



Research paper

Linear and crosslinked Polyurethanes based catalysts for reduction of methylene blue



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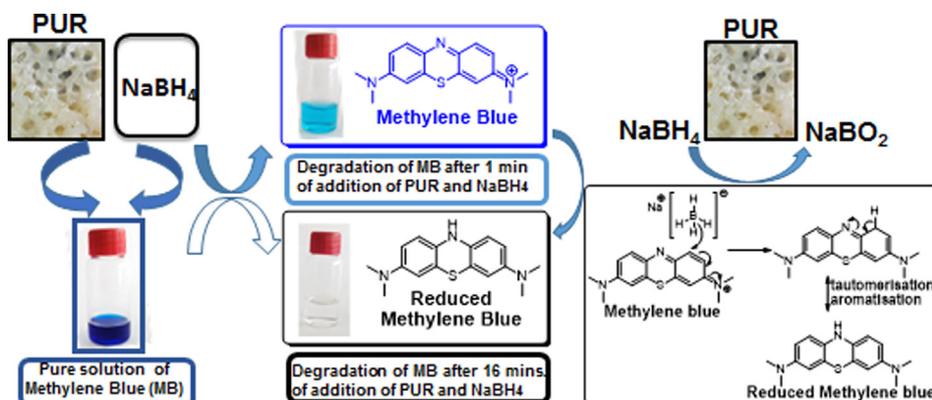
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HIGHLIGHTS

- Linear & crosslinked polyurethanes were prepared at room temperature.
- Polyurethanes were cellular in morphology as confirmed by SEM & BET analysis.
- Polyurethanes successfully catalyzed the reduction of Methylene blue in aqueous medium.
- Crosslinked polyurethane was more efficient and stable with surplus surface area.

GRAPHICAL ABSTRACT



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ABSTRACT

The large amount of synthetic dyes in effluents is a serious concern to be addressed. The chemical reduction is one of the potential way to resolve this problem. In this study, linear and crosslinked polyurethanes i.e. LPUR & CLPUR were synthesized from toluene diisocyanate (TDI), polyethylene glycol (PEG; 1000 g/mole) and tetraethylenepentamine (TEPA). The structure and morphology of synthesized materials were examined by FTIR, SEM and BET. The CLPUR was found stable in aqueous system with 0.80 g/cm³ density and 16.4998 m²g⁻¹ surface area. These materials were applied for the reduction of methylene blue in presence of NaBH₄. Both, polymers catalyzed the process and showed 100% reduction in 16 and 28 mins., respectively, while, the reduction rate was significantly low in absence of these materials, even after 120 mins. Furthermore, negligible adsorption was observed with only 7% removal of dye. The best reduction rates were observed at low concentration of dye, increasing concentration of NaBH₄ and with more dosage of polymeric catalyst. The kinetic study of process followed zero order kinetics. It

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was hence concluded that both synthesized polymers played a catalytic role in reduction process. However, stability in aqueous system and better efficiency in reduction process endorsed CLPUR as an optimal choice for further studies.

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1. Introduction

Synthetic organic dyes are dominating the market with an annual production of over 7×10^5 metric tons. They are used in diverse consumer products from textile to food items [1]. A huge amount of these dyes is present in the effluents causing serious concern of water pollution. These dyes are damaging water bodies physically as well as biologically. A number of physical, chemical and biological technologies have been developed to address this environmental issue [2]. The chemical reduction is one of the common, fast and effective methods for the removal of dyes like methylene blue (MB) from aqueous solution [3]. The MB is very sensitive for redox activities as it gives blue color in oxidized state which quickly disappear in reduced form. It is a well-known dye for analytical purposes and widely reported in characterization of innovative catalytic systems [4]. On the other side, MB has been reported to cause severe central nervous system toxicity by blocking certain oxidase enzyme in the body [5].

An intelligent approach is the use of a catalyst or redox mediator in reduction processes. The review of literature reveals that metals such as Au, Ag, Mn, Zr and TiO_2 based catalysts have extensively been used for this purpose [6–9]. These metallic catalysts are normally found in pure inorganic form or dispersed in some organic matrix [4,10]. These catalysts generally assist the interaction between the electron donor and acceptor resulting in accelerated redox process [3,11]. These materials are employed for wastewater treatment and encouraged for better output. However, water-added catalysts increase process cost due to required separation strategies. In addition, they can be a cause of secondary pollution if their separation is ignored after wastewater treatment. Therefore, an attractive catalyst should facilitate wastewater treatment in an economic way, without causing secondary pollution.

Polyurethane (PUR) is an organic polymer prepared by the polyaddition of isocyanates with different polyols. It is reported as a versatile material for use in a wide range of applications including oil removal [12], metal ion adsorption [13], removal of dyes and organic pollutants [14–17]. The PUR is appreciated due to simple preparation, low cost and high surface area [15]. They are also known for their remarkable chemical and thermal resistance along with high polarity in structure [18].

Herein we have studied a novel application of PUR, acting as redox catalyst in removal of MB. The linear and crosslinked PUR were synthesized by one-step simple method at room temperature and employed for reduction of MB in the presence of NaBH_4 . The possibility of secondary pollution and need of separation cost can be eliminated with this catalytic material as it was in cellular form which does not dissolve in the testing aqueous media. Before this, PUR and its modified forms have extensively been investigated for removal of dyes, but via adsorption mechanism [1]. This is the

first time; we are reporting PUR as redox catalyst in removal of MB from aqueous solution through reduction. To validate our observations, further experiments were performed which suggested the prevalence of PUR acting as redox catalyst instead of adsorption process.

2. Experimental

2.1. Materials

Toluene diisocyanate (TDI), Polyethylene glycol (PEG, Mw: 1000 g/mole), Tetraethyl pent amine (TEPA), Sodium borohydride (NaBH_4) and Methylene blue (MB) were purchased from Sigma Aldrich, and Acros Organics, USA.

2.2. Synthesis and characterization of polyurethanes

Two types of polyurethane i.e. linear and crosslinked were synthesized by using TDI, PEG and TEPA. The exact mole ratios of monomers are given in Table 1. As such synthesized samples were cellular in appearance as shown in Fig. 1. The synthesis process was as follows:

- For linear polyurethane (LPUR), firstly, weighed amount of PEG (10 g) was melted in an open glazed bowl by heating upto 50°C . Then calculated amount of TDI (1.74 mL) and water (0.84 mL) were sprinkled simultaneously on the melted PEG along with vigorous stirring. The blowing and gelling reaction was completed in 1–2 mins. Then bowl was placed in an oven at 50°C for 4–8 h before further use.
- The crosslinked polyurethane (CLPUR) was also prepared following parallel process. The PEG (10 g) was melted in the similar manner and crosslinker i.e. TEPA (1 g) was mixed in melted PEG. Then, 3.5 mL of TDI and 0.84 mL of water were sprinkled along with vigorous stirring. Similarly, reaction was completed in 1–2 mins. and bowl was placed in an oven at 50°C for 4–8 h

The physical and chemical characterization of synthesized polymers were performed as; solubility in various solvents, density determination according to ISO 845: 2016, morphological analysis by scanning electron microscope (SEM, TESCAN Vega LMU), pore size, pore volume and surface area determination by Brunauer-Emmett-Teller (BET; Tristar II 3020, USA) and recording of IR spectra by 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 400 cm^{-1} to 4000 cm^{-1} .

2.3. Reduction of Methylene Blue (MB)

The catalytic role of LPUR and CLPUR in acceleration of reduction of MB was studied in an aqueous solution. In a typical experiment, two independent test tubes were charged with 2.5 mL of MB ($2.5 \times 10^{-5}\text{ M}$), 2.5 mL of NaBH_4 (0.1 M) and 0.5 g of each sample (LPUR & CLPUR). Further, one more set was prepared as blank which contains only dye and NaBH_4 solutions of same volume and concentration. The progress of reduction process was monitored

Table 1
Monomers and mole ratios used for synthesis of LPUR and CLPUR.

Monomers	Mole ratio for LPUR	Mole ratio for CLPUR
TDI	1	2
PEG	1	1
TEPA	0	1
H_2O	7% by weight	7% by weight

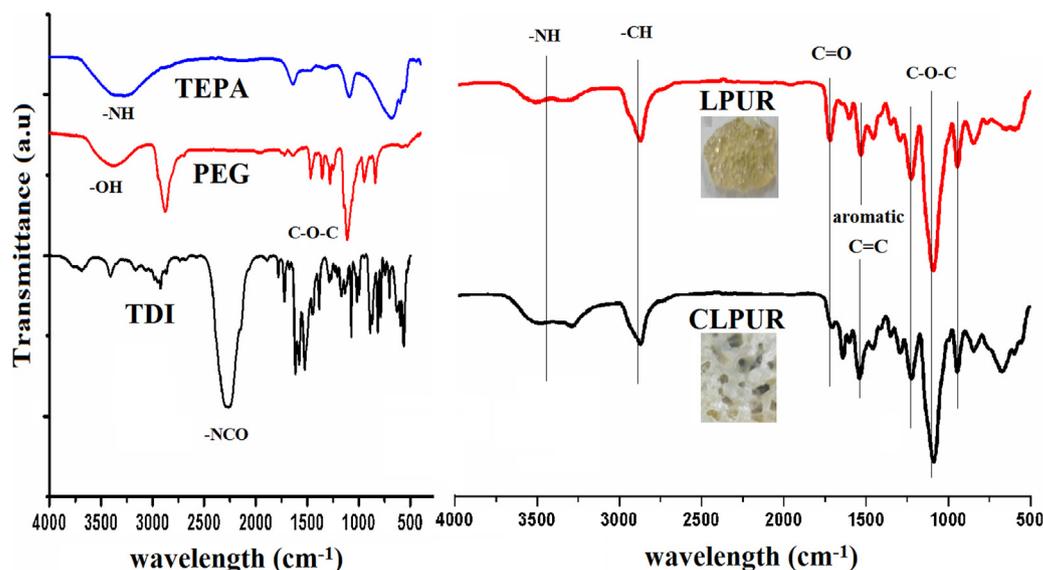


Fig. 1. FTIR spectra of monomers (TDI, PEG and TEPA) and synthesized linear (LPUR) and crosslinked (CLPUR) polymers. Inset shows digital camera images of CLPUR and LPUR.

Table 2
Experiments with different concentration levels of MB, NaBH₄ and doses of CLPUR.

Experiments	MB (M)	NaBH ₄ (M)	CLPUR (g)
1.	1.5×10^{-5}	0.1	0.5
2.	2.0×10^{-5}	0.1	0.5
3. ^a	2.5×10^{-5}	0.1	0.5
4.	2.5×10^{-5}	0.15	0.5
5.	2.5×10^{-5}	0.5	0.5
6.	2.5×10^{-5}	0.1	0.25
7.	2.5×10^{-5}	0.1	0.75

^a optimized experimental conditions.

continuously by UV/Vis spectrophotometer (T90, PG Instruments Ltd).

2.4. Effect of initial concentration of MB dye & NaBH₄ and dose of CLPUR

To study the effect of initial concentration of MB & NaBH₄ and dose of CLPUR, series of experiments were performed. The typical experiments were conducted as described in section 2.3. However, three different levels of each variable were studied keeping others constant. Similarly, progress of each experiment was recorded by UV/Vis spectrophotometer with regular time intervals till the completion of process. The details of variation are compiled in Table 2. The % age removal of dye for all experiments was calculated by using the formula given below

$$Pr = \frac{C_0 - C_t}{C_0} \times 100$$

Where;

Pr = percent removal of MB dye

C₀ = concentration of dye at zero time

C_t = concentration of dye at time t

2.5. Evaluation of adsorption process

Before this, PUR has extensively investigated as adsorbent for dyes. However, the observations were different in this study i.e. PUR acting as catalyst in removal of MB. Therefore, to clarify this observation, adsorption of MB on synthesized CLPUR (0.5 g) was also studied. An experiment was carried out in which only a weighed

piece of polymer was placed in 2.5 mL of MB (2.5×10^{-5} M) solution. Any change in color of dye was monitored with UV/Vis spectrophotometer for 120 mins. In addition, the polymeric material used in this experiment was separated at the end, dried and examined by FTIR to evaluate any chemical changes.

2.6. Kinetic study of reduction process

To determine the order of reaction and rate of reaction, the kinetic study of reduction process was carried out at 33 ± 2 °C. For comparison, the optimized reaction conditions with both CLPUR & LPUR were selected against blank reduction of MB, without any catalyst. The obtained values of $\ln C_t/C_0$ were plotted against time of reaction, where C_t is A_t (absorbance at time t) and C₀ is equivalent to A₀ (absorbance at zero time).

2.7. Reusability of catalyst

The determination of reusability of stable catalyst i.e. CLPUR was performed up to ten runs. In a typical run, a weighed amount of CLPUR was used for the reduction of MB according to the procedure given in section 2.3. The time required for completion of process was recorded with the help of spectrophotometer. The used CLPUR was separated by filtration, dried in oven at 50 °C till constant weight and then applied for the next run in similar manner.

3. Results & discussion

3.1. Characterization of LPUR and CLPUR

The monomers used to synthesize LPUR & CLPUR were TDI, PEG and TEPA. The FTIR spectrum of each monomer and samples was recorded and presented in Fig. 1. The FTIR spectra confirmed the synthesis of PURs as characteristic bands of TDI (-NCO at 2250 cm^{-1}), PEG (-OH at 3400 cm^{-1}), and TEPA (broad -NH band at 3300 cm^{-1}) have disappeared. Moreover, appearance of a typical -NH urethane stretching band (H bonded and non-bonded) between 3250 and 3590 cm^{-1} and -C=O urethane stretching band near 1720 cm^{-1} for LPUR and at 1640 cm^{-1} with a weak shoulder near 1710 cm^{-1} for CLPUR supported the proposed synthesis. In spectrum of CLPUR, the shifting of -C=O stretching band towards lower wavelength suggested the incorporation of TEPA which,

Table 3
Solubility of LPUR and CLPUR in different polar and non-polar solvents at $33 \pm 2^\circ\text{C}$.

Solvents used	Solubility of LPUR	Solubility of CLPUR
Water	Fragmented	Insoluble
Ethanol	Swollen	Insoluble
<i>n</i> -Hexane	Insoluble	Insoluble
DMF	Soluble	Fragmented
THF	Fragmented and swollen	Insoluble

offered more options for H bonding at molecular level. Furthermore, multiple characteristic bands of C–O–C stretching near 933 cm^{-1} , 1093 cm^{-1} and 1226 cm^{-1} and aromatic C=C stretching bands at 1520 cm^{-1} and 1605 cm^{-1} confirmed the assimilation of PEG and TDI in LPUR and CLPUR. Other prominent bands were associated with –NH bending at 1448 cm^{-1} and C–H stretching between 2862 and 2875 cm^{-1} [19–21].

3.2. Solubility of LPUR and CLPUR
Solubility of LPUR and CLPUR was observed at ambient temperature i.e. $33 \pm 2^\circ\text{C}$. A small piece of each sample was placed in 2.5 mL of different solvents and any change in physical state of sample was observed within 4 h. These observations were recorded in Table 3. These results showed that LPUR was soluble in DMF, insoluble in *n*-hexane, swollen in ethanol, fragmented and swollen in THF and water. On the other hand, CLPUR was only fragmented in DMF and quite stable in all other solvents. This difference in behavior can be attributed to the linear and crosslinked structure of LPUR and CLPUR, respectively. CLPUR due to its crosslinked network showed higher resistance towards different solvents. While, LPUR being linear, was unstable in all polar solvents [22]. However, these results were supportive for the more appropriate use of CLPUR in aqueous system. Due to enhanced stability, it was selected for further experiments in this study.

3.2. Density of LPUR and CLPUR

Average density of LPUR and CLPUR were calculated according to the standard method by taking measurements of three different sample sections. According to the average density, LPUR was denser (1.40 gcm^{-3}) as compared to the CLPUR (0.80 gcm^{-3}). This difference in the densities can be accredited to linear and crosslinked structures of polymers as decrease in mass per unit volume due to crosslinking is an obvious fact [23–25]. The low density of CLPUR offered more surface area for further applications.

3.3. Catalytic activity of LPUR and CLPUR

In evaluation of catalytic activity of PURs, Fig. 2 (a, b, c) showed that there was no appreciable reduction of MB with NaBH_4 in the absence of PURs. The NaBH_4 was able to reduce only 30% dye in 120 mins. of reaction time (Fig. 2c). However, in the presence of LPUR, 100% reduction of dye was attained only in 28 mins and CLPUR showed equivalent performance in just 16 mins. These results clearly revealed the catalytic role of PURs in observed reduction process. The presence of these cellular materials has accelerated the reduction of MB, especially CLPUR has pronounced effect on this process. It might be possible due to the stable cross linked network structure and enhanced surface area of CLPUR.

The MB dye is electrophilic in nature and BH_4^{-1} acts as a nucleophile. A most probable mechanism may involve the simultaneous adsorption of dye molecules and BH_4^{-1} on the cellular structure of LPUR and CLPUR, thus providing surface for their interaction and redox reaction to take place. General process and mechanism for reduction of MB in presence of synthesized polymeric catalysts is shown in Fig. 3. The presence of conjugation site on the LPUR and CLPUR as part of the urethane functional group placed next to the aromatic ring may also be involved in the accelerated electrons transfer from nucleophile to electrophile [26–28]. The stability in

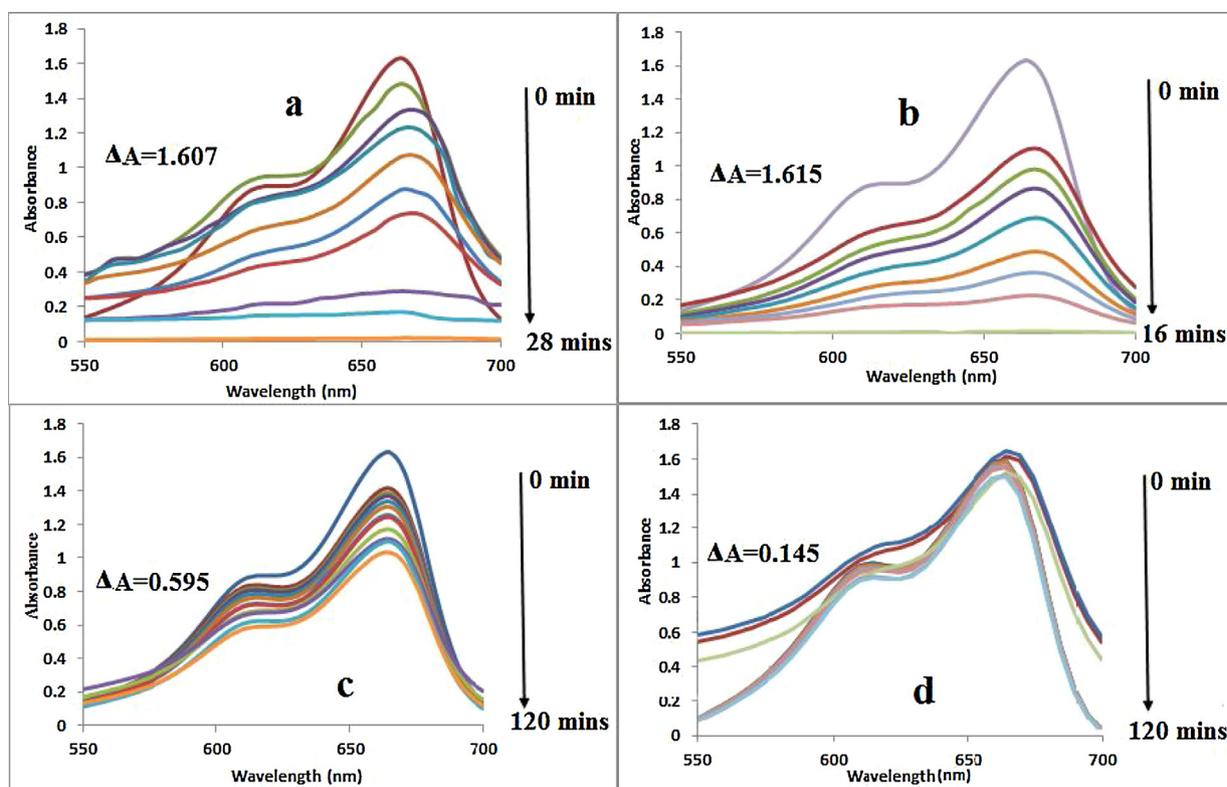


Fig. 2. Changes in the UV–vis absorption spectra of MB dye ($2.5 \times 10^{-5}\text{ M}$) using: a) NaBH_4 (0.1 M) and 0.5 g of LPUR; b) NaBH_4 (0.1 M) and 0.5 g of CLPUR; c) NaBH_4 only (0.1 M); d) 0.5 g of CLPUR only.

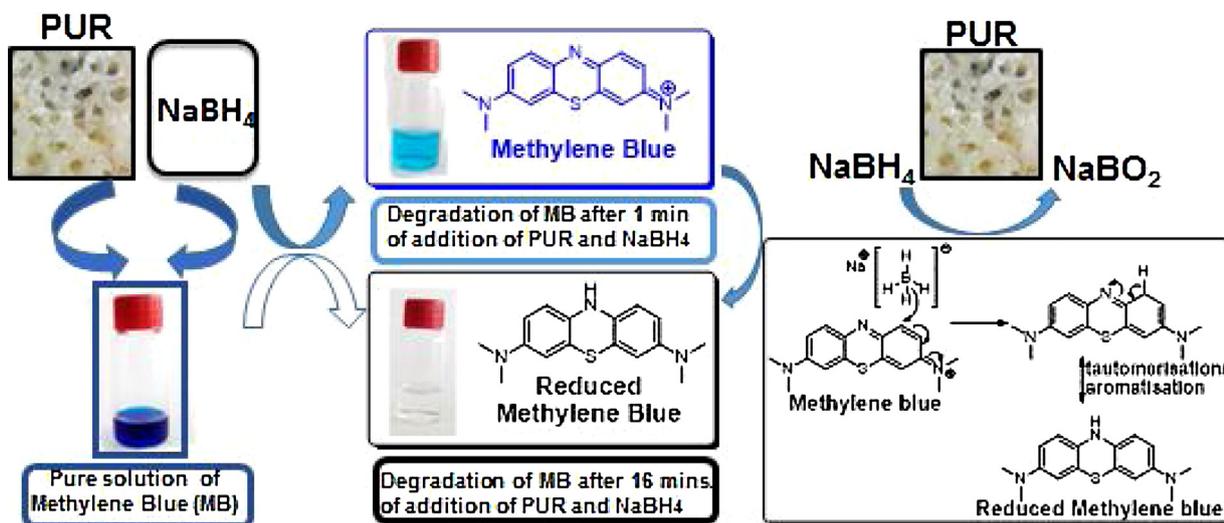


Fig. 3. Proposed process and mechanism for reduction of MB in presence of synthesized polymeric catalysts.

aqueous system and better efficiency in reduction process endorsed CLPUR as an optimal choice for further studies.

3.4. Evaluation of adsorption process

Before this, PUR has been praised as excellent, economic and efficient adsorbent for removal of various dyes [29–34]. However, the catalytic role of PUR in reduction of dye was observed in current study. To evaluate any chance of adsorption, an additional experiment was performed with 2.5 mL of MB (2.5×10^{-5} M) and CLPUR (0.5 g) in absence of NaBH_4 . The respective UV–vis spectra are displayed in Fig. 2d. The CLPUR was able to remove only 8% MB in 120 mins. These results indicated negligible adsorption of dye molecules on CLPUR. In addition, this slight adsorption of dye molecules may facilitate in reduction process.

The FTIR was also employed as a key tool, to predict the catalytic role of CLPUR in the reduction of MB dye. The FTIR spectra of pure and used CLPUR are given in Fig. 4, which eliminate any adsorption based interaction between polymer and dye molecules. Characteristic bands of urethane were observed in all these spectra with similar intensities. For instance $-\text{NH}$ stretching band (H bonded and non-bonded) at $3230\text{--}3590\text{ cm}^{-1}$, $-\text{C}=\text{O}$ stretching band at 1640 cm^{-1} with a weak shoulder at 1710 cm^{-1} , aromatic $\text{C}=\text{C}$ stretching bands at 1540 cm^{-1} and 1603 cm^{-1} along with three characteristic bands of $\text{C}-\text{O}-\text{C}$ between 940 cm^{-1} to 1219 cm^{-1} appeared with same intensities in a, b, c spectra of Fig. 3. Hence, these observations supported the only catalytic role of CLPUR in reduction process of MB. There was no evidence of adsorption phenomena as repudiated by these FTIR spectral details [35].

3.5. Effect of initial concentration of MB, NaBH_4 and CLPUR

Multiple series of experiments were conducted to investigate the effects of concentration of dye and NaBH_4 and catalyst dose i.e. CLPUR, on reduction process while keeping other reaction parameters constant. Fig. 5 depicted the effect of different dye concentrations i.e. 2.5×10^{-5} M, 2.0×10^{-5} M and 1.5×10^{-5} M on decolorization process. These results indicated a linear relationship between concentration of dye and time required for complete decolorization. With increased concentration of dye, number of molecules to be reduced increased, thus time required for complete reduction process was also increased [36,37].

The Fig. 6 presented the decolorization process with different concentrations of NaBH_4 while keeping other conditions constant.

Here, decolorization time was decreased with increase in NaBH_4 concentration. This relation is adequate as NaBH_4 was the reducing agent, so, its concentration can directly accelerate the process of reduction [38].

As shown in Fig. 7 with increasing amount of catalyst i.e. CLPUR the time required for decolorization process was decreased greatly [37]. At higher dose level, decrease in reduction time was more pronounced. The increased amount of catalyst facilitated for more simultaneous adsorption of dye molecules and BH_4^{-1} , as more cellular area became available.

3.6. Analysis by SEM and BET

To explore the morphology of polymer, SEM was used. Both, pure CLPUR and used CLPUR were examined. The images recorded are presented in Fig. 8. Apparently, CLPUR was a cellular material which could be confirmed in SEM images as well. These cells of CLPUR supported in reduction of dye where oxidizing and reducing species may come closer. This morphology of CLPUR is quite stable which can be observed in SEM image of used CLPUR which helped in reusability of the material.

The BET analysis was carried out for synthesized polymers to determine the pore size, pore volume and surface area. The results obtained are presented in Table 4. These results proved the cellular morphology of polymers as shown by SEM analysis. Furthermore, this BET analysis provide the information regarding surface area of CLPUR ($16.5\text{ m}^2\text{g}^{-1}$) and LPUR ($3.7\text{ m}^2\text{g}^{-1}$).

3.7. Reusability of CLPUR

The reusability and stability are important criteria for catalysts. The catalyst, CLPUR was applied for reduction of MB dye in multiple experiments. The maximum time required for 100% reduction of dye was recorded and presented in Fig. 9. Progressive decrease in time indicated increasing efficiency. These results showed unique and interesting trend in reusability of catalyst being polymeric in

Table 4
Pore size, pore volume and surface area of LPUR & CLPUR as determined by BET.

Sr. No.	BET Analysis parameter	LPUR	CLPUR
1.	Pore size (Å)	183.167	165.633
2.	Pore volume (cm^3/g)	0.884458	0.237350
3.	Surface area (m^2/g)	3.7	16.5

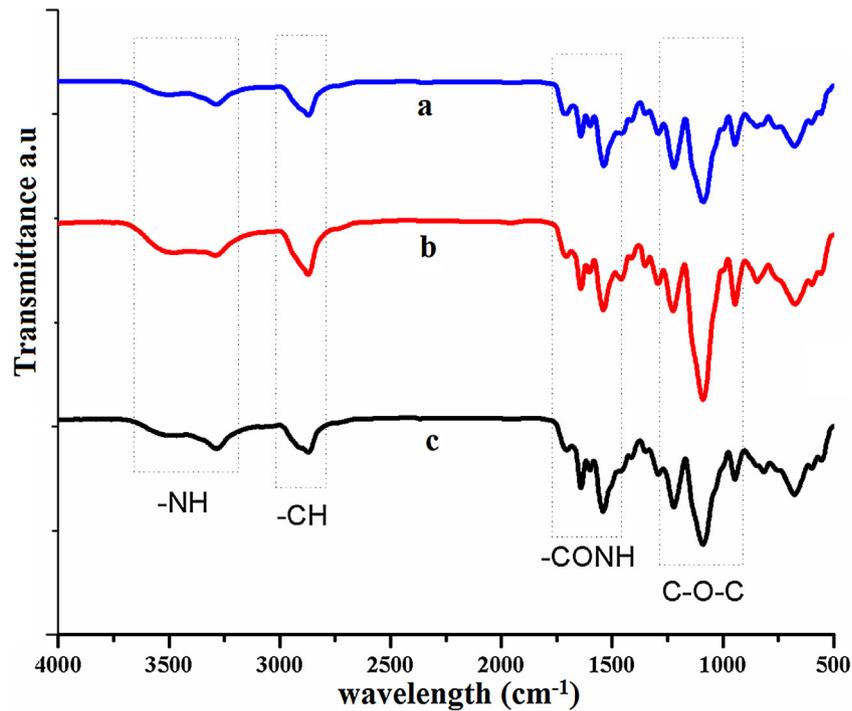


Fig. 4. FTIR spectra of CLPUR: a) CLPUR used in catalytic reduction of MB in presence of NaBH₄; b) pure CLPUR; c) CLPUR used for removal of MB in absence of NaBH₄.

nature in contrast to the previous reports related to inorganic catalysts [6,7]. The catalyst was not poisoned or deactivated during the reduction or separation processes. It exhibited progressively enhanced efficiency in initial five cycles. The time required for maximum reduction of dye was decreased in each successive cycle. This

escalating trend in efficiency may be due to more exposure of active sites on polymer network with washing and dislodging involved in each next cycle. However, this change was diminished from fifth to tenth cycle with almost constant efficiency.

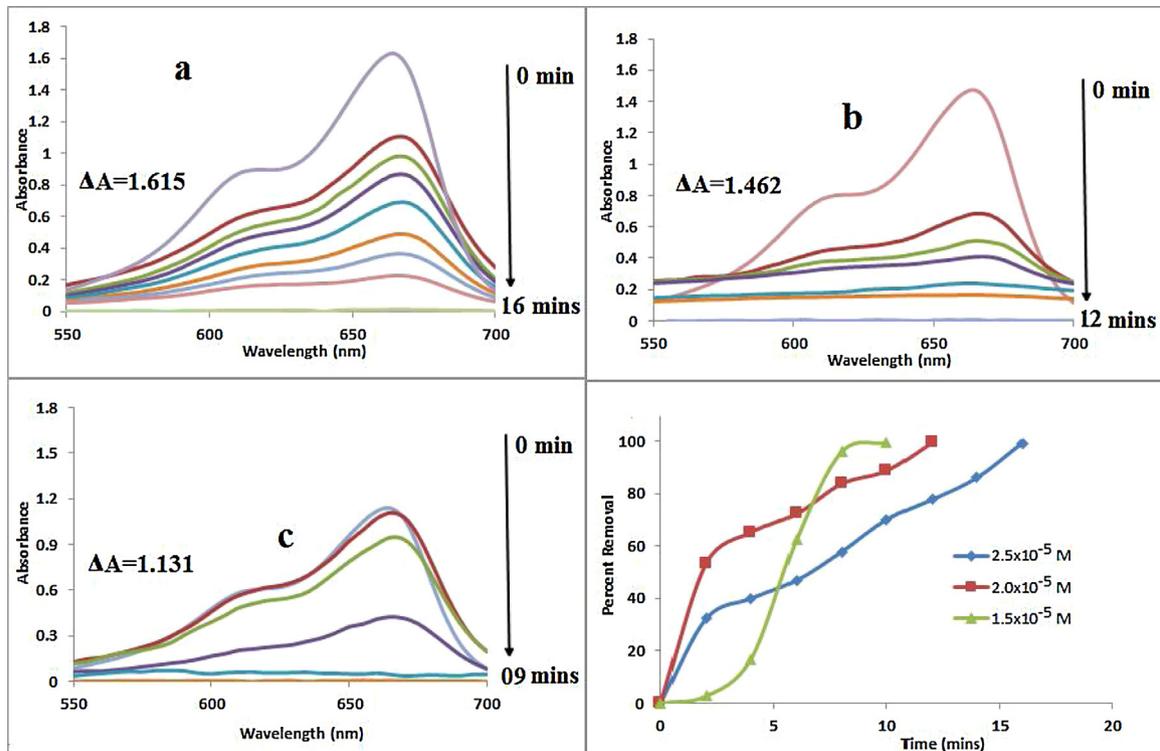


Fig. 5. Effect of MB dye concentrations on the UV-vis absorption spectral pattern with CLPUR (0.5 g) and NaBH₄ (0.1 M): a) 2.5 × 10⁻⁵ M MB; b) 2.0 × 10⁻⁵ M MB; c) 1.5 × 10⁻⁵ M MB and d) comparison of percent removal of dye with three different concentration levels of MB.

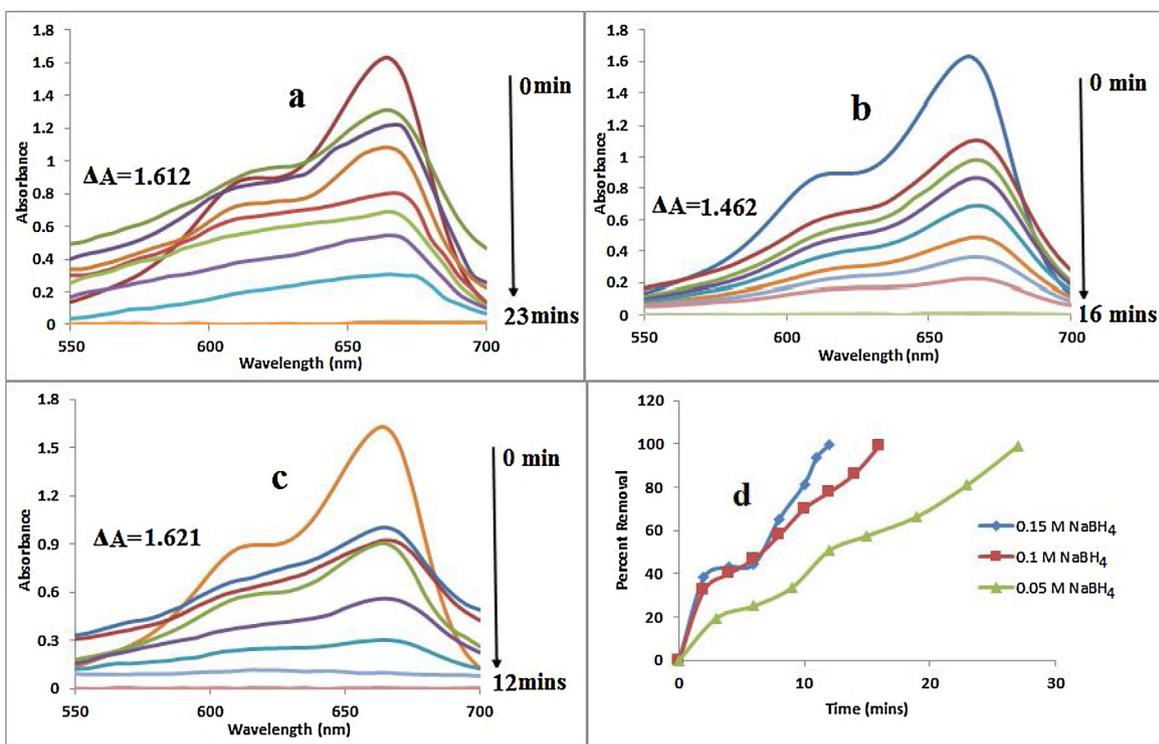


Fig. 6. Changes in the UV–vis absorption spectra of MB dye (2.5×10^{-5} M) with different concentrations of NaBH_4 in presence of CLPUR (0.5 g): a) 0.05 M NaBH_4 b) 0.1 M NaBH_4 ; c) 0.15 M NaBH_4 and d) comparison of percent removal of dye with three different concentrations of NaBH_4 .

3.8. Kinetic study of catalytic process

The kinetic analysis of catalytic reduction process was carried out to determine the rate constant and order of the reaction. To compare the kinetic parameters, optimized reduction processes

with CLPUR and LPUR were selected. Various standard kinetic models i.e. zero order, first order and second order were applied. The values of R^2 and apparent rate constant (k) for reduction of methylene blue in the presence of synthesized catalysts are given in Table 5. These R^2 values revealed that catalytic reduction process

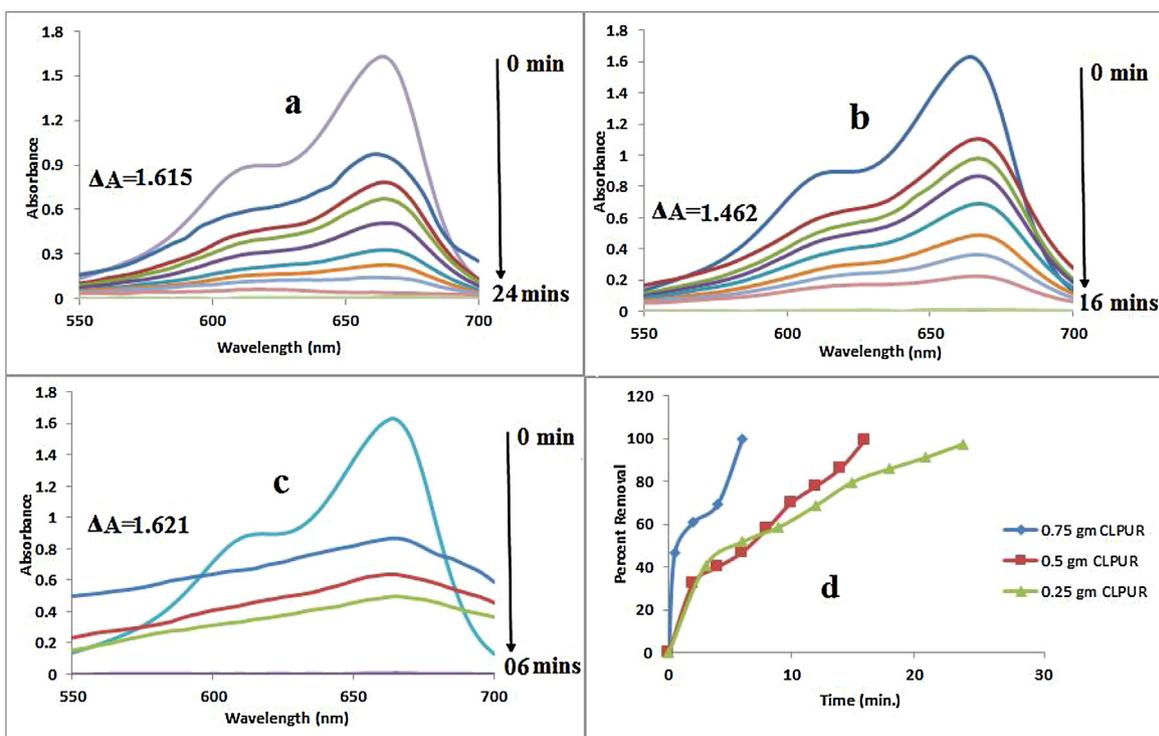


Fig. 7. Changes in the UV–vis absorption spectra of MB dye (2.5×10^{-5} M) with different doses of CLPUR in presence of NaBH_4 (0.1 M): a) 0.25 g CLPUR; b) 0.5 g CLPUR; c) 0.75 g CLPUR and d) comparison of percent removal of dye with three different dose levels of CLPUR.

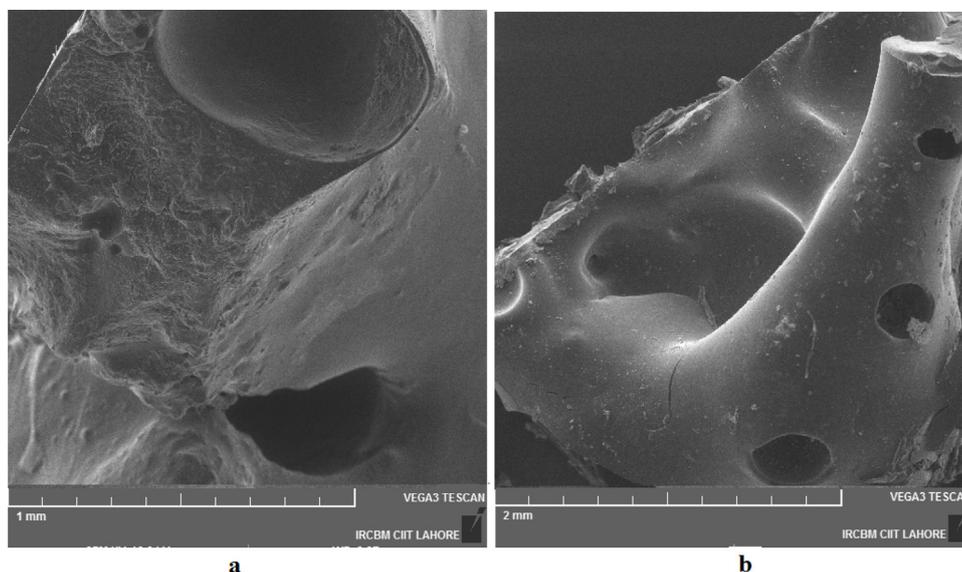


Fig. 8. SEM images of polymer: a) pure synthesized CLPUR and b) Used CLPUR.

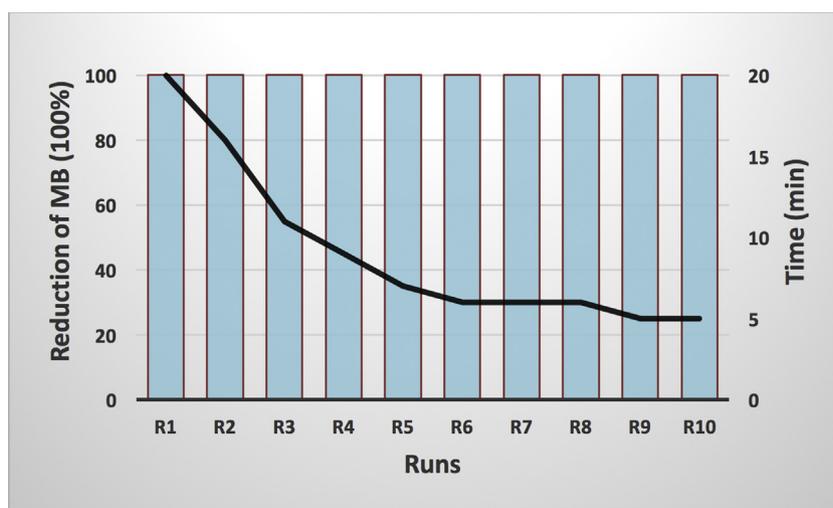


Fig. 9. Reusability studies of CLPUR for complete reduction of MB; R1 for first run, R2 is second run and so on. Primary y-axis shows reduction of MB (%) and secondary y-axis shows time (min) required for complete reduction of MB in each respective runs.

Table 5

Name of the kinetic models used, mathematical form of kinetic models, regression coefficient (R^2) and rate constant (k) for reduction of MB with CLPUR & LPUR at temperature $30^\circ\text{C} \pm 2$.

Sr. No.	Name of Kinetic Model used	Mathematical form of Kinetic Model	Regression Coefficient (R^2)		Rate constant (k)	
			LPUR	CLPUR	LPUR	CLPUR
1.	Zero order	$C_0 - C_t = kt$	0.9745	0.9615	0.607 $\text{mol.dm}^{-3}.\text{min}^{-1}$	0.891 $\text{mol.dm}^{-3}.\text{min}^{-1}$
2.	1st order	$\ln(C_t/C_0) = -kt$	0.7588	0.7050	0.1289 min^{-1}	0.2218 min^{-1}
3.	2nd order	$1/C_t = kt + 1/C_0$	0.3861	0.3396	0.9806 $\text{mol}^{-1}.\text{dm}^3.\text{min}^{-1}$	2.6674 $\text{mol}^{-1}.\text{dm}^3.\text{min}^{-1}$

follows zero order kinetics as presented in Fig. 10 as well. The values of apparent rate constant were $0.0891 \text{ mol dm}^{-3}.\text{min}^{-1}$ and $0.0607 \text{ mol dm}^{-3}.\text{min}^{-1}$ for optimized reduction processes with CLPUR and LPUR, respectively. Hence, apparent rate constant supported for more efficient reduction process on the surface of CLPUR.

4. Conclusions

In this study, cellular LPUR and CLPUR were prepared by single step process at room temperature. The FTIR confirmed the proposed synthesis of polymers. The SEM and BET analysis showed cellular

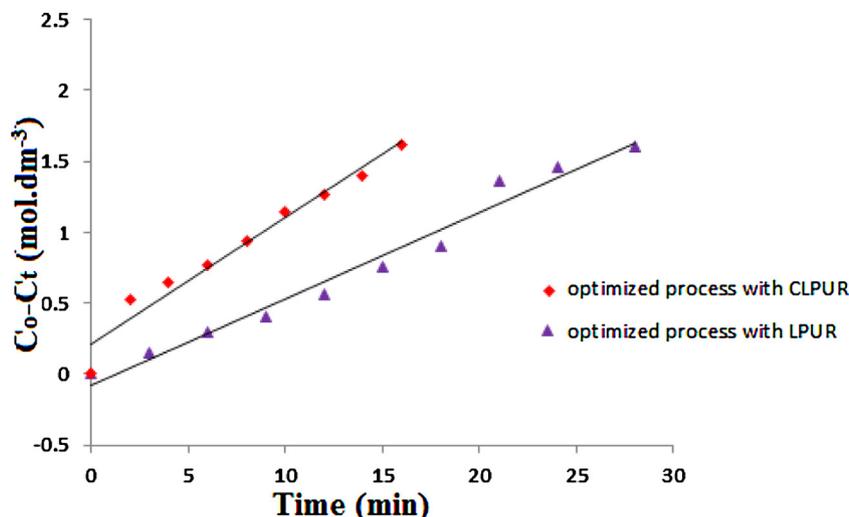


Fig. 10. Plot of $C_0 - C_t$ (mol.dm^{-3}) as a function of time (min.) for reduction of MB with catalysts.

morphology of both polymers. They catalyzed the reduction of MB dye in presence of NaBH_4 . The catalytic role of both polymers was validated with UV–vis spectroscopy focusing on maximum absorption at 665 nm. However, CLPUR was more effective and stable. The comparative kinetic study of this catalytic reduction process followed zero order kinetics. Hence, these materials can be potential catalysts in other important redox processes. They can be preferred to avoid secondary contaminations in treated water. In addition, minimum separation efforts will be required as CLPUR was stable in aqueous systems. In future directions, these materials can be shaped into filter columns for treatment of wastewater for removal of other hazardous pollutants. In addition, this system may also be tested to develop quick water based de-staining solution for stained SDS-PAGE gels.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jhazmat.2017.10.019>.

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