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## A novel, efficient, and recyclable biocatalyst for Michael additions and its iron (III) complex as promoter for alkyl oxidation reactions

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**Abstract**. Chitosan-*g*-poly(2-cyano-1-(pyridin-3-yl)allyl acrylate) (**Cs-***g*-**PCPA**), having a grafting percentage G% of 64%, was prepared and was then subjected to complexation with iron (III) (**Cs-***g*-**PCPA**/**Fe**(III)). The results of catalytic studies demonstrated that **Cs-***g*-**PCPA** serves as an efficient, recyclable and eco-friendly, basic catalyst for Michael additions, which produce adducts in high yields under mild conditions. Moreover, **Cs-***g*-**PCPA** supported Iron (III) complex was prepared and was then characterized by using FESEM, XRD, TGA, and XPS. In addition, EDS plot of the Fe(III)-chelate, confirms the presence of a relatively high amount (13%) of Fe(III). **Cs-***g*-**PCPA** (G% = 64) supported Iron (III) complex (**Cs-***g*-**PCPA/Fe(III)**) in presence of H<sub>2</sub>O<sub>2</sub> can be used to oxidize methyl pyridazinyl carbonitriles to form the corresponding fused furan derivatives efficiently. These polymeric catalysts are stable so that they can be recycled and reused more than five times without losing their catalytic activity.

#### 1. Introduction.

Many investigations carried out recently have focused on the development of new green synthetic methodologies, which reduce and/or prevent the use and/or production of environmental pollutants.<sup>1-3</sup> "Twelve Principles of Green Chemistry" have been suggested as guidelines to increase the efficiencies of synthetic methods, use less toxic solvents, reduce the steps of the synthetic routes and minimize wastes.<sup>3-5</sup> Catalysis of chemical reactions has many green beneficial features including lower activation energies that results in lower temperature processes, the use of catalytic rather than stoichiometric amounts of materials, increased chemo- and stereo-selectivities that cause less by-product formation, and the decreased utility of processing and separation agents.<sup>6</sup> Heterogeneous catalysis, in particular, conforms to the goals of green chemistry by providing simple methods for product/catalyst separations.<sup>7,8</sup> Chitosan, Cs, is a

alkaline hydrolysis of chitin. This polymer has many advantages, including being renewable, biodegradable, relatively economical, and having a low toxicity. Recently, chitosan has been used as a "green" support for several transitional metal catalysts and as a solid base catalyst for many organic reactions.<sup>9-11</sup> Much earlier, chitosan was successfully used as an efficient biocatalyst for Michael addition reactions of active methylene compounds to electron poor alkenes.<sup>12,13</sup> This process, which has attracted enormous attention as one of the most efficient C-C bond forming reaction in organic synthesis, is typically carried out in presence of homogeneous or heterogeneous basic catalysts.<sup>14-</sup> <sup>16</sup> The major problems associated with the use of chitosan as a catalyst for these processes are its lower catalytic activity and difficulty of being recycled because it forms a gel. To overcome these problems, a new catalyst, Cs-g-PCPA, was generated by homogeneous grafting of the novel monomer, 2-cyano-1-(pyridin-3-yl)allyl acrylate (CPA), onto chitosan using similar reported methodology.<sup>17-19</sup> The chitosan graft cross-linked copolymer Cs-g-PCPA was found to have higher thermal stability than the unmodified chitosan and, as a result, it can be used effectively for higher temperature catalytic reactions.<sup>20</sup>

naturally occurring polysaccharide that is usually obtained by

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Electronic Supplementary Information (ESI) available: Application of Cs-g-PCPA, graft copolymer, against unmodified chitosan beads, for some Michael addition reactions and also, application of the Cs-g-PCPA/Fe(III) chelate as an oxidizing catalyst are provided as supporting data. See DOI: 10.1039/x0xx00000x

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Chitosan has been reported to a have high metal ion adsorption affinity.<sup>21,22</sup> Tomczak et al. has shown that the chitosan Fe(III) chelate contains surface adsorbed Fe<sup>3+</sup> ions through nitrogen and oxygen atoms on the surface of chitosan.<sup>23,24</sup> The Fe(III) ions adsorption capacity of chitosan grafted with pyridine containing monomers is expected to be higher than that of the non-grafted chitosan owing to the presence of pyridine moieties in graft side chains. Recently, Tang et al. prepared chitosan-supported iron (III) chelates and used them as powerful catalysts for the oxidation of cyclohexane with air.<sup>25</sup>

Based on the above observation, chitosan-g-poly(2-cyano-1-(pyridin-3-yl)allyl acrylate) supported iron(III) complex, **Cs-g-PCPA**/Fe(III), was prepared in the form of beads and shown to be an effective promoter of methyl group specific oxidation reactions of methylpyridazinone in the presence of hydrogen peroxide.

#### 2. Results and discussion.

#### 2.1 Preparation of graft copolymer Cs-g-PCPA

2-cyano-1-(pyridin-3-yl)allyl acrylate (**CPA**, **1**) was prepared and was then employed in homogeneous grafting to chitosan using potassium persulfate and sodium sulfite as redox promoters (Scheme 1).<sup>20</sup> The grafting was demonstrated by analysing FTIR spectral differences between the chitosan and the copolymer.<sup>25</sup>



**Scheme 1.** Homogeneous grafting of 2-cyano-1-(pyridin-3-yl)allyl acrylate (1) onto chitosan to yield the grafted polymer **Cs-g-PCPA (2)**.

#### 2.2 Preparation of Chitosan-g-iron (III) supported catalyst

The chitosan graft copolymer Cs-g-PCPA (64%G) was converted into a Fe(III) chelate (Cs-g-PCPA(64%G)/Fe(III)) by stirring in a pH 1.8 aqueous solution containing  $Fe(NO_3)_3$  for 5 h.<sup>21-23</sup> The degree of Fe(III) incorporation of the polymer was determined by calculating the difference between the Fe<sup>3+</sup> concentration of the aqueous solution before and after adsorption onto the polymer by using atomic absorption spectrophotometry. Under these conditions, the maximum adsorption of Cs-g-PCPA(64%G)/Fe(III) was 0.089 mmol Fe<sup>3+</sup>/g chitosan. The formed Fe(III) supported catalyst was converted into dark brown spherical beads by neutralization with sodium hydroxide, which were kept under distilled water before use. Various Fe (III) ion binding sites exist in the graft copolymer, including s C-2 (NH2), C-3 (OH) of the chitosan backbone and in the CN, C=O, N centres of the graft side chains. As a consequence, the iron chelates are likely heterogeneous in nature.

# 2.3 Characterization of Chitosan-g-(PCPA) copolymer and its iron (III) complex

The **Cs-g-PCPA** graft copolymer sample, with 64%G, was prepared and confirmed by studying the FTIR spectra which was in agreement with our reported data.<sup>20</sup>

Surface morphologies of chitosan, Cs-g-PCPA graft copolymer (64%G), and iron(III) chelated Cs-g-PCPA (64%G) (see below) are displayed in Fig. 1 A, B, and C. By viewing these images, it can be seen that the surface of chitosan is fibrous in shape while that of the grafted sample is less fibrous. The FESEM of Cs-g-PCPA (64%G)/Fe(III), displayed in Fig. 1C, shows that the surface has undergone a remarkable change owing to coordination with Fe(III) ions. The unique structure of the chitosan is completely destroyed and replaced by irregular shapes with some large, well-developed crystals distributed on the surface. The energy dispersion composition (EDS) plot of the Fe(III)-chelate, given in Fig. 1D, confirms the presence of a relatively high amount (13%) of Fe(III). Interestingly, the amount of Fe(III) has not changed markedly (12%) after carrying out the catalytic oxidation reaction of the product 15 for 3 times (Scheme 5).



Fig. 1. FESEM images of A) chitosan; B) Cs-g-PCPA (64%G); C) Cs-g-PCPA(64%G)/Fe(III); D) EDS of Cs-g-PCPA (64%G)/Fe(III).

In Fig. 2 A, B, and C are shown XRD patterns of pure chitosan powder, chitosan graft 64% copolymer, and its Fe(III) chelate respectively. The pattern of chitosan contains a characteristic peak at  $2\theta = 19.8^{\circ}.^{26,27}$  Inspection of the XRD patterns of the chitosan and 64%G copolymer, Fig. 2 A and B, show weakness in the intensity peak of chitosan ( $2\theta = 19.8^{\circ}$ ) upon grafting and that at the same time appearance of new peak at  $2\theta = 17.1^{\circ}$ . The intensity increase of the ( $2\theta = 17.1^{\circ}$ ) peak is associated with the production of long polymer chains in poly-2-cyano-1-(pyridin-3-yl)allyl acrylate moieties introduced by grafting. Moreover, in Fig 2 C, Fe(III) chelates showed a clear improvement in the crystallinity which is attributed to the coordination of Fe with the binding sits of the copolymer.



Fig. 2. XRD patterns of (A) chitosan<sup>25</sup>; B) Cs-g-PCPA (64%G)<sup>25</sup>;
 C) Cs-g-PCPA (64%G )/ Fe(III).

XPS spectroscopy was employed to obtain information about the elemental composition and chemical states on the surface of **Cs-g-PCPA**(64%G)/Fe(III) (Fig. 3 A and B) analysis of the spectra shows that a peak exists that corresponds to a binding energy between 700-720 eV, which is characteristic of Fe<sup>3+</sup> cations. In addition, in a manner characteristic for Fe<sup>3+, 28</sup> satellite peaks are observed at ca. 720 and 733 eV on the high binding energy sides of the main peaks in the Fe(2p) spectrum (Fig. 3 B). These findings indicate that chelation of Fe(III) with the copolymer has taken place in the bulk and at the surface of the grafted polymer, a phenomenon that is in accord with the results of FESEM measurements which show that large regular crystals are present on the surface of the particles.



Fig. 3. (A) XPS spectra for Fe(III)-grafted chitosan (64%G), (B) Fe(2p) spectrum.

AFM provides a high resolution, sub-nanometre scale mapping of the topography of the surface of a material. The AFM of chitosan (Fig. 4 A) yields a 3D image that shows the presence of a smooth textured surface topography, indicating the absence of detectable agglomerates. In Fig. 4 B is displayed the AFM of the %G = 64 copolymer, which shows that it has an irregular undulating surface, attributed to the randomly distributed graft regions. In Fig. 4 C is displayed the 3D image of the surface of **Cs-g-PCPA**(64%G)/Fe(III), which is comprised of a random distribution of broad and intense peaks associated with the presence of Fe(III).

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**Fig. 4.** AFM – 3D images of (A) chitosan **Cs**, (B) **Cs-g-PCPA** (64%G), and (C) **Cs-g-PCPA** (64%G)/Fe(III).

# 2.4 Application of the graft copolymer as a basic heterogeneous Michael addition catalyst

The effectiveness of the grafted chitosan polymer Cs-g-PCPA as a basic catalyst in Michael addition reactions was explored. Benzylidene-malononitrile 3 was observed to participate in a Michael addition reaction with dimedone 4 promoted by 10%wt Cs-g-PCPA beads to yield the chromene-3-carbonitrile derivative 5 in an excellent yield (>95%) (Scheme 2). Moreover, this compound 5 has been prepared previously by employing other homogeneous basic catalysts.<sup>12,13,15,16</sup> One of the difficulties associated with using the unmodified chitosan as a catalyst for these reactions is that separation of the product from the catalyst. This difficulty is caused by the fact that this polysaccharide readily forms a gel. In contrast, the catalytically more active grafted copolymer does not form a gel during workup and, as a result, it is a superior catalyst for these reactions. Accordingly, the grafted copolymer catalyst can be readily separated by simple filtration and reused after it is washed with hot methanol and dried in an oven at 100 °C for 2 h for more than five times without loss of catalytic activity.

In order to estimate the appropriate catalyst loading, a model reaction of benzylidene-malononitrile **3** (1.54 g, 10 mmol) and

dimedone **4** (1.40 g, 10 mmol) was carried out in 25 mL absolute ethanol using 1, 5, 10, 15, and 20% wt. of catalyst under the same conditions (Fig. 5). The catalyst loading 10%wt was found to be the optimal quantity. Moreover, the catalyst was reused four times and the results showed that the graft copolymer can be reused as such without significant loss in its catalytic activity (Table 1).

**Table 1.** Recyclability of the chitosan graft copolymer as basiccatalyst.

	Fresh	Recycled Catalyst			
State of Catalyst					
	Catalyst	(1)	(2)	(3)	(4)
Product 5	05	0.4	02	0.2	0.2
(%Yield)	95	94	93	92	92
· · ·					



Fig. 5. Optimization of the chitosan graft copolymer as basic catalyst.

Reactions of benzylidene-malononitrile **3** with barbituric and thiobarbituric acids **6a** and **b** have been described earlier.<sup>29-31</sup> These processes produce the pyridopyrimidines **8** when ammonium acetate is employed as the catalyst. In contrast, reactions of **3** with **6a** and **b** occur more efficiently (80%) to produce pyranopyrimidines **7a** and **b** when carried out in ethanolic solutions containing 10%wt of **Cs-g-PCPA** beads (Scheme 2). In a study evaluating the possibility of carrying out a one pot reaction, we observed that stirring independent

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mixtures of **6a** and **b** containing benzaldehyde, malononitrile and **Cs-g-PCPA** beads leads to efficient formation of **7a** and **b**, respectively. The results of additional investigations demonstrated that **Cs-g-PCPA** serves as a catalyst for classical Gewald's reactions<sup>29,30</sup> of 3-oxoalkanenitriles **9a** and **b** with ethyl cyanoacetate **10** in 1,4-dioxane solutions containing elemental sulfur. These processes generate the thiophene derivatives **11a** and **b** (Scheme 3).



Scheme 2. Cs-g-PCPA (64%G) catalysed Michael addition reactions.

A plausible mechanism for this process involves the formation of ylidene intermediate **A**, which is cyclization of intermediate B occurs readily to form the aromatic thiophene products, **11a** and **b** via elimination of the catalyst (Scheme 3). The findings of a further exploration of this process showed that the yields of the thiophenes are highly dependent on the nature of solvent, with the use of 1,4-dioxane leading to much higher yields than with ethanol.



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**Scheme 3. Cs**-*g*-**PCPA** (64%G) catalysed Gewald's synthesis of thiophene.

Substituted enaminonitriles **12a** and **b** are promising substrates for the synthesis of new quinolinone derivatives **13a** and **b**, containing piperidenyl or morpholinyl substituents at the C-2 position (Scheme 4). In fact, **12a** and **b** were found to react with dimedone in ethanol in the presence of 10%wt of **Cs-g-PCPA** as heterogeneous catalyst to afford quinolinone derivatives **13a** and b in high yields (*ca*. 90%). The structures of these products were assigned based on the results of X ray crystallographic analysis (Fig. 6A and B).



Fig. 6. (A) X-ray crystal structure of **13a**; (B) X-ray crystal structure of **13b**.

A reasonable mechanism for these processes involves initial **Cs-g-PCPA** catalysed Michael addition reaction between the enaminonitriles and dimedone to produce intermediate **I**. This intermediate then cyclizes to give the aminopyran intermediate **II** that undergoes an allowed 1,3-nitrogen shift, in agreement with that previously published by our group, <sup>13,32,33</sup>

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accompanied by ring opening to afford imine intermediate IV. Finally, IV intermediate readily cyclizes to give **13a** and **b**.



Scheme 4. Cs-g-PCPA (64%G) catalysed synthesis of quinolinone derivatives 13a and b.

1.6 Applying the chitosan graft–Fe(III) chelate as a co-catalyst for oxidation of alkyl pyridazinones

One of the major challenges in organic synthesis is the development of methods for the controlled oxidation of nonactivated alkyl C-H bonds.<sup>3</sup> Earlier reports<sup>24</sup> of the use of Fe(III) supported chitosan chelates in oxidations of alkyl groups encouraged us to carry out a brief exploration of oxidation reactions of heterocyclic compounds promoted by **Cs-g-PCPA** /Fe(III) chelates. In this effort, we observed that controlled oxidation at the methyl groups in the pyridazinones **14a** and **b** can be performed utilizing the **Cs-g-PCPA** (64%G)/Fe(III) chelate as an efficient Fe(III)-supported catalyst. Accordingly, independent mixtures of **14a** and **b** containing **Cs-g-PCPA** (64%G)/Fe(III) react in the presence of excess hydrogen peroxide to form the fused furan derivatives **15a** and **b** in relatively higher yields than previously reported<sup>34</sup> (Scheme 5). The reaction mixture of the catalyst in glacial acetic acid with  $H_2O_2$  afforded the maximum yield of the oxidation products (Table 2). As shown in Table 2, it is clear that the solvent of choice for this reaction is the glacial acetic acid where higher yields were obtained.



Scheme 5. Oxidation of alkyl pyridazinones utilizing Cs-g-PCPA (64%G)/Fe(III).

**Table 2.** Solvent effects on the oxidation reaction of methyl

 pyridazinones <sup>a</sup>

Entry	Substrate	Solvent	Product	Yield
1		H <sub>2</sub> O		N.R. <sup>b</sup>
2		EtOH		8
3	14a	AcOEt	15a	44
4		CH₃CN		66
5		AcOH		72
6		H <sub>2</sub> O		N.R. <sup>b</sup>
7		EtOH		14
8	14b	AcOEt	15b	48
9		CH₃CN		58
10		AcOH		66

<sup>a</sup> Reactions were conducted with 1 mmol substrate, with 10% wt of the Cs-g-PCPA (G=64%)/Fe(III) chelate and 5 mmol of 30% hydrogen peroxide.

#### <sup>b</sup> N.R. Reaction didn't occur.

The proposed mechanism of oxidation of pyridazinones via chitosan graft–Fe(III) chelate may be postulated as in Scheme 6. The reaction was started with oxidation of methyl

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substituent utilizing  $H_2O_2/Fe^{3+}$  oxidizing mixture to afford the corresponding 1° alcohol. Because of the binding capability of Fe(III) catalyst with CN group, non-isolable intermediate was catalysed to underwent heterocyclization process to afford the final product **15a** and **b** via intermediates B and C.



**Scheme 6.** Proposed mechanism for oxidation of alkyl pyridazinones utilizing **Cs-g-PCPA** (64%G)/Fe(III) as a catalyst.

### 3. Experimental

3.1 Materials

Medium molecular weight grade chitosan (deacetylated 90%, M = ca. 35.000) was purchased from Aldrich. DABCO (1,4diazabicyclo[2.2.2]octane) was purchased from Aldrich. Potassium persulfate K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (KSS) and sodium sulfite Na<sub>2</sub>SO<sub>3</sub> (SS) were purchased from Riedel-deHaen and Fluka, respectively. Acrylonitrile was purchased from Aldrich and purified by treatment with 10% NaOH for 30 min to remove the inhibitor and then distilled at 77°C. Pyridine-3-carbonitrile was purchased from Aldrich. All other chemicals of analytical grade were used without further purification.

#### 3.2 Apparatus and Instrumentation

Field emission scanning microscopy (FESEM) was carried out using a model Leo (Zeiss) Remotely Operationable Variable Pressure Field Emission SEM with EDX (Energy Dispersive X-Ray Spectrometers) and Cryo attachment. Powder samples used in the measurements were made by compression of the polymer and then coating with gold. The degree of Fe<sup>3+</sup> adsorption on the chitosan grafted copolymer was calculated based on the difference of Fe<sup>3+</sup> concentration in aqueous solutions before and after adsorption at wavelength 248 nm using an atomic absorption spectrophotometer (Perkin-Elmer 3100 Model). Single crystal X-ray crystallographic analysis was performed by using a RIGAKU RAPID II. The XRD measurements were performed at room temperature on chitosan, grafted chitosan and Fe(III)/copolymer. Siemens diffractometer model D500 (Germany) operating in the reflection mode with Cu-Ka radiation (35kV, 30mA) was used for the analysis. X-ray photoelectron spectroscopy (XPS) was conducted using a model VG Scientific 200 spectrometer (UK) equipped with MgKa radiation (1253 eV) and operated at 23 kV and 13 mA. All binding energy values (in eV) were determined with respect to the C1s line (284.6 eV) originating from adventitious carbon, the standard deviation of the peak position being within ±0.02 eV. Surface topography was analysed via AFM using the Nanoscope IV Multimode Atomic Force Microscope.

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#### 3.3 Preparation of Basic Catalyst Chitosan-g-PCPA (Cs-g-PCPA) beads

### 3.3.1 Preparation of 2-Cyano-1-(pyridin-3-yl)allyl acrylate, CPA, vinyl monomer

Recently, Fakhreia *et al* has reported a novel methodology to modify chitosan through grafting with 2-Cyano-1-(pyridin-3yl)allyl acrylate, **CPA**.<sup>25</sup> The latter vinyl monomer was synthesized by reacting 2-(Hydroxy(pyridin-3yl)methyl)acrylonitrile, Morita Baylis Hillman (MBH) adduct of acrylonitrile and nicotinaldehyde in the presence of DABCO as a catalyst under neat conditions, with acryloyl chloride.

# 3.3.2 Preparation of the graft copolymer **Cs-g-PCPA**, under optimum conditions <sup>25</sup>

A 1.00 g chitosan powder was stirred in 50 mL distilled water to which  $K_2S_2O_7$  (3.5 x 10<sup>-3</sup> M) and NaHSO<sub>3</sub> (1.75 x 10<sup>-3</sup> M) with a ratio of 1:0.5 were added respectively. CPA (2.14 g, 10 mmol) was added and then mixture was stirred at 65°C for 4 h. Filtration gave the graft copolymer, which was washed with water and was then extensively extracted with hot ethanol using the *soxhlet* extraction technique to remove the unreacted monomer. Finally the graft copolymer **Cs-g-PCPA** was dried.

### 3.3.3 Preparation of Cs-g-PCPA – supported Iron(III) chelate: Fe / Cs-g-PCPA

An aqueous solution containing  $Fe(NO_3)_3$  was used to absorb Fe(III) ions on the surface of Cs-g-PCPA grafted chitosan beads of 64 %G.<sup>20,21</sup> The degree of adsorption was calculated based on the difference of Fe<sup>3+</sup> concentration in aqueous solution before and after adsorption at wavelength 248 nm. For Fe(III) adsorption onto **Cs-g-PCPA**, a contact time of 5 h at pH 1.8 was used for stirred mixture of **Cs-g-PCPA** beads (0.05 g) and 100 mL (10 mM) of Fe(NO<sub>3</sub>)<sub>3</sub> solution in 250 mL beaker. The amount adsorbed on the beads was calculated according to the following equation:

Adsorption Capacity 
$$(q_e) = \frac{(C_0 - C_e) V}{W}$$

Where  $C_0$  is the initial Fe(III) concentration (ppm),  $C_e$  is the final concentration of Fe(III) after the adsorption time, V is the volume of Fe(III) solution (mL) and W is the used weight of graft copolymer **Cs-g-PCPA** beads (g). The yellowish-coloured beads containing adsorbed Fe<sup>3+</sup> were washed thoroughly with distilled water and stored in the distilled water for further use. Under the previous conditions, the maximum adsorption capacity was obtained as 0.091 mmol Fe<sup>3+</sup>/g chitosan.

# 3.3.4 Conversion of catalyst powder to the form of spherical beads

Chitosan (or modified chitosan) was converted to spherical bead shapes as previously reported<sup>35</sup> by dissolving 2.00 g of powder in 60 mL of 5% (v/v) acetic acid solution. The viscous solution was sprayed into 500 mL of a stirred 0.50 M NaOH solution as a precipitation bath. In the bath neutralization of the acetic acid occurred within the chitosan gel and thereby promoting coagulation to form spherical uniform chitosan gel beads. Impurities trapped in the pores of chitosan beads were removed by rinsing with distilled water. Filtration and air-drying gave beads that could be stored under distilled water.

#### Conclusions

In the investigation described above, we have shown that the grafted chitosan, **Cs-g-PCPA** (G = 64%) beads were employed as an efficient basic, recyclable, reusable, and green

heterogeneous catalysts for Michael addition reactions. The results of this study show that **Cs-g-PCPA** (G = 64%) serves as a superior catalyst for Michael additions as compared to chitosan itself and suggest that the new basic catalyst can replace other more toxic old organic catalysts, like piperidine and pyridine, in Michael additions. The chitosan graft crosslinked copolymer **Cs-g-PCPA** was found to have higher thermal stability than chitosan and, as a result, it can be used effectively for higher temperature reactions. Finally, the iron (III)-supported chitosan copolymer complex, **Cs-g-PCPA** (G = 64%)/Fe (III), was shown to be a promising catalyst for selective methyl group oxidation reactions of methyl substituted heterocycles.

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## Graphical Abstract

A novel, efficient, and recyclable biocatalyst for Michael additions and its iron (III) complex as promoter for alkyl oxidation reactions

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