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Research Article

Ecofriendly Reduction of Methylene Blue with Polyurethane Catalyst

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A number of physical, chemical, and biological technologies have been developed to address the issue of synthetic dyes in wastewater. One of the important chemical methods involves reduction of these stringent pollutants into less hazardous products. In this study, a cross-linked polyurethane foam (CPUF) was prepared from toluene diisocyanate (TDI), tetraethylenepentamine (TEPA), and polycaprolactone diol (PCL; Mw: 1000 g/mole). To avoid harmful reducing agents, ecofriendly reduction of methylene blue (MB) was executed with CPUF as catalyst where ascorbic acid and fresh juice extracts were applied as reducing agents. The FTIR and SEM analysis confirmed the chemical composition and porous morphology of CPUF, respectively. The 100% reduction of MB was recorded in just 15 minutes with ascorbic acid and CPUF, while similar result was obtained in 37 minutes in blank experiment composed of only MB and ascorbic acid. Thus, catalytic role of CPUF in reduction process was proved. Fresh fruit extracts also participated in the reduction process, but rate of reaction was accelerated in the presence of CPUF. The reusability study of the catalyst supported its stability and efficiency. All the successful reduction processes followed 1st-order kinetics with highest apparent rate constant for ascorbic acid. Furthermore, phytotoxicity evaluation proved safe reduction of MB with 60% germination index. Hence, it can be concluded that catalytic role of CPUF has been established with safe and biodegradable reducing agents which can be extended to other redox processes.

1. Introduction

Synthetic dyes are an indispensable contributor of modern civilization. They are involved all around from textile to pharmaceuticals. Above 10^5 different types of dyes are produced annually in a huge volume of $>7 \times 10^5$ metric tons. A large amount of these dyes is added into wastewater during application and postapplication stages in industries which builds a serious concern. They are considered hazardous since they damage the physical and chemical characteristics of water and propagate harm to living organisms [1, 2]. Therefore, a very active area of research is dedicated to eradicate these dyes from wastewater. Various physical, chemical, and biological technologies are developed to address the issue of organic dye pollutants [3]. One of the chemical methods involves reduction of these stringent pollutants into less hazardous metabolites [4].

These reduction treatments are usually accompanied by some catalysts to speed up the process. Mostly, inorganic catalysts are used which poses issues of secondary pollution or regeneration after treatment. To overcome these obstacles, polymeric catalysts such as polyurethanes have been proposed [5].

Polyurethane is an exclusive class of synthetic polymers which contains urethane link (-NHCOO). It is well known for versatile applications from cushioning to coatings due to tunable properties [6–8]. Polyurethane foams are extensively involved in water treatment processes, directly and indirectly [9]. Mostly, such treatments are reported with adsorption mechanisms due to polarity containing active

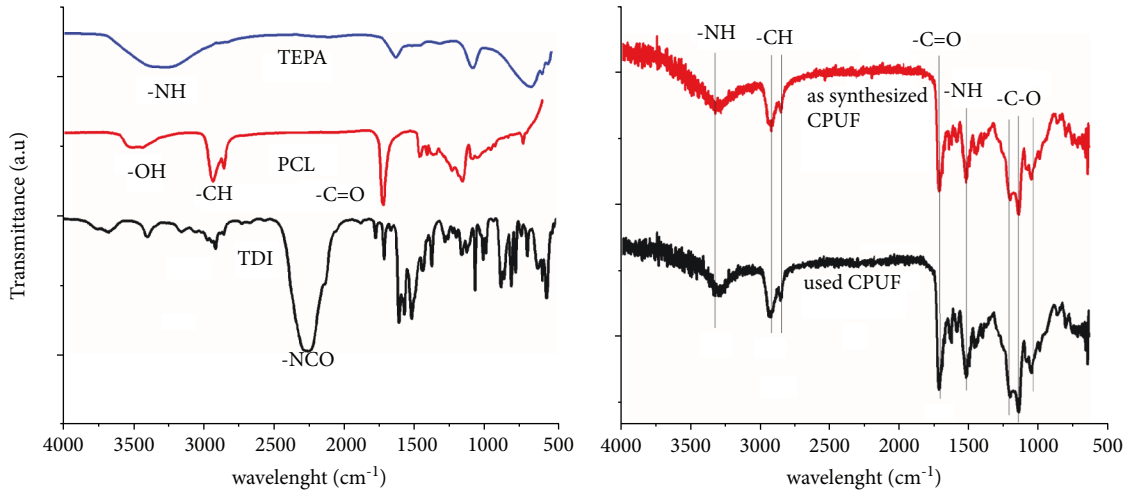


Figure 1: FTIR spectra of monomers (TDI, PCL, and TEPA) and cross-linked polyurethane foam (CPUF) as (a) synthesized CPUF and (b) used CPUF.

sites in the structure of polyurethane. However, catalytic role of polyurethane during reduction treatments has been investigated as well [5].

Previously, we studied reduction of methylene blue (MB) dye with linear and cross-linked polyurethane catalysts in the presence of sodium borohydride ($NaBH_4$) as a reducing agent [5]. But, $NaBH_4$ is a known hazardous substance which can penetrate through the skin and eye and inhalation. Therefore, in this study, the objective was to replace hazardous $NaBH_4$ with some safe and ecofriendly reducing agents. To accomplish this objective, pure ascorbic acid and fresh juice extracts of *Citrus limon* (lemon) and *Psidium guajava* (guava) were applied as reducing agents. Ascorbic acid is a natural reducing agent well known for its antioxidant properties. It is also appreciated to protect the reducing power of other antioxidants such as tocopherol. In the human body, it is essential for anti-inflammatory actions, collagen synthesis, to prevent tissue damages and for basic cell organization. These functions are performed by ascorbic acid through redox circuits present in the cell [10–12]. Furthermore, the motivation to select fruit juices was the presence of soluble ascorbic acid in fruit juices especially in citrus family [13, 14].

2. Materials and Methods

2.1. Materials. Toluene diisocyanate (TDI) and tetraethylenepentamine (TEPA) were purchased from Sigma-Aldrich Co., USA. The polycaprolactone diol (PCL, Mw: 1000 g/mole) was obtained from Acros Organics, USA. Methylene blue (MB) and ascorbic acid were procured from Avonchem Ltd., UK, and Honeywell, USA, respectively.

2.2. Synthesis and Characterization of Cross-Linked Polyurethane Foam (CPUF). The synthesis of CPUF was performed following the previous reported method [5]. The mole ratio of monomers was 2 : 1 : 1 for TDI, PCL, and TEPA, respectively. In a typical experiment, a weighed amount of PCL (5.5 g) was heated to melt at >40°C in an open glazed bowl. Then appropriate amount of TEPA (0.4 mL) was mixed

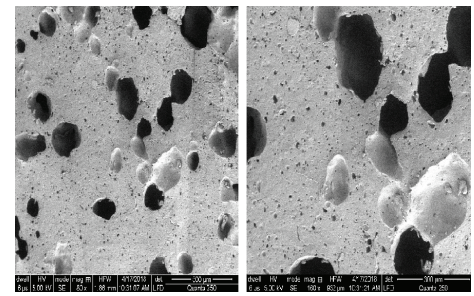


Figure 2: Images of CPUF captured by SEM.

in melted PCL with stirring of few seconds. In the next step, the calculated amounts of TDI (2.3 mL) and water (1 mL) were speckled promptly on the melted mixture of PCL and TEPA along with vigorous stirring. The whole blowing and gelling reaction was accomplished in 1-2 minutes. The cellular polyurethane sample was placed in an oven at 50°C for 4-8 h before further use.

The morphological characterization of synthesized polyurethane was performed by scanning electron microscope (SEM; QUANTA250, UK). The tracking of synthesis through chemical link development was monitored by Fourier transform infrared spectroscopy using ATR-FTIR spectrophotometer (Shimadzu IR Prestige-21, USA). The numbers of scans were 70 and resolution was 4.0. The spectra were recorded in transmission mode from 600 cm^{-1} to 4000 cm^{-1}.

2.3. Reduction of Methylene Blue (MB) with CPUF and Ascorbic Acid. The catalytic activity of CPUF was verified by reduction of MB dye in aqueous solution where ascorbic acid was used as a reducing agent. A set of three test tubes was prepared in a typical experiment. One of these was charged with 2.5 mL of MB (2.5×10^{-5} M) solution, 2.5 mL of ascorbic acid (1.5×10^{-5} M) aqueous solution, and 0.25 g of CPUF. The second test tube was prepared as a blank I which contained only MB and ascorbic acid solutions of the same volume and concentration. The third one was

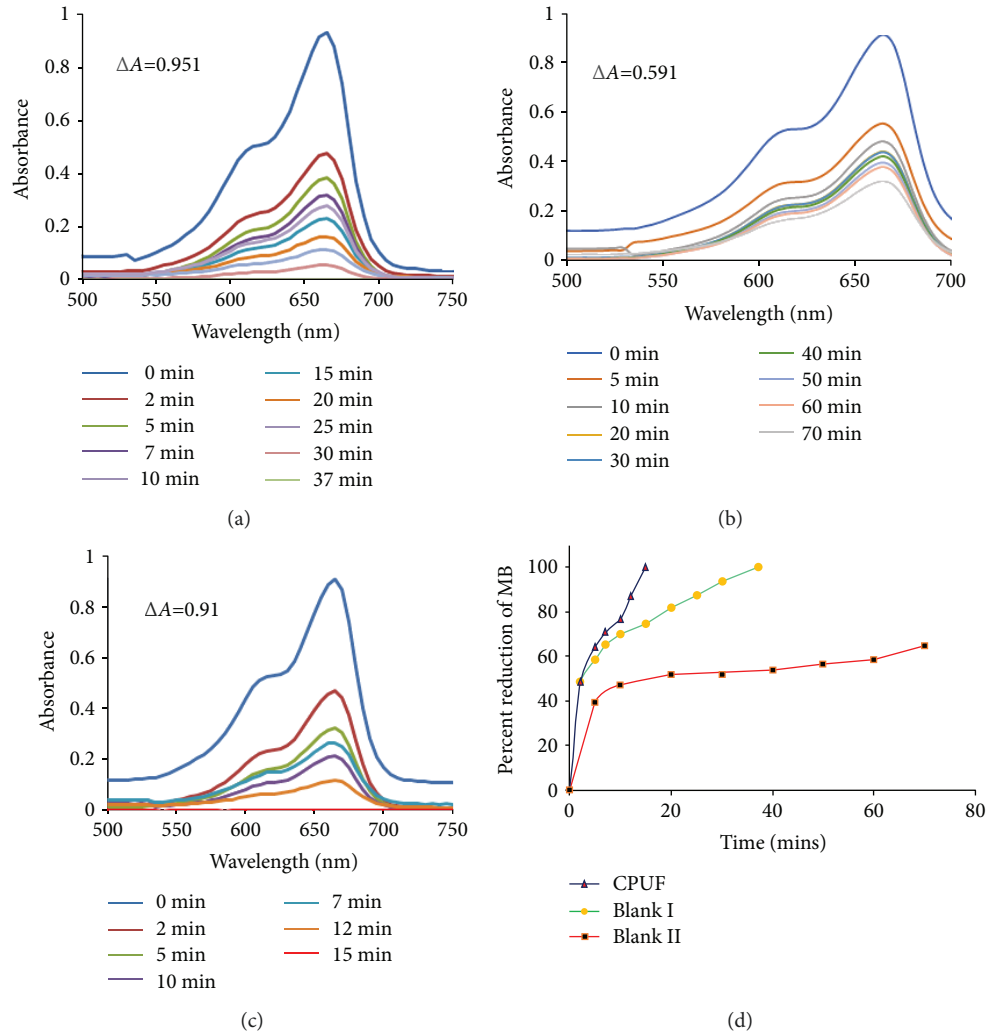


Figure 3: UV-Vis absorption spectra recorded for the progress in reduction of MB dye: (a) 2.5 mL of MB (2.5×10^{-5} M) solution and 2.5 mL of ascorbic acid (1.5×10^{-5} M) solution named as blank I, (b) 2.5 mL of MB (2.5×10^{-5} M) solution with 0.25 g of CPUF named as blank II, (c) 2.5 mL of MB (2.5×10^{-5} M) solution and 2.5 mL of ascorbic acid (1.5×10^{-5} M) solution with 0.25 g of CPUF, and (d) comparison of percent reduction of MB as a function of time in (a), (b), and (c).

considered as blank II and charged with only 2.5 mL of MB solution of the same concentration and 0.25 g of CPUF. Whole experimental setup was carried out at room temperature (25°C ± 3) in the laboratory. At regular time intervals, an aliquot was taken in quartz cell to record the progress of the catalytic process in terms of disappearance of blue color of MB by UV-Vis spectrophotometer (T90, PG Instruments Ltd). The reduction of MB (%) for all these experiments was calculated by using the formula as follows:

$$\text{Reduction of MB}\,(\%) = \frac{C_0 - C_t}{C_0} \times 100, \qquad (1)$$

where C_0 is the concentration of MB at zero time and C_t is the remaining concentration of MB at any time t of the process in terms of absorbance.

2.4. Reduction of Methylene Blue (MB) with Psidium guajava and Citrus limon Extracts. The natural extracts of fruits, i.e., *Psidium guajava* and *Citrus limon*, were also used as reducing agents in this study. Fruits were purchased from the local market. The *Citrus limon* was washed, cut at half, and squeezed, while *Psidium guajava* was grinded homogeneously with distilled water. Both of the extracts were filtered and centrifuged. The supernatants were used in further experiments. The experiments were conducted with 2.5 mL of MB (2.5×10^{-5} M) solution, 2.5 mL of fresh extract, and 0.25 g of CPUF along with a blank. This blank was composed of 2.5 mL of MB and 2.5 mL of fresh extract. In the next experiment, a mixture of ascorbic acid (1.5×10^{-5} M) solution and *Psidium guajava* or *Citrus limon* (50 : 50) was added with MB solution in the presence of CPUF. A parallel blank of the same composition was also monitored in the absence of CPUF.

2.5. Reusability of CPUF. The evaluation of reusability of CPUF was carried out up to five runs. In the first run, a specific amount of CPUF was used for the reduction process

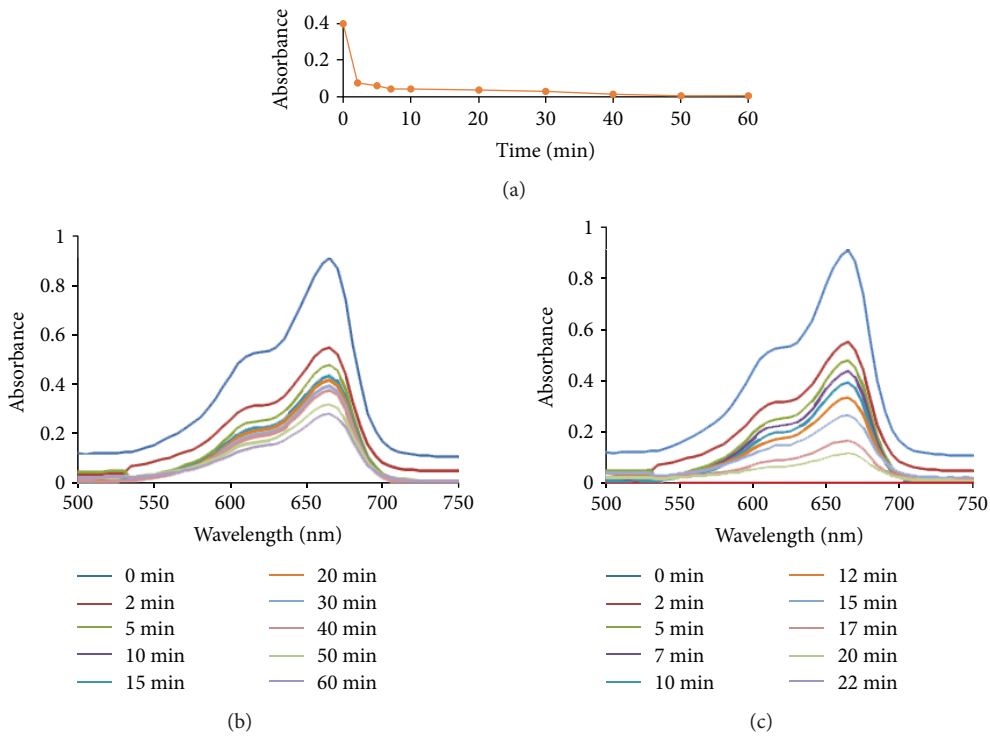


Figure 4: UV-Vis absorption spectra recorded for the progress in reduction of MB dye: (a) 2.5 mL of MB (2.5×10^{-5} M) solution and 2.5 mL of fresh *Psidium guajava* extract, (b) 2.5 mL of MB (2.5×10^{-5} M) solution and 2.5 mL of fresh *Psidium guajava* extract with 0.25 g of CPUF, and (c) 2.5 mL of MB (2.5×10^{-5} M) solution, *Psidium guajava* extract, and ascorbic acid (50 : 50) with 0.25 g of CPUF.

according to the procedure described above. The required time for completion of reduction process was examined with UV-Vis spectrophotometer. At the end of the first run, used CPUF was separated, washed, and dried in an oven at 50°C till constant weight before employing for the next run in a similar manner.

2.6. Phytotoxicity Study of Treated MB Solution. The phytotoxicity of treated and untreated MB solutions was evaluated through seed germination assay. The germination of the seeds of *Triticum aestivum* was observed according to the protocol set by Bibi et al. [15]. The seed germination was carried out on a filter paper in petri dishes containing appropriate volume of solution. This assay was conducted for 7 days at 33 ± 3°C in darkness. The numbers of germinated seeds and root length were recorded at the end. All the procedure was performed in two replicates. Germination index (GI) was calculated by the following equation:

$$\text{GI} = \frac{\text{number of seeds germinated}}{\text{total number of seeds}}. \quad (2)$$

2.7. Kinetic Study of Reduction Process. The order of reaction and rate of reaction was determined by the kinetic study of reduction process at 33°C ± 3. All successfully catalyzed experiments with three proposed reducing agents, i.e., ascorbic acid, *Psidium guajava*, and *Citrus limon*, were selected. The standard kinetic models for zero order, 1st order, and 2nd order were applied. It was considered that C_0 is equivalent to A_0 (absorbance at zero time) and C_t is equivalent to A_t (absorbance at time t), where A was determined by UV-Vis spectrophotometer at the λ_{max} of MB, i.e., 665 nm.

3. Results and Discussion

3.1. Characterization of Cross-Linked Polyurethane Foam (CPUF). The FTIR spectra of monomers (TDI, PCL, and TEPA) and synthesized CPUF are shown in Figure 1. These spectra supported the development of urethane links in CPUF. The characteristic bands of TDI (-NCO at 2268 cm^{-1}), PCL (-OH at 3496 cm^{-1} and –C=O at 1729 cm^{-1}), and TEPA (broad –NH band at 3275 cm^{-1}) are clearly evident in respective spectra. However, all of these bands of monomers were replaced with characteristic band of urethane links such as –NH stretching vibration band at 3316 cm^{-1}, –NH bending vibration band at 1537 cm^{-1}, and –C=O stretching vibration band at 1723 cm^{-1} with a slight shoulder at 1700 cm^{-1}. The shoulder of –C=O may appear due to the intermolecular H bonding in polymer structure. These transitions of IR bands strongly established the synthesis of polyurethane sample [6, 16–18]. Other noticeable bands in IR spectra of synthesized CPUF were symmetric and antisymmetric bands of aliphatic –CH at 2933 cm^{-1} and 2855 cm^{-1}, aromatic C=C stretching band at 1645 cm^{-1} and 1595 cm^{-1}, and multiple stretching bands of ester C-O at 1064 cm^{-1}, 1160 cm^{-1}, and 1214 cm^{-1}. These bands additionally confirmed the incorporation of TDI and PCL in structure of CPUF.

Furthermore, the FTIR spectrum of CPUF used in the reduction process of MB is also documented and presented in Figure 1. This spectrum was recorded to make a structural

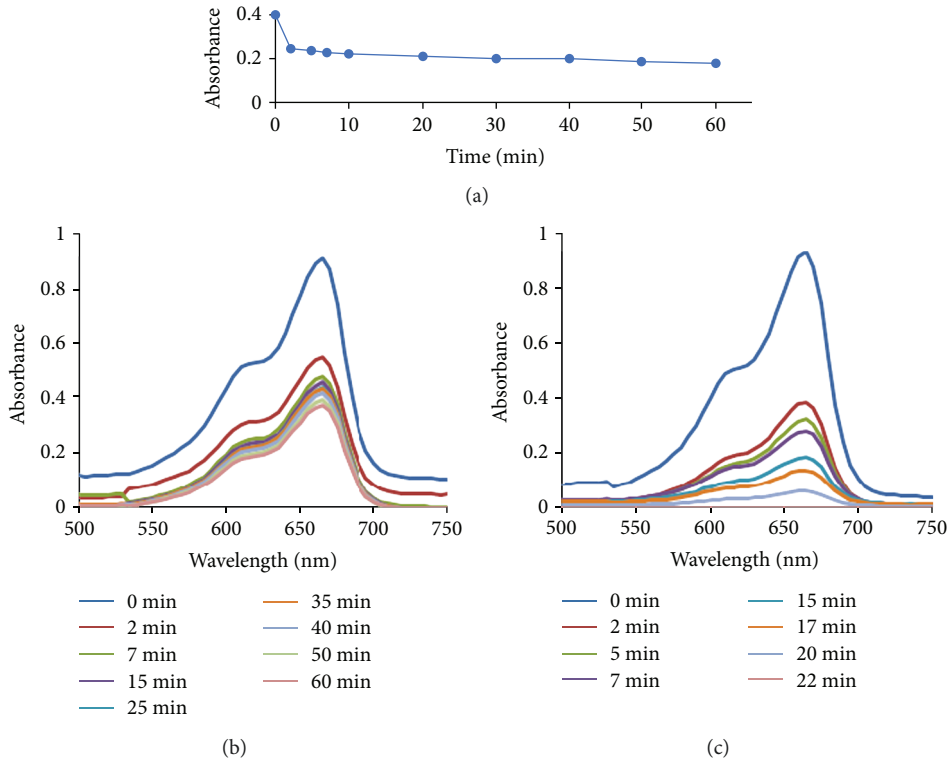


Figure 5: UV-Vis absorption spectra recorded for the progress in reduction of MB dye: (a) 2.5 mL of MB (2.5×10^{-5} M) solution and 2.5 mL of fresh *Citrus limon* extract, (b) 2.5 mL of MB (2.5×10^{-5} M) solution and 2.5 mL of fresh *Citrus limon* extract with 0.25 g of CPUF, and (c) 2.5 mL of MB (2.5×10^{-5} M) solution, *Citrus limon* extract, and ascorbic acid (50 : 50) with 0.25 g of CPUF.

comparison between as such synthesized and used CPUF. Figure 1 has repudiated any chemical change in the structure of CPUF even after its application in reduction process. Hence, it can be concluded that CPUF has provided a reaction site and just acted as a catalyst in the observed reduction process [5].

Apparently, synthesized CPUF was cellular in nature. Its morphology was analyzed by SEM. Multiple images were recorded at different magnifications and two are presented in Figure 2. These images revealed the open porous structure of CPUF with an average size of 35.75 μm. These pores facilitated the reduction process by bringing reactants closer to each other [5].

3.2. Reduction of Methylene Blue (MB) with CPUF and Ascorbic Acid. The reduction of MB was recorded with the UV-Vis spectrophotometer, and results are displayed in Figure 3. These spectra showed that there was a remarkable role of CPUF in the reduction process. The time required for complete reduction of MB in the presence of only ascorbic acid was 37 minutes (Figure 3(a), blank I), whereas complete reduction was observed in just 15 minutes in the presence of CPUF (Figure 3(c)). These results clearly exposed the catalytic role of cellular CPUF in the observed reduction process. The most plausible mechanism may involve the simultaneous adsorption of MB and ascorbic acid on the cellular structure of CPUF, thus providing the surface for their mutual interaction leading to redox reaction between them. In another supportive judgment, this redox reaction may be accelerated due to the presence of conjugated site, located next to the aromatic ring in the CPUF urethane link [19–21].

Furthermore, the UV-Vis spectra of blank II, composed of 2.5 mL of MB (2.5×10^{-5} M) solution with 0.25 g of CPUF, are also presented in Figure 3(b). It was observed that about 64.94% MB was removed from solution in 70 minutes. It may be accredited to the adsorption of MB on cellular CPUF as polyurethane has been extensively reported for adsorption processes [22–28]. This adsorption of dye molecules may facilitate the redox process in the presence of ascorbic acid. Hence, CPUF acted as a catalyst in the reduction of MB as well as provided sufficient support matrix for the process.

3.3. Reduction of Methylene Blue (MB) with CPUF and Psidium guajava Extract. For safe and ecofriendly reduction study, *Psidium guajava* and *Citrus limon* were also applied to exploit their reducing activity. Both of these fruits are well known for ascorbic acid content in their extracts [13]. Therefore, fresh extracts were prepared and used in the reduction experiments. The progress of process was monitored and displayed in Figures 4 and 5. Figure 4(a) shows 98% reduction of MB with pure *Psidium guajava* extract in the presence of CPUF. The time for accomplishment of this process was almost 60 minutes. This long time indicated low efficiency of *Psidium guajava* extract in reduction process. To boost the reduction speed, ascorbic acid solution (1.5×10^{-5} M) was mixed with *Psidium guajava* extract in a 50 : 50 ratio. But this mixture was also less effective, only 71% reduction was observed in 60 minutes (Figure 4(b)). However, similar

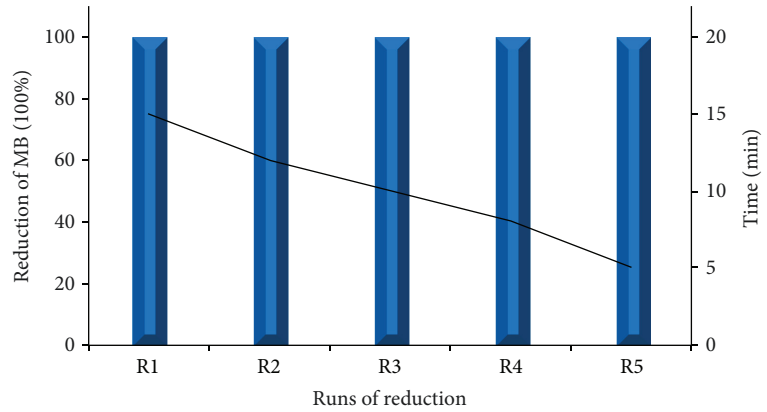
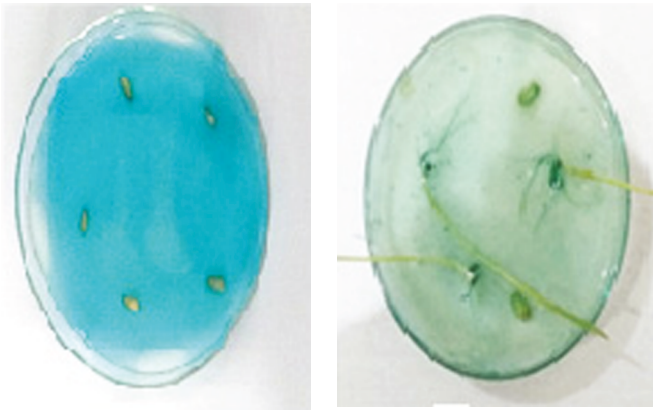


Figure 6: Reusability of CPUF for 100% reduction of MB. R1 represents first run, R2 is for second run, and so on. Primary y-axis shows reduction of MB (%) and secondary y-axis shows time (min) required for 100% reduction of MB in each respective runs.



(a) (b)

Figure 7: (a) Germination of seeds in the original MB solution. (b) Germination of seeds in the treated MB solution.

Table 1: Name of the kinetic models used, mathematical form of the kinetic models, regression coefficient (R^2), and rate constant (k) for reduction of MB with CPUF, ascorbic acid, and mixtures of ascorbic acid and *Psidium guajava* or *Citrus limon* extracts at temperature 33° C ± 3.

Sr. no.	Name of the kinetic model used	Mathematical form of the kinetic model	Regression coefficient (R^2)			Rate constant (k)		
			A^a	L^b	G^c	A	L	G
1.	Zero order	C_0-C_t = kt	0.8341	0.7157	0.9009	0.0501 mol dm^{-3} min^{-1}	0.0289 mol dm^{-3} min^{-1}	0.0325 mol dm^{-3} min^{-1}
2.	1st order	$\ln(C_t/C_0) = -kt$	0.9464	0.8869	0.9356	0.1485 min^{-1}	0.1048 min^{-1}	0.0885 min^{-1}
3.	2nd order	$1/C_t = kt + 1/C_0$	0.8622	0.7093	0.7992	0.5304 mol^{-1} dm^3 min^{-1}	0.585 mol^{-1} dm^3 min^{-1}	0.3133 mol^{-1} dm^3 min^{-1}

[a]Reduction of MB in the presence of ascorbic acid and CPUF (0.25 g). [b]Reduction of MB in the presence of *Citrus limon* extract and ascorbic acid (50 : 50) with CPUF (0.25 g). [c]Reduction of MB in the presence of *Psidium guajava* extract and ascorbic acid (50 : 50) with CPUF (0.25 g).

experiment with 0.25 g of CPUF showed appreciable results as shown in Figure 4(c). The reaction speed was accelerated to achieve 100% reduction in just 22 minutes. These results demonstrated the catalytic role of CPUF.

3.4. Reduction of Methylene Blue (MB) with CPUF and Citrus limon Extract. Similar experiments were carried out with fresh *Citrus limon* extract, and results are given in Figure 5. Figure 5(a) shows 54% reduction in 60 minutes with pure *Citrus limon* extract. Thus, *Citrus limon* was less effective even than *Psidium guajava* in reduction process. A mixture of *Citrus limon* and ascorbic acid also showed low reduction, i.e., 58.68% in 60 minutes (Figure 5(b)), comparatively. Yet, 100% reduction of MB was recorded in 22 minutes with addition of CPUF as revealed in Figure 5(c). Hence, safe reduction process was possible with fruit extracts but rate was low. However, rate was accelerated with ascorbic acid and CPUF.

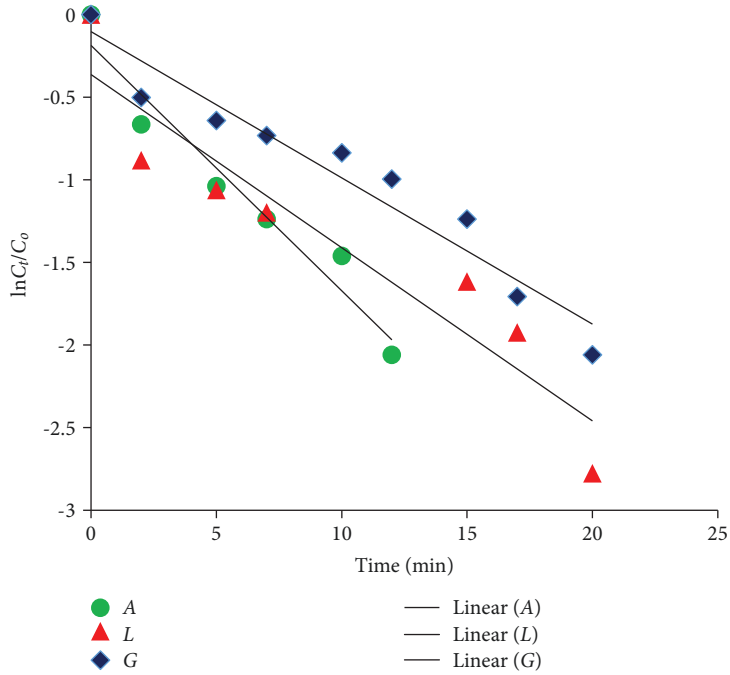


FIGURE 8: Plot of $\ln(C_t/C_0)$ as a function of time (min) for reduction of MB; *A*: reduction of MB in the presence of ascorbic acid and 0.25 g of CPUF, *L*: reduction of MB in the presence of *Citrus limon* extract and ascorbic acid (50 : 50) and 0.25 g of CPUF, and *G*: reduction of MB in the presence of *Psidium guajava* extract and ascorbic acid (50 : 50) and 0.25 g of CPUF.

3.5. Reusability of CPUF. The stability of a catalyst can be evaluated in terms of reusability. The prepared catalyst, CPUF, was applied multiple times for reduction of MB, and time required for 100% reduction is documented and presented in Figure 6. The results showed very distinctive trend of catalyst reusability in contrast to the previous reports related to inorganic catalysts [29, 30]. This catalyst exhibited progressively enhanced efficiency in five runs of reduction of MB. It was observed that the completion time for reduction process was decreased in each succeeding run. This unique trend in efficiency may be appeared due to the exposure of more active sites on polymeric structure of catalyst with cleaning and detaching involved in each successive run [5].

3.6. Phytotoxicity of Treated MB Solution. The objective of the study was to use safe and ecofriendly reducing agents. The phytotoxicity results supported the achievement of the said goal. The 0% germination index or 100% germination inhibition was observed for *T. aestivum* seeds in pure MB solution (Figure 7(a)).

However, 60% germination index was calculated for dye solution treated with ascorbic acid in the presence of CPUF catalyst. An average shoot length and root length were 4.6 cm and 8.5 cm, respectively. Hence, the phytotoxicity experiment clearly showed that reduction of MB resulted in its transformation into the less toxic product [15].

3.7. Kinetic Study of Reduction Process. To determine the rate constant and order of reaction, kinetic analysis of reduction processes was carried out. The standard kinetic models for zero order, 1st order, and 2nd order were applied on successfully catalyzed reactions. The values of rate constant (k) and R^2 are presented in Table 1. These results revealed that all catalytic processes followed 1st-order kinetics as highest R^2 were obtained. The graphic presentation of results is displayed in Figure 8. The highest apparent rate constant was 0.1485 min^{-1} for reduction of MB with ascorbic acid and CPUF experiment. Hence, these results confirmed the ascorbic acid as most efficient reducing agent along with catalytic role of CPUF.

4. Conclusion

In this study, cross-linked polyurethane foam (CPUF) was prepared from TDI, TEPA, and PCL (1000 g/mole). The chemical composition of CPUF was confirmed by characteristic bands of urethane link (–NHCOO) present in FTIR spectra. The SEM images showed porous morphology which supported cellular appearance of the polymer. The catalytic activity of CPUF was evaluated by the reduction of MB solution. Safe and ecofriendly reducing agents such as ascorbic acid and fresh extracts of *Psidium guajava* and *Citrus limon* were used. All of these participated actively in reduction process with CPUF, but ascorbic acid was the most efficient reducing agent. Phytotoxicity analysis through seed germination assay supported ecofriendly reduction of MB with ascorbic acid. All the successful reduction processes obeyed the 1st-order kinetic model. Hence, catalytic role of CPUF has been established with safe and biodegradable reducing agents which can be extended to other redox processes.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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