Chemical Science International Journal

19(4): 1-7, 2017; Article no.CSIJ.34270
ISSN: 2456-706X
(Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

Synthesis and Characterization of Cellular Polyurethane as Redox Catalyst

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Authors' contributions

This work was carried out in collaboration between all authors. Author MS designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors YN, AK and MI managed the analyses of the study. Author YS helped honorably through expertise of her field. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2017/34270
Editor(s):
(1) Francisco Marquez-Linares, Full Professor of Chemistry, Nanomaterials Research Group, School of Science and Technology, University of Turabo, USA.
Reviewers:
(1) Birsa Mihail Lucian, Alexandru Ioan Cuza University of Iasi, Romania.
(2) Leo Baldenegro, Center of Engineering and Industrial Development, Mexico.
(3) M. Mupa, Bindura University of Science Education, Zimbabwe.
Complete Peer review History: http://www.sciencedomain.org/review-history/19948

Original Research Article

Received 22nd May 2017
Accepted 7th June 2017
Published 8th July 2017

ABSTRACT

Dyes are coloring materials used extensively in common consumer products. A large amount of dye effluent is produced mainly by textile industry. These dye effluents need remediation as they are damaging water bodies and biological organisms including human beings. Polyurethane is one of the potential materials which can be used to solve this problem. In this study, polyurethane was synthesized by a simple method using toluene diisocyanate (TDI), Polyethylene glycol (PEG; 1000 g/mol) and Butanediol (BDO). The synthesis was confirmed by the FTIR bands of –NH, C=O, C–N and C–O–C at 3390 cm^{-1}, 1735 cm^{-1}, 1420 cm^{-1} and 1094 cm^{-1}, respectively. This synthesized material was applied in degradation of Methylene blue dye through reduction reaction which was monitored by UV-Vis spectroscopy. The color of the dye was removed 100% in just 7 min. Where, more than 70% dye was reduced in just first 3 mins. Consequently, synthesized material can be a potential catalyst in reduction processes.

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Keywords: Polyurethane; dyes; catalyst; methylene blue; spectroscopy.

1. INTRODUCTION

Dyes are coloring materials used in color commodities of our day to day use. Dye effluents are among the major pollutants discharged into the environment. Wastewater from textiles, food coloring, paper, pharmaceuticals and cosmetic industries are polluted by dyes. When these colored effluents are entered into the rivers or lakes they damage the aesthetics and upset the biological activities in these water bodies [1]. The textile industry is the main contributor in production of colored wastewater as approximately 100 L of water is wasted during processing of 1 kg of fabrics [2-3]. In Pakistan, situation becomes more serious, where textile industry is the backbone of economy and export. These dyes are a great concern in effluent treatment due to their color and potential toxicity to animals and humans [4]. The common removal techniques for dyes include coagulation, ozonation, membrane process, filtration, adsorption and bioremediation [5]. All of these techniques have their own pros and cons. However, when color is removed from wastewater, not only it regains original aesthetic look, also becomes less hazardous for further applications. Furthermore, removal of color minimize the interference in advanced wastewater treatment steps. A number of synthetic and natural materials are used in these techniques. Polyurethane is one of potential material to be used for treatment of wastewater.

Polyurethane (PUR) is produced by the polyaddition or ring opening type of reactions [5-6]. It is a versatile and very important class of synthetic polymers. They are block copolymers made up of soft and hard segments alternating each other, linked together with urea or urethane linkage. Soft segments are mostly with low glass transition temperature such as polyesters with free –OH groups [7-8]. The hard segments are composed of diisocyanates, possessing high glass transition temperature [9-10]. They are used in variety of applications such as high-performance air filters, sensors, coatings, protective textiles, wound dressing materials, binder resins, fibers and elastomeric products [11]. The versatile applications of PUR are associated with its adaptable properties such as elasticity, flexibility, high abrasion resistance, tear strength and excellent shock absorption. The molecular structure of PUR has a number of polar sites which can play important role in removal of pollutants such as metals and dyes etc.

In this study a novel aspect of polyurethane applications was observed. As we are reporting the catalytic role of polyurethane in removal of Methylene blue (MB) through reduction process. Here simple PUR polymer was synthesized at ambient temperature and characterized. It was applied for removal of a model dye that is MB from aqueous solution. The observed process was based on reduction of dye resulting in complete removal of blue color from aqueous system. The effect of variables such as dye concentration and dose of PUR etc. was investigated in terms of time required to complete the process. The PUR has shown an excellent catalytic activity in reduction of dye.

2. MATERIALS AND METHODS

2.1 Materials

Toluene-2,4-diisocyanate (TDI) was purchased from Sigma Aldrich Chemical Co., USA. Polyethylene glycol (PEG; Mw: 1000 g/mole), Butanediol (BDO) and Sodium borohydride ($NaBH_4$) was procured from Acros Organics, USA. Methylene blue was provided by Avonchem Limited UK.

2.2 Synthesis of Polyurethane

PUR was prepared using TDI, PEG and BDO. The PEG (20 g) was melted in a china clay glazed bowl. Then 7 ml of TDI and 2 ml of BDO were added drop wise into the melt with continuous stirring. The distilled water (1.9 mL) was added into the materials parallel to the stirring which started formation of cellular PUR [5]. Whole process was completed in few minutes. The above synthesized sample was kept in an oven for 48 hours at 50℃.

2.3 Characterizations

The molecular composition of synthesized PUR was confirmed by Fourier Transform Infrared spectroscopy (FTIR; Agilent Technologies Carry 630, USA). The spectrum was recorded in the range of 4000 cm^{-1} to 600 cm^{-1}.

The solubility of sample was studied at ambient temperature and 50℃ in different solutions like

acetone, n-Hexane, N, N'-dimethyl formamide (DMF), tetrahydrofuran (THF), and ethanol. A weighed amount (0.3 g) of sample was placed in 5 ml of each solvent and solubility was noted after 24 hours [5].

The catalytic property of PUR sample was examined by using MB dye solution in the presence of $NaBH_4$ using UV-visible spectrophotometer (UVD-3500 Labomed, Inc., USA). The spectrum was collected using a quartz cuvette with 1 cm optical path length. Sodium borohydride, 0.5 M solution was freshly prepared along with $4.6x10^{-5}$ M solution of MB. Two set of experiments were carried out simultaneously. One experiment was performed with 0.1 g PUR while the other one was used as a blank without sample. Then change in absorbance was recorded continuously till the solutions became colorless.

Effect of experimental variables on catalytic activity was studied separately with different levels of each variable. Three different concentrations of dye, 30 ppm, 40 ppm and 50 ppm were used with constant sample dose of 0.1 g and 1% solution of $NaBH_4$. In the similar manner, the effect of three different levels of $NaBH_4$, 1%, 1.33% and 2% was investigated with 0.1 g sample dose and 50ppm dye solution. Also, effect of sample dose was monitored using three different doses, 0.1 g, 0.5 g and 1.5 g with 50 ppm dye solution and 1% $NaBH_4$. In each case change in absorbance was recorded at 665 nm till complete decolorization. The percentage color removal of the dye was calculated from the following formula.

$$D = \frac{A_0 - A_t}{A_0} \times 100$$

Where, D is percentage removal of color; A_o is absorbance at zero time and A_t is the absorbance at time t.

3. RESULTS AND DISCUSSION

3.1 Fourier Transform-Infrared (FT-IR) Spectroscopy

The IR spectrum of PUR is shown in Fig. 1. This spectrum confirmed the formation of required product. In this spectrum characteristic bands of urethane are following; N–H stretching band at about 3390 cm^{-1}, C–H symmetric and antisymmetric stretching at 2890 cm^{-1}, C=O stretching at 1735 cm^{-1}, C=C stretching at 1600 cm^{-1}, N–H bending around 1530 cm^{-1}, N–C band at 1420 cm^{-1} and characteristic band of ether linkage, C–O–C at 1094 cm^{-1} [12-14]. Also, –NCO band of TDI around 2300 cm^{-1} and –OH bands of PEG and BDO were disappeared which supports the formation of PUR [15].

3.2 Solubility of PUR

The solubility of sample is important in order to direct its application in different media. Therefore, solubility in different polar and non-polar solvents was examined at ambient and 50℃ temperature and results are presented in Table 1.

These results indicated the complete solubility of synthesized PUR in DMF. But, it showed partial solubility in water, ethanol and THF. At higher temperature, solubility in THF was increased. However, sample was insoluble in n-hexane being a non-polar solvent. An important point to

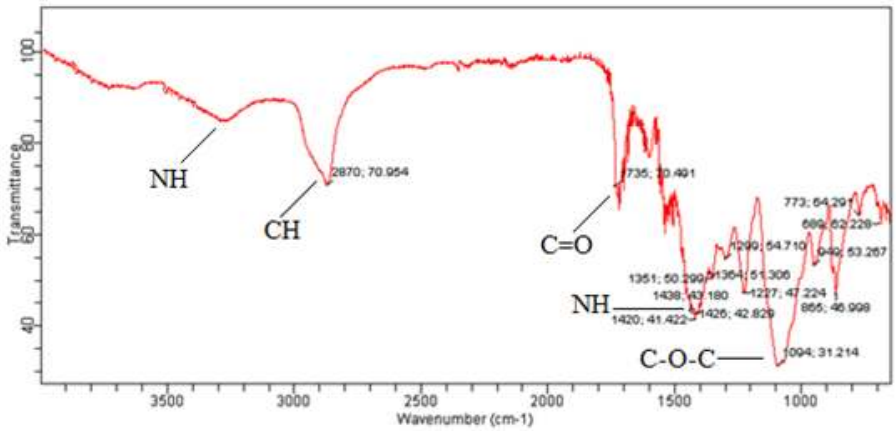

Fig. 1. IR spectrum of synthesized PUR sample

Table 1. Solubility of PUR in different solvents at ambient temperature and at 50℃

Sr. No.	Solvents	Solubility at ambient temperature	Solubility at 50℃
1	Water	±	±
2	Ethanol	±	±
3	n-Hexane	_	_
4	THF	±	+
5	DMF	+	+

+ = soluble; - = insoluble; ± = partially soluble

consider here is that partial solubility in water can affect the ultimate application of PUR. It suggested more structural improvement in PUR which can make it more stable.

3.3 Reduction of MB

The progress of catalytic activity was monitored by recording UV-Vis. spectrum of MB dye with time. The proposed reaction for reduction of dye is presented in Fig. 2.

The spectra of catalyzed experiment (with dye solution, $NaBH_4$ and PUR) and blank experiment (with dye solution and $NaBH_4$ only, without PUR) are given in Figs. 3 and 4, respectively. The absorbance at λ_{max} of dye was decreased with time which was an indicative of reduction of the dye. These spectra clearly showed catalytic property of synthesized PUR. It can be seen that 71.5% color removal was attained in 22 min. in case of blank experiment. Conversely, almost equal result was obtained in just 3 min. in presence of PUR. And 100% color removal was observed in only 7 min. Similar results has been reported earlier with silica supported Ag nano particles [16]. This catalytic activity of PUR may be possible because of presence of $–NH–H_4C_6–NH–COO$ groups in structural backbone. These groups may able to act as electron mediator in redox reaction just like natural catalytic systems (17). Also cellular nature of the material provides cavities for close and confined interaction of electrophile i.e. dye and nucleophile i.e. BH_4^-.

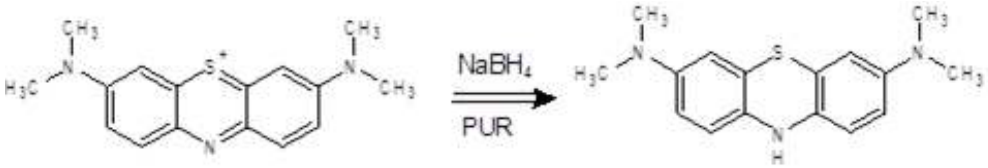

Fig. 2. Schematic reaction for reduction of Methylene blue

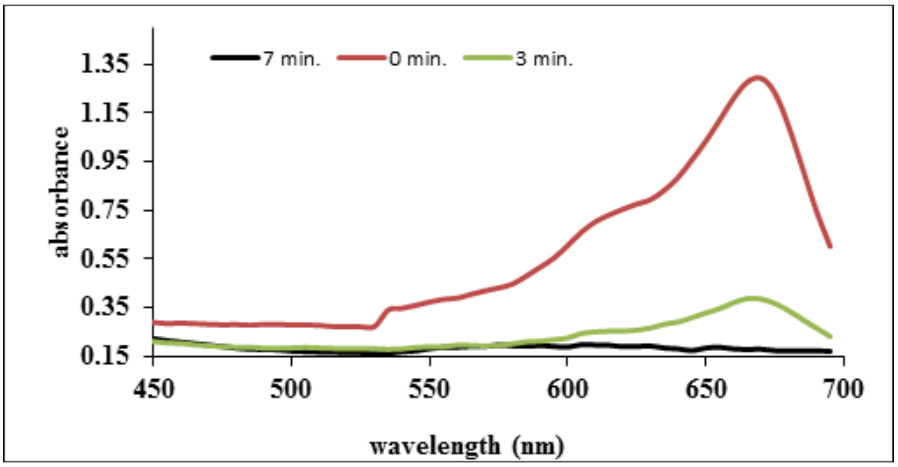

Fig. 3. UV-Vis spectra of MB during catalyzed reduction reaction. MB= $4.6x10^{-5}$; $NaBH_4$= 0.5 M and PUR= 0.1 g

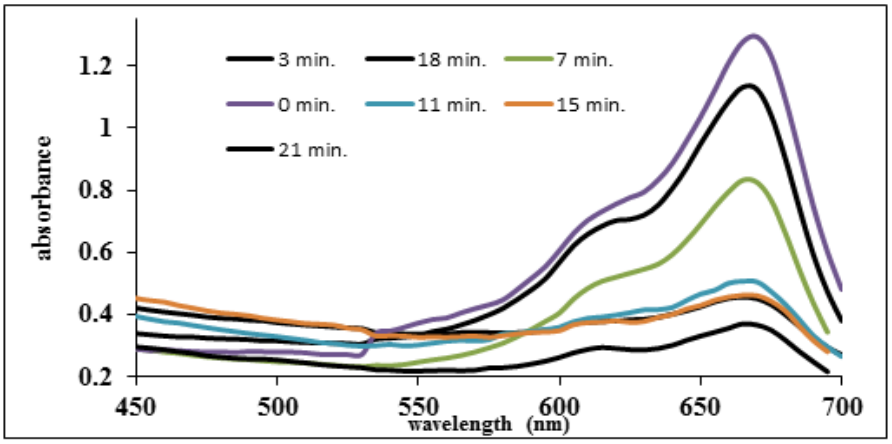

Fig. 4. UV-Vis spectra of MB during blank experiment in absence of PUR; MB= $4.6x10^{-5}$; $NaBH_4$=0.5M

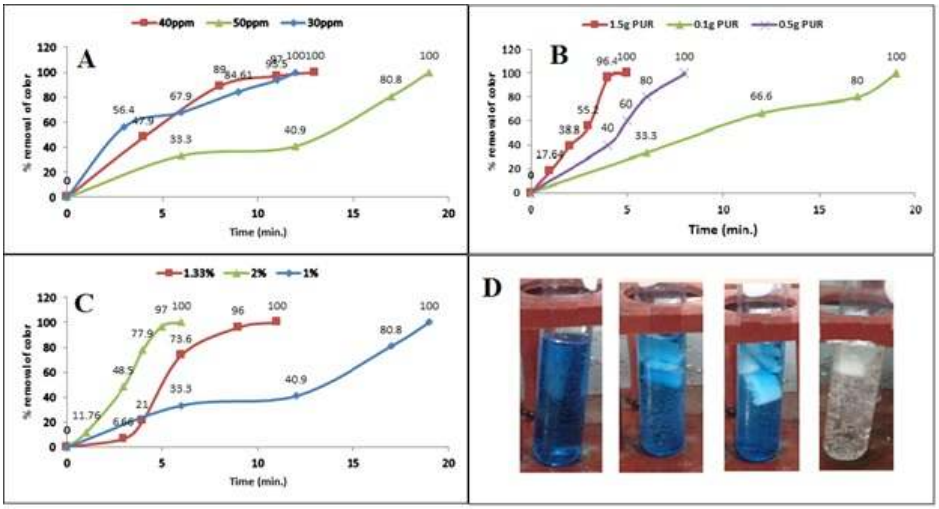

Fig. 5. Removal of dye (%) at different time intervals; A) 50 ppm, 40 ppm and 30 ppm dye concentrations with 0.1 g PUR and 1% $NaBH_4$, B) 0.1 g, 0.5 g, 1.5 g PUR with 1% $NaBH_4$ and 50ppm dye solution, C) 1%, 2% and 1.33% $NaBH_4$ with 50 ppm dye solution and 0.1 g PUR, D) progressive decrease in color of dye recorded by digital camera images

3.4 Effect of Variables on Catalytic Activity of PUR

The amount of catalytic material, concentration of $NaBH_4$ and concentration of MB were main possible variables during catalytic reduction process. Therefore, to investigate their effect on catalytic activity of synthesized PUR, three different set of experiments were carried out. In each experimental set, three levels of one specific variable were used keeping others constant.

Effect of concentration of dye was monitored with 50 ppm, 40 ppm and 30 ppm solutions. While, $NaBH_4$ and PUR dose were fixed such as 1% and 0.1 g, respectively. The results recorded in terms of time required for disappearance of color are presented in Fig. 5A. It can be seen that time for removal of color has increased with an increase in dye concentration; more dye will take longer time to be reduced.

Fig. 5B demonstrated the linear relationship between PUR dose and reduction time. As more catalyst was available, reduction process was accelerated even in presence of same concentration of reducing agent. Also, Fig. 5C shows effect of concentration of $NaBH_4$ on reduction time. With increase in concentration of

reducing agent, time for reduction has shortened significantly. All these results are quite justified, as concentration of $NaBH_4$ and PUR dose directly affect the reduction time by facilitating the process positively. However, study of effect of variables can be exploited to sketch the commercialization cost of the process.

4. CONCLUSION

A simple polyether based PUR was prepared at room temperature. The synthesis of PUR was confirmed by typical FTIR bands of –NH, C=O, C–N and C–O–C at 3390 cm^{-1}, 1735 cm^{-1}, 1420 cm^{-1} and 1094 cm^{-1}, respectively. The prepared sample was applied as a catalyst in reduction of MB dye in terms of removal of color from aqueous system. The complete color removal was obtained just in 07 min. which was quite rapid as compared to the control. The reduction time was increased with increasing dye concentration while decreased with decreasing the amount of reducing agent and PUR dose. However, it is important to mention that PUR was partially soluble in water. It can interfere in proper application of material. Therefore, more improvement in stability of PUR is required which can be achieved through tailoring of its composition.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
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