixture was filtered and then precipitate was dried in oven at 60°C to obtain a co-polymer of TDH and glutaraldehyde [1:1].

TDH solution [0.94 g (5 mmol) in 30 mL DMSO] was added to 20 mL glutaraldehyde [0.94 mL (10 mmol) in 20 mL DMSO] and the reaction mixture was heated at 45°C for 3 h. The white color reaction mixture was obtained. The reaction mixture was filtered and then precipitate was dried in oven at 60°C to obtain a co-polymer of TDH and glutaraldehyde [1:2].

TDH solution [0.94 g (5 mmol) in 30 mL DMSO] was added to 20 mL glutaraldehyde [1.88 mL (20 mmol) in 20 mL DMSO] and the reaction mixture was heated at 45°C for 3 h. The white color reaction mixture was obtained. The reaction mixture was filtered and then precipitate was dried in oven at 60°C to obtain a co-polymer of TDH and glutaraldehyde [1:4].

*Preparation of standard curve of pesticide solution:*

The stock standard solution was prepared by dissolving the known quantity of acephate (organophosphate pesticide) in distilled water. 100 mL of acephate solution of different concentrations in the range 0.1–1.0 mg/mL was prepared from stock solution and its absorption was noted at wavelength  $\lambda_{\max}$  255 nm by UV-Visible double beam spectrophotometer. The standard curve was prepared between absorbance and concentration at  $\lambda_{\max}$  255 nm of known concentrations of acephate solution.

*Determination of adsorption capacity of co-polymer:*

100 mL of pesticide stock solution at initial concentration of 1.0 mg/mL was prepared and a fixed dose of 0.1 g co-polymer of TDH and glutaraldehyde [1:4] was added to this solution. The beaker was kept at room temperature (25°C  $\pm$  2°C), for contact time of 2 h with frequent agitation to reach equilibrium. After 2 h, absorbance of pesticide solution was observed at  $\lambda_{\max}$  255. A decrease in the adsorption of pesticide solution was observed. Further, concentration of the given pesticide solution was estimated by prepared standard curve. The same experiment was repeated at the same

concentration and experimental condition at different time intervals (2 h, 4 h, 6 h etc.).

The adsorption capacity of 0.1 g of synthesized co-polymer with respect to time can be calculated using the equation.

$$\text{Adsorption capacity} = [(C_A - C_B)/C_A] \times 100 \quad (1)$$

where  $C_A$  = original concentration of pesticide without co-polymer.  $C_B$  = concentration of pesticide with co-polymer after time interval.

Various parameters are used for adsorption studies like adsorbent dose, contact time and pesticide concentration.

## Results and discussion

### *Chemistry of synthesis:*

PET waste was degraded using hydrazine monohydrate by simple aminolysis reaction without the use of any catalyst at ambient temperature and pressure condition. The reaction proceeds via nucleophilic mechanism. The amines of hydrazine monohydrate act as nucleophile which reacts with carbonyl group of PET, thereby breaking ester linkage. The by-product formed is ethylene glycol. The aminolysis reaction of PET with hydrazine monohydrate is proposed in Fig. 1(A). TDH is used as a precursor in the co-polymer synthesis. The co-polymer of TDH and glutaraldehyde was synthesized based on Schiff base chemistry. Poly-Schiff bases are also known as polyimines. Imines are established as nitrogen analogs of carbonyl functional group. In nucleophilic addition-elimination reaction, imines are formed by the reaction of aldehydes or ketones with primary amines and ammonia derivatives<sup>13</sup>. Here in this mechanism of Schiff base formation, the non-bonded electrons on nitrogen cause water to be eliminated as by-product and further there is subsequent loss of proton from the protonated imine to form a stable imine. In this work, dialdehyde react with diamine to form polyimine. The low cost compound TDH were reacted with glutaraldehyde to form synthetic co-polymer. Fig. 1(B) shows the mechanism of synthesis of co-polymer.

### *Characterization:*

#### *FTIR analysis:*

FTIR spectra of TDH showed absorption bands at 3310  $\text{cm}^{-1}$  and 1602  $\text{cm}^{-1}$  which was assigned to N-H and C=O stretching, respectively. A medium bifurcated band was observed at 3310  $\text{cm}^{-1}$  that showed coupled N-H stretching

indicating the presence of primary amide. The absorption bands obtained at 1600, 1536, 1487  $\text{cm}^{-1}$  showed C=C stretching indicating the presence of an aromatic ring. The absorptions at 1290, 1233, 1100  $\text{cm}^{-1}$  showed C-O stretching. The spectral values of TDH synthesized in lab were in good agreement with that of literature reported<sup>11</sup>. Fig. S1(A) (Supplementary files) shows FTIR spectrum of TDH.

FTIR of co-polymer of TDH and glutaraldehyde in the given ratios of [1:1], [1:2] and [1:4] are shown in Fig. S1(B) (Supplementary files). Absorption band at 3310  $\text{cm}^{-1}$  indicated coupled N-H stretching showing the presence of secondary amide. A sharp peak at 1652  $\text{cm}^{-1}$  showed C=N (imine) stretching indicating the presence of imine. The absorption band obtained at 1490  $\text{cm}^{-1}$  showed C=C stretching indicating the presence of an aromatic ring. The absorption band at 2932  $\text{cm}^{-1}$ , showed C-H stretching. The presence of C=N confirmed the reaction product obtained was polyimine. Fig. S1(B) (Supplementary file) shows FTIR spectra of co-polymer of TDH and glutaraldehyde [1:1], [1:2] and [1:4].

#### *Raman spectroscopy:*

Raman spectroscopy is a technique complementary to FTIR analysis. Raman spectroscopy was done for co-polymer of TDH and glutaraldehyde. C=N stretch was found at 1640  $\text{cm}^{-1}$  confirming the presence of imine group. The band at 3050  $\text{cm}^{-1}$  denotes the presence of C-H stretch. The band obtained at 1560  $\text{cm}^{-1}$  and 1300  $\text{cm}^{-1}$  showed the presence of C=C stretching indicating the presence of an aromatic ring and C-C stretch, respectively. Fig. S2 (Supplementary file) shows Raman spectrum of co-polymer of TDH and glutaraldehyde.

#### *Elemental analysis:*

CHN analysis was done to identify the percentage of carbon, hydrogen and nitrogen in co-polymer of TDH and glutaraldehyde. Table 1 shows that theoretical and experimental % of CHN is in good agreement with each other.

#### *Thermal analysis:*

TGA/DTA and DSC were performed for co-polymer of TDH and glutaraldehyde [1:4] to study the physical behavior of the compound with respect to temperature. TGA/DTA was performed from ambient temperature upto 720°C (heating rate 20°C/min) in nitrogen atmosphere using 10 mg sample.

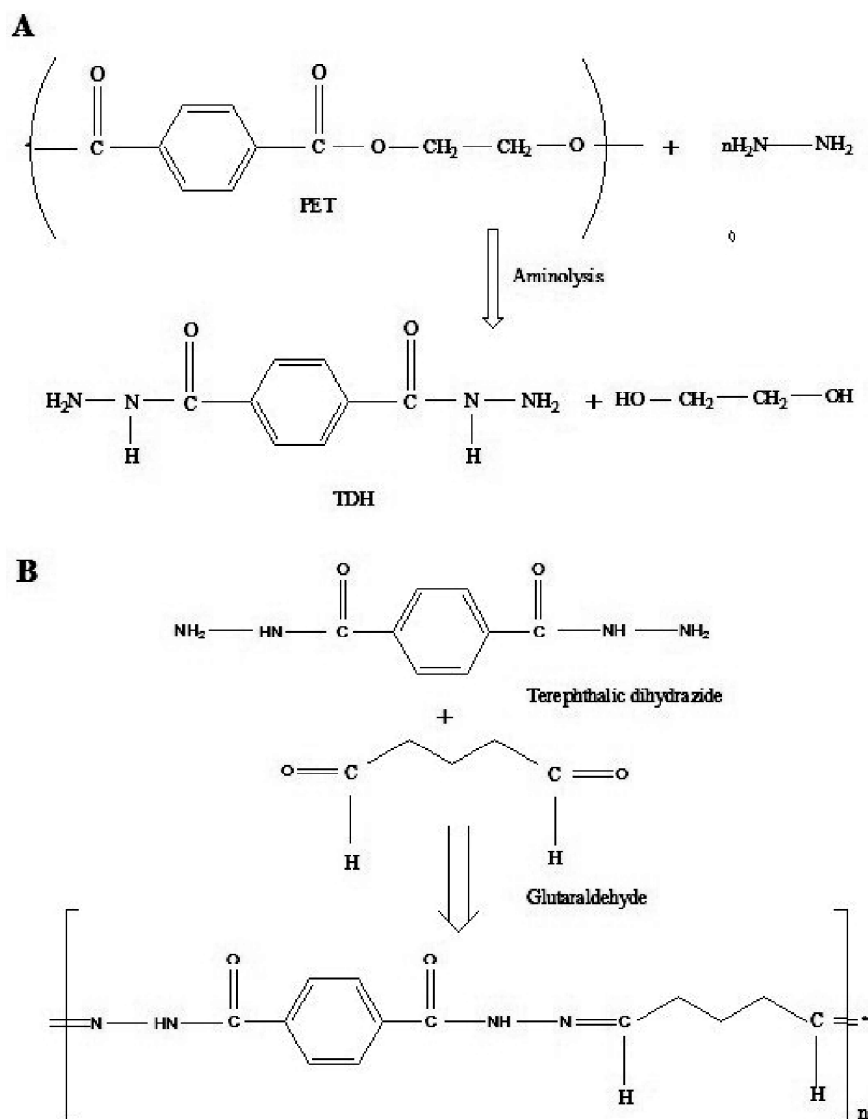


Fig. 1. (A) Synthesis of precursor TDH from PET. (B) Synthesis of co-polymer of TDH and glutaraldehyde.

TGA was performed for co-polymer to give an insight into structure with respect to temperature. The loss in weight of co-polymer was observed after 275°C, hence establishing that co-polymer was thermally stable till 275°C (Fig. S3). Fig. S3 (Supplementary files) shows TGA curve of co-polymer. The degradation pattern for all the three co-polymer was similar.

DSC was performed using 10 mg sample from ambient to 300°C at a heating rate 20°C/min in nitrogen atmosphere. The optimum temperature to melt the co-polymer of TDH and glutaraldehyde 1:1(A) was found to be 164.1°C (broad

peak). The melting temperature of the co-polymer of TDH and glutaraldehyde 1:2(B) was 248.7°C. The thermogram of co-polymer 1:4(C) showed two step degradations. The first degradation showed melting temperature at 246.1°C and second degradation temperature at 256.3°C. The copolymer showed good thermal stability as well as storage stability [Fig. S4 (Supplementary file)]. The polymer was stored at room temperature and pressure condition for prolonged period. FTIR analysis of the compound was done at different time interval and found that the co-polymer was stable after storing the polymer for prolonged period.

**Table 1.** Comparison of theoretical and experimental (%) of CHNS of TDH and co-polymer of TDH and glutaraldehyde

Compd.	Theoretical (%)				Experimental (%)			
	C	H	N	S	C	H	N	S
TDH	49.48	5.15	28.86	0	49.05	5.01	28.13	0.01
Co-polymer of TDH and glutaraldehyde [1:4]	60.23	5.79	21.63	0	59.14	6.10	20.70	0

*Application of co-polymer as an adsorbent:*

100 mL of the pesticide stock solution of initial concentration 1 mg/mL was prepared and a fixed dose of 0.1 g co-polymer of TDH and glutaraldehyde [1:4] was added to this solution. The beaker was kept at room temperature (25°C ± 2°C), for contact time of 2 h with frequent agitation to reach equilibrium. After 2 h, pesticide solution was tested to get the absorbance at  $\lambda_{max}$  255 nm. A decrease in the absorption of pesticide solution was observed from the prepared standard curve. The same experiment was repeated for 4 h with 1 mg/mL pesticide solution and concentration was estimated. The same experiment was repeated after 6 h with 0.1 g of co-polymer and 1 mg/mL concentration of pesticide solution. Table 2 shows the adsorption capacity of 0.1 g of synthesized co-polymer with respect to time.

**Table 2.** Adsorption capacity of synthesis co-polymer with respect to time

Time interval (h)	Absorbance	Concentration (mg/mL)	Adsorption capacity (%)
0 (blank)	0.083	1.0	–
2	0.069	0.82	18
4	0.051	0.63	37
6	0.047	0.58	42

In this study, removal capacity of acephate pesticide from water by synthetic co-polymer which is a low-cost and waste adsorbent was investigated. The synthesized (0.1 g) co-polymer of TDH and glutaraldehyde [1:4] was kept in the pesticide solution (1 mg/mL) for 2 h, which showed the adsorption capacity of 18% and after 4 h it showed adsorption capacity of 37%. It reached equilibrium in 6 h with adsorption capacity 42%. The results show that the use of polymer has decreased the concentration of the pesticide in pesticide

contaminated water. Thus synthetic copolymer can be used as an adsorbent for contaminated water.

The results show that co-polymer [1:4] with maximum adsorption capacity of 42% (0.1 g of co-polymer) can be used as a good alternative synthetic adsorbent for treatment of pesticide contaminated water.

**Conclusions**

In recent years, due to agrochemical applications in crop farms and in forest lands a very serious environmental issue has developed which has led to contamination over surface and ground water by pesticides. An economic equilibrium separation process is adsorption which is effective method for various applications such as decontamination and is preferred over other methods due to flexibility, simplicity of design, initial cost, ease of operation, and resistance to toxic pollutants. In this research work, an attempt was made to develop a potentially applicable compound TDH from PET waste water bottles by aminolysis method at ambient temperature and pressure condition. PET was aminolysed to aromatic amide TDH by hydrazine monohydrate. The low cost industrial chemical, TDH (difunctional amine) were reacted with the glutaraldehyde (difunctional aldehyde) to form the synthetic co-polymer via nucleophilic addition elimination reaction. The synthesized co-polymer of TDH and glutaraldehyde have been carried out in various ratios viz. [1:1], [1:2] and [1:4] and well characterized by using FTIR and Raman spectroscopy, element analysis and thermal analysis. The synthesized co-polymer has been used as a non-conventional and low-cost adsorbent for organophosphate removal from waste water. The adsorption capacity of co-polymer of TDH and glutaraldehyde [1:4] was estimated experimentally and it was concluded that co-polymer showed maximum adsorption capacity of 42% (0.1 g co-polymer) after 6 h. Hence, the synthetic co-polymer can be used as an alternative for treatment of pesticide contaminated water.

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