Synthesis of N-Benzylideneaniline by Schiff base reaction using Kinnow peel powder as Green catalyst and comparative study of derivatives through ANOVA techniques

Renu Verma1, Narendra Pal Lamba1, Anshu Dandia2, Anamika Srivastava3, Kanak Modi1, Mannmohan Singh Chauhan1,2 & Jagdish Prasad1*

The cheap and easy availability of the Kinnow peel waste has reported various applications due to presence of multifunctional groups. Therefore, in present study we explored its application to synthesize N-Benzylideneaniline and its derivatives based on Schiff base reaction. Kinnow peel powder is characterized by FTIR, TEM, SEM, XRD, EDX, and TGA for functional groups, morphology, surface, elements and thermal stability. Benzaldehyde, aniline, and their derivatives such as 4-methyl benzaldehyde, 4-hydroxy benzaldehyde, 4-methoxy benzaldehyde, and 4-methoxy aniline have been used to compare the efficacy of the Schiff base reaction using analysis of variance (ANOVA) and it has been observed that combination of Aniline and benzaldehyde for Schiff base reaction provided 85% yield of relative product.

In the present time, it becomes a new challenge to reduce chemical waste, reaction time, economically efficient and toxic chemicals in organic transformations for the researchers. Green chemistry plays the most fundamental role in synthetic chemistry because it maximize the yield of reaction product and minimize the side product without using any hazardous chemicals and specific reaction conditions, so it become possible to minimize the harassment of environment. Green catalyst is only the path, which can resolve all these issues. There are many green catalysts and green methods are reported to make environment toxic free like modified of mesoporous halloysite nanotubes (HNTs) by using CuFe2O4 nanopartical1, synthesized the imidazole heterocycles via green NiFe2O4/geopolymer nanocatalyst2, and preparation of nickel nanoparticles by green method3. Green catalysts are also used in synthesis of 2,4,6-tri-arylpyridines, diazepine, organic transformation, pyrido-imidazo-isoquinolines, synthesis of chromene-linked nicotinonitriles, and aminonitriles by using the environmentally-friendly and highly efficient LPSF magnetic4, Fe3O4/SiO25, iron oxide nanoparticles6, multiple carbon nanotubes and TiO2 catalyst7, Fe3O4@SiO2-OSO3H8, Fe3O4@SiO2-NH2-GA9 nanocatalyst are reported respectively. Cellulose based nanocomposite with Fe3O4 nanoparticles is reported as a recoverable catalyst for condensation reaction11. A novel and green nanocomposite Fe3O4@PEO-SO3H, (PEG-400)-SO3H-coated Fe2O3 and copper oxide nanoparticles were prepared for green synthesis of polyhydroquinolines12, aminocarbonyl13, and 1, 2,3-triazoles 14 respectively.

Biomass is a cheap carbon material, so, it is important and abundant in nature15. Biomass is generally derived from mesoporous carbon, which has great potential because of its chemical, mechanical and physical properties16,17. Hence, biomass have wide applications in the field of sensors18–20, catalysis21–25, gas storage26–28, energy storage29–35, and waste-water treatment36,37. Biomass contains many oxygen functional group and other elements at their surface, which makes it a good support material for catalytic17. However, many biomass-based catalysts were reported and obtained from fruits peel and were found to be inefficient for catalytic purposes38–40.

1ASAS, Amity University Rajasthan, Jaipur, Rajasthan 303002, India. 2Department of Chemistry, University of Rajasthan, Jaipur 302004, India. 3Department of Chemistry, Banssthali Vidyapith, Banasthali 304022, India. *email: phd8du@gmail.com; jprasad@jpr.amity.edu
such as catalyst developed from leftover pulp of *Citrus limetta* (Mausambi) which was waste material\cite{41,42}. Therefore, it is necessary to develop novel biomass catalyst that will be more stable and reliable for many applications.

Hugo Schiff reported the Schiff base by condensation reaction between aldehyde and amine in 1864\cite{43}. These compounds contains azomethine group (–HC=N–) and behaves like Flexi-dentate ligand. Schiff base have wide applications in many types of biological activities like antibacterial\cite{44}, antitumor\cite{45}, anti-oxidant\cite{46}, anti-inflammatory activity\cite{47}, antifungal\cite{48} and industrial applications. Schiff base ligand is generally used in the development of inorganic chemistry, co-ordination chemistry because they are able to generate complex with metal ions. Some of the Schiff base shows good catalytic performance at high temperature\cite{49}. Synthesis of Schiff base is catalyzed by various type of chemical catalyst. However, these catalysts may be harmful for environment as well as for human being. To overcome these issues, some eco-friendly catalyst developed and reported.

Due to the high importance of eco-friendly catalysis in the Schiff Base reaction and potential of cost effectively, available fruit peel experiments have been designed to investigate its application as a catalyst in the present study. This is very first report where Kinnow peel powder is used as organic catalyst for Schiff base reaction between aniline and benzaldehyde.

**Experimental methodology**

**Materials.** Waste peels of Kinnow mandarin is selected and used as a catalyst in this study. Kinnow peels are collected from local fruit stalls in Jaipur, Rajasthan. Bruker Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA), Energy dispersion X-ray spectroscopy (EDS), X-ray diffraction (XRD), Transmission emission spectroscopy (TEM), and Thin layer chromatography (TLC) are performed for characterization of Kinnow peel powder. All chemicals and solvents are used without any purification: DMSO, DCM, acetonitrile, pet-ether, diethyl ether, aniline, benzaldehyde, 95% ethanol, and distilled water.

**Preparation of the catalyst.** Kinnow peel wastes are washed with di-ionized water to remove dirt particles and cleaned well. The peel is dried in an oven for 24 h at 70 °C to remove moisture content. The dried peel waste is converted into powder form and then the powder is stored for further experiment (Fig. 1).

**Preparation of Schiff base and their derivatives.** 10 mg of Kinnow peel powder is added in reaction mixture of 1 mmol of Benzaldehyde and 1 mmol of Aniline in a test tube and allowed to stir it for 3 min on the magnetic stirrer at room temperature. The performance of the reaction is checked by the TLC plates with mobile phase [9:1 ratio of hexane and ethyl acetate] and after the completion of catalytic reaction the desired product is recrystallized by ethanol. Similar method is used for Schiff base reaction between derivatives of aniline and benzaldehyde.

**Results and discussion**

Herein, synthesis and to obtained high yield of the Schiff base product with green catalyst (organic material) is developed. This is achieved by adopting the green method for Schiff base reaction between benzaldehyde and aniline with Kinnow peel powder. It is observed that the desired product N-Benzylideneaniline is formed with 85% yield in 3 min (Scheme 1).

**Optimization for Schiff base reaction:** The Schiff base reaction in between benzaldehyde and aniline is performed with various solvents (Table 1). From Table 1 it is clear that, 72% yield of relative product is observed with DCM (Table 1, entry 1), while DMSO provides only 70% yield (Table 1, entry 2). We also used diethyl ether, pet ether, acetonitrile for Schiff base reaction and 65–75% yield of relative products was found respectively
We also investigated the effect of catalyst loading, it is observed that 10 mg catalyst provides best results (Table 1, entry 7) but without catalyst Schiff base reaction provides only 48% yield of relative product (Table 1, entry 9). The bare component also provides moderate yield (60%) of Schiff base product (Table 1, entry 10).

Therefore, Kinnow peel powder is high stable and eco-friendly catalyst for synthesis of Schiff base and providing best results under mild reaction conditions.

Derivative of N-Benzylideneaniline also synthesized using same experimental procedure. The different derivatives such as 4-methyl benzaldehyde, 4-hydroxy benzaldehye, 4-methoxy benzaldehyde, and 4-methoxy aniline are used for Schiff base reaction by following optimized reaction conditions. Further more, it has been also observed that derivatives of aniline and benzaldehyde also affect the yield of relative Schiff base products. After that to confirm the yield of respective reaction, each derivative reaction of Schiff base put on five times and observed the result (As shown in Table 2) (Scheme 2).

The total number of sampled observation of the yield of six derivatives are not the same, therefore the difference among the effect of the derivatives to obtain by considering the following hypothesis.

### Table 1. The effect of solvents and different amount of catalyst on Schiff base reaction between aniline and benzaldehyde.

| Entry | Solvents | Catalyst (mg) | Time (min) | Yield (%) |
|-------|----------|---------------|------------|-----------|
| 1     | DCM      | 10            | 180        | 72        |
| 2     | DMSO     | 10            | 240        | 70        |
| 3     | Diethyl ether | 10      | 210        | 65        |
| 4     | Pet ether | 10            | 150        | 68        |
| 5     | Acetonitrile | 10      | 240        | 75        |
| 6     | Neat     | 5             | 5          | 75        |
| 7     | Neat     | 10            | 3          | 85        |
| 8     | Neat     | 20            | 3          | 85        |
| 9     | Neat     | Without catalyst | 10  | 48        |
| 10    | Neat     | Bare component | 10  | 60        |

### Table 2. Schiff base reaction by using different derivatives of aniline and benzaldehyde.

| Entry | Aromatic amine | Aldehyde derivatives | Product | %Yield in consecutive 5 cycles |
|-------|----------------|-----------------------|---------|-------------------------------|
| 1     | NH₂            | CHO                   | ![Product Image] | 85, 85, 85, 84, 85           |
| 2     | NH₂            | H₃C-CHO               | ![Product Image] | 80, 80, 80, 79, 78           |
| 3     | NH₂            | HO-CHO                | ![Product Image] | 80, 80, 78, 80, 80           |
| 4     | NH₂            | H₃CO-CHO              | ![Product Image] | 82, 80, 82, 83, 83           |
| 5     | H₃CO-NH₂       | CHO                   | ![Product Image] | 83, 83, 84, 83, 83           |
| 6     | H₃CO-NH₂       | H₃C-CHO               | ![Product Image] | 80, 80, 81, 80, 80           |
The null hypothesis (H0): is that there is no difference among the effect of six derivatives on the yield of the product against the alternative hypothesis (H1): is that there is a difference among the effect of six derivatives on the yield of the product.

To test the above null hypothesis one-way analysis of variance (ANOVA) technique is used. Before applying the ANOVA technique, the assumption for homogeneity of variances is tested through Levene's test. For analysis of the data the software SPSS is used. From SPSS following Descriptive statistics is obtained (Table 3).

The analysis of variance table for testing the difference among the derivatives on the yield is given below (Table 4).

From the above table, it is concluded that there is a difference of the yield among the six derivatives. Since, there is a difference among six derivatives then a multiple comparison test that is a Tukey test is applied to find out the significant difference between any two derivatives.

From the above table, it is concluded that there is a difference among the yield among the six derivatives. Since, there is a difference among six derivatives then a multiple comparison test that is a Tukey test is applied to find out the significant difference between any two derivatives.

The null hypothesis (H0): is that there is no difference among the effect of six derivatives on the yield of the product against the alternative hypothesis (H1): is that there is a difference among the effect of six derivatives on the yield of the product.

To test the above null hypothesis one-way analysis of variance (ANOVA) technique is used. Before applying the ANOVA technique, the assumption for homogeneity of variances is tested through Levene's test. For analysis of the data the software SPSS is used. From SPSS following Descriptive statistics is obtained (Table 3).

The analysis of variance table for testing the difference among the derivatives on the yield is given below (Table 4).

From the above table, it is concluded that there is a difference among the yield among the six derivatives. Since, there is a difference among six derivatives then a multiple comparison test that is a Tukey test is applied to find out the significant difference between any two derivatives.

The IR spectrum of fresh and recovered Kinnow peel powder. The IR spectrum of fresh Kinnow peel powder and recovered Kinnow peel powder is compared (Fig. 2), which shows a broad peak at 3325 cm\(^{-1}\) and 3328 cm\(^{-1}\) in the high-frequency area attributed to the stretching mode of the O–H bond, which reveals the presence of hydroxyl groups in both Kinnow peel powder. The C–H stretching observed at 2920 cm\(^{-1}\) and 2918 cm\(^{-1}\). The bands observed at 1718 cm\(^{-1}\) and 1720 cm\(^{-1}\) are assigned to the carboxyl group. The sharp peak found at 1605 cm\(^{-1}\) and 1603 cm\(^{-1}\) is a resonance peak which assigned to C=C (aromatic ring). The peak at 1419 cm\(^{-1}\) and 1406 cm\(^{-1}\) denotes COO\(^{-}\) bond and the peak at 1093 cm\(^{-1}\) and 1094 cm\(^{-1}\) corresponds to the vibrational mode of the C-O group.
TEM. The TEM is used to determine the morphology of Kinnow peel powder. TEM images confirmed that the samples' particles are spherical having diameter of >100 nm and rod shaped with >50 nm in length (Fig. 3) and that the particles are largely agglomerated at 200 nm. The larger and variable sizes of Kinnow peel powder particles are visible in the TEM images.

SEM-EDX analysis. The scanning electron microscopy (SEM) has been used to study the morphology of Kinnow peel powder particles. Figure 4 shows the spectra obtained in SEM using EDX of the particle core. SEM spectra show the irregular particles with heterogeneous morphology. The size of the particle is 0.95 μm (calculated by imageJ). Figure 5 presents the result of EDX analysis for the cracked surface of Kinnow peel powder's particle after autoclave. It is evident that oxygen (O) and Ca are found as major (93.9%) and minor (6.1%) elements in the sample.

TGA analysis. Thermogravimetric analysis (TGA) is used to confirm Kinnow peel powder's thermal stability throughout a temperature range of 10 °C to 800 °C. As seen in Fig. 6. The removal of the chemisorbed and physisorbed solvent over the Kinnow peel powder's surface was clearly responsible for the weight loss below 200 °C. The huge weight loss has been observed in the temperature range of 230 °C to 510 °C.

Table 5. Homogeneity test results of Tukey HSD for the yield of Schiff base reaction.

| (I) Substrate                        | (J) Substrate                        | Mean difference (I-J) | Std. error | Sig | 95% confidence interval |
|-------------------------------------|-------------------------------------|-----------------------|------------|-----|-------------------------|
| Aniline + Benzaldehyde              | Aniline + 4methyl Benzaldehyde      | 5.00000*              | .53541     | .000| 3.3445 6.6555           |
| Aniline + 4-hydroxy Benzaldehyde    | 4.80000*                            | .53541                | .001       | .7445 4.0555            |
| Aniline + 4 Methoxy Benzaldehyde    | 2.40000*                            | .53541                | .002       | .7445 4.0555            |
| 4 Methoxy Aniline + Benzaldehyde    | 1.20000*                            | .53541                | .256       | 1.4555 2.8555           |
| 4 Methoxy Aniline + 4 Mtheyl Benzaldehyde | 4.20000*                            | .53541                | .000       | 2.5445 5.8555           |

Figure 2. IR spectrum of fresh Kinnow peel powder (black) and recovered Kinnow peel powder (red).
X-ray diffraction (XRD) of Kinnow peel powder. Figure 7 shows the X-ray diffraction (XRD) of Kinnow peel powder with key diffractions at 2θ = 15°, 19.7°, and 21° and it is observed with Cu Kα (λ = 1.5405 Å) radiation in the 2θ range from 10° to 90°.

The activity of the catalyst (Kinnow peel powder), is compared with the reported methods for Schiff base reaction and the data shown in Table 6. From the data, it is clearly shows that the high efficiency of the present work while comparing on the literature reported catalysts for the Schiff base reaction.

Mechanism of Schiff base formation reaction of benzaldehyde and aniline via catalyst involves four steps: (1) Reaction of aniline with benzaldehyde in the presence of kinnow peel powder (Step 1, Scheme 3), (2) formation of intermediate (Step 2, Sheme 3), (3) Formation of carbinolamine (Step 3, Scheme 3) and (4) Formation of Schiff base product (Step 4, Scheme 3)63,64.
Figure 4. Scanning electron micrographs of the Kinnow peel powder.

Figure 5. Spectrum of cracked surface of Kinnow peel powder particle based on EDX.
Figure 6. TGA analysis of Kinnow peel powder.

Figure 7. XRD data of Kinnow peel powder.
| Serial no | Catalyst                          | Solvent     | R (R-NH₂) | R (R-CHO) | Reaction condition | Time     | Yield % |
|-----------|-----------------------------------|-------------|-----------|-----------|--------------------|----------|---------|
| 1         | Calcined eggshell (CES)⁹⁰         | Solvent free| 4-OCH₃    | 4-OH      | RT grinding        | 10–15 min| 98      |
| 2         | Montmorillonite K-10 clay⁹¹       | –           | H         | H         | MW                 | 3 min    | 98      |
| 3         | Acetic acid⁹²                      | –           | H         | H         | Grinding           | 2 h      | 89      |
| 4         | Mg(CH₃COO)₂⁹³                     | DCE         | 4-NO₂     | 4-OME     | RT                 | 8 h      | 95      |
| 5         | P₂O₅/Al₂O₃⁹⁴                      | –           | H         | H         | RT string          | 20 min   | 80      |
| 6         | CeCl₃·7H₂O⁹⁵                      | Ethanol     | H         | 2-OH      | Reflux             | 2 h      | 68      |
| 7         | Montmorillonite⁹⁶                 | Chloroform  | H         | H         | RT grinding        | 10 min   | 95      |
| 8         | Cu/Co metal complexes⁹⁷           | Ethanol     | 4-NO₂     | H         | Reflux             | 3 h      | –       |
| 9         | Glacial acetic acid⁹⁸             | Ethyl alcohol| 4-F-2-CH₃| H         | Reflux             | 2 h      | –       |
| 10        | Hot ethanoic solution⁹⁹          | Ethanol     | Substituted(1,3-dihydrobenzoimidazole-2-ylidene)amide| Reflux| 4 h | 78 |
| 11        | Acid catalysis⁹⁹                  | Trimethyl orthoformate| H | H | Stirring | 8 h | – |
| 12        | Alumina⁹⁹                        | –           | H         | H         | Stirring 20 °C     | 2 h      | 99      |
| 13        | Conc. H₂SO₄⁹²                     | Ethanol     | –         | –         | Reflux             | 1 h      | 70      |
| 14        | Kinnow peel powder (Present work)| Solvent free| H         | H         | Stirring           | 3 min    | 85      |

Table 6. Efficiency of the Schiff based reaction using various substrates and catalysts.

Scheme 3. Possible Mechanism of Schiff base reaction with kinnow peel powder.
Conclusion

N-Benzalideneaniline and their derivatives are synthesized by using benzaldehyde and aniline derivatives where Kinnow peel powder has been used as a catalyst. This reaction resulted into 85% to 78% yield in neat condition. Comparisons of the yield of the six derivatives have also been done and comparative study done by ANOVA technique.

Received: 14 December 2021; Accepted: 10 May 2022
Published online: 10 June 2022

References

1. Maleki, A., Hajizadeh, Z. & Salehi, P. Mesoporous halloysite nanotubes modified by CuFe 2 O 4 spinel ferrite nanoparticles and study of its application as a novel and efficient heterogeneous catalyst in the synthesis of pyrazolopyridine derivatives. Sci. Rep. 9(1), 1–8 (2019).
2. Hajizadeh, Z., Radinekian, E., Eivazzadeh, R. & Maleki, A. Development of novel and green NiFe 2 O 4 /geopolymer nanocatalyst based on bentonite for synthesis of imidazole heterocycles by ultrasonic irradiations. Sci. Rep. 10(1), 1–11 (2020).
3. Alghari, M. R., Soltaninejad, V. & Maleki, A. Synthesis of nickel nanoparticles by a green and convenient method as a magnetic mirror with antibacterial activities. Sci. Rep. 10(1), 1–10 (2020).
4. Maleki, A. & Firoozni-haji, R. One-pot three-component synthesis of pyrido [2,1:2,3]imidazo [4,5-c]isoquinolines using Fe 3 O 4 @SiO 2 –OSO 3 H as an efficient heterogeneous nanocatalyst. RSC Adv. 4(109), 64169–64173 (2014).
5. Maleki, A. & Movahed, H. & Ravaghi, P. Magnetic cellulose/Ag as a novel eco-friendly nanobiocatalyst to catalyze synthesis of chromene-linked nicotinonitriles. Carbohydr. Polym. 156, 259–267 (2017).
6. Maleki, A., Azadeeghan, S. & Rahimi, J. Gallium acid grafted to amine-functionalized magnetic nanoparticles as a proficient catalyst for environmentally friendly synthesis of aminonitritoles. Appl. Organomet. Chem. 33, 1–7 (2019).
7. Maleki, A. Fe 3 O 4 /SiO 2 nanoparticles : an efficient and magnetically recoverable nanocatalyst for the one-pot multicomponent synthesis of diazepine derivatives. Tetrahedron 68, 3–9 (2012).
8. Maleki, A. One-pot three-component synthesis of pyrido [2,1:2,3]imidazo[4,5-c]isoquinolines using Fe 3 O 4 @SiO 2 –OSO 3 H as an efficient heterogeneous nanocatalyst. RSC Adv. 4(109), 64169–64173 (2014).
9. Maleki, A. & Movahed, H. & Ravaghi, P. Magnetic cellulose/Ag as a novel eco-friendly nanobiocatalyst to catalyze synthesis of chromene-linked nicotinonitriles. Carbohydr. Polym. 156, 259–267 (2017).
10. Maleki, A. & Firouzi-Haji, R. L-Proline functionalized magnetic nanoparticles: A novel magnetically reusable nanocatalyst for the green synthesis of 1,2,3–triazoles. Green Chem. Lett. Rev. 13, 395–406 (2019).
11. Maleki, A. & Firouzi-Haji, R. L-Proline functionalized magnetic nanoparticles: A novel magnetically reusable nanocatalyst for the green synthesis of 1,2,3–triazoles. Green Chem. Lett. Rev. 13, 395–406 (2019).
12. Maleki, A. Green oxidation protocol: selective conversions of alcohols and alkenes to aldehydes, ketones and epoxides by using a new multimwll carbon nanotube-based hybrid nanocatalyst via ultrasound irradiation. Ultras. Sonochem. 40, 460–464 (2017).
13. Maleki, A. & Firoozni-haji, R. Green synthesis of aminoacarbonyl compounds using a nanostructured heterogeneous catalyst under mild reaction conditions. Inorg. Nano-Metal Chem. 49, 132–135 (2019).
14. Maleki, A., Panahzadeh, M. & Eivazzadeh-keihan, R. Agar: a natural and environmentally-friendly support composed of copper oxide nanoparticles for the green synthesis of 1,2,3–triazoles. Green Chem. Lett. Rev. 12, 395–406 (2019).
15. Brin, B., Qiu, K., Shang, C. & Guo, Z. Naturally derived porous carbon with selective metal- and/or nitrogen-doping for efficient CO 2 capture and oxygen reduction. J. Mater. Chem. A 3(9), 5212–5222 (2015).
16. Sevilla, M., Ferrero, G. A. & Fuertes, A. B. One-pot synthesis of biomass-based hierarchical porous carbons with a large porosity development. Chem. Mater. 29, 6900–6907 (2017).
17. Veerakumar, P. et al. Porous carbon-modified electrodes as highly selective and sensitive sensors for detection of dopamine. Analyst. 139, 4994 (2014).
18. Madhu, R., Karuppiiah, C., Chen, S.-M., Veerakumar, P. & Liu, S.-B. Electrochemical detection of 4-nitrophenol based on biomass derived activated carbons. Anal. Methods, 6, 5274 (2014).
19. Veeramani, V. et al. Heteroatom-enriched porous carbon/nickel oxide nanocomposites as enzyme-free highly sensitive sensors for detection of glucose. Sens. Actuators B Chem. 221, 1384–1390 (2015).
20. Veeramani, V. et al. Cajeput tree bark derived activated carbon for the practical electrochemical detection of vanillin. New J. Chem. 39, 9109–9115 (2015).
21. Liu, L., Zhu, Y.-P., Su, M. & Yuan, Z.-Y. Metal-free carbonaceous materials as promising heterogeneous catalysts. Chem. Cat. Chem. 7, 2765–2787 (2015).
22. Subodh, N. K., Chaudhary, K., Kumar, G. & Masram, D. T. Fur-imine-functionalized graphene oxide-immobilized copper oxide nanoparticle catalyst for the synthesis of xanthene derivatives. ACS Omega 3, 16377–16385 (2018).
23. Sun, X. et al. Single cobalt sites in mesoporous N-doped carbon matrix for selective catalytic hydrogenation of nitroarenes. J. Catal. 357, 20–28 (2018).
24. Veerakumar, P., Dhenadhayalan, N., Lin, K.-C. & Liu, S.-B. Highly stable ruthenium nanoparticles on 3D mesoporous carbon: an excellent opportunity for reduction reactions. J. Mater. Chem. A, 3, 23448–23457 (2015).
25. Veerakumar, P. et al. Biomass-derived activated carbon supported Fe 3 O 4 nanoparticles as recyclable catalysts for reduction of nitroarenes. ACS Sustain. Chem. Eng. 4, 6772–6782 (2016).
26. Balahmar, N., Al-Jumialy, A. S. & Mokaya, R. Biomass to porous carbon in one step: directly activated biomass for high performance CO 2 storage. J. Mater. Chem. A, 5, 12330–12339 (2017).
27. Manyà, J. J., González, B., Azzura, M. & Arger, G. Ultra-microporous adsorbents prepared from vine shoots-derived biochar with high CO 2 uptake and CO 2/N 2 selectivity. Chem. Eng. J. 345, 631–639 (2018).
28. Zhang, C. et al. Porous carbons derived from hypercrosslinked porous polymers for gas adsorption and energy storage. Carbon 114, 608–618 (2017).
29. Chang, H., Joo, S. H. & Pak, C. Synthesis and characterization of mesoporous carbon for fuel cell applications. J. Mater. Chem. 17, 3078 (2007).
30. Jain, A. et al. Highly mesoporous carbon from Teak wood sawdust as prospective electrode for the construction of high energy Li-ion capacitors. Electrochim. Acta. 228, 131–138 (2017).
31. Ma, H., Liu, Z., Wang, X., Zhang, C. & Jiang, R. Supercapacitive performance of porous carbon materials derived from tree leaves. J. Renew. Sustain. Energy. 9, 044105 (2017).
32. Tang, W. et al. Natural biomass-derived carbons for electrochemical energy storage. Mater. Res. Bull. 88, 234–241 (2017).
33. Wang, J. et al. Biomass derived carbon for energy storage devices. J. Mater. Chem. A, 5, 2411–2428 (2017).
34. Zhang, G., Chen, Y., Chen, Y. & Guo, H. Activated biomass carbon made from bamboo as electrode material for super capacitors. Mater. Res. Bull. 102, 391–398 (2018).
35. Yao, Y. et al. Synthesis of “sea urchin”-like carbon nanotubes/porous carbon superstructures derived from waste biomass for treatment of various contaminants. Appl. Catal. B Environ. 219, 563–571 (2017).
36. Zhu, L. et al. An environmentally friendly carbon aerogels derived from waste pomelo peels for the removal of organic pollutants/oils. Microporous Mesoporous Mater. 241, 285–292 (2017).
37. Hu, B. et al. Engineering carbon materials from the hydrothermal carbonization process of biomass. Adv. Mater. 22, 813–828 (2010).
38. Ahirrao, D. J., Tambat, S., Pandit, A. B. & Jha, N. Sweet-time-peels-derived activated-carbon-based electrode for highly efficient supercapacitor and flow-through water desalination. Chem. Select. 4, 2610–2625 (2019).
39. Senopahyay-Mary, J., Thomas, T., Loganath, R. & Meenambal, T. Optimisation of Copper Removal from E-Waste Using Bioleaching Technique by Activated Mosambi Peels in Waste Valorisation and Recycling, 363–371 ( Springer Singapore, 2019).
40. Yadav, S. & Sharma, C. S. Novel and green processes for citrus peel extract: a natural solvent to source of carbon. Polym. Bull. 75, 3133–3142 (2018).
41. Bhatnagar, A., Sillanpää, M. & Witek-Krowiak, A. Agricultural waste peels as versatile biomass for water purification – A review. Chem. Eng. J. 270, 244–271 (2015).
42. Mondal, N. K., Basu, S., Sen, K. & Debnath, P. Potentiality of mosambi (Citrus limetta) peel dust toward removal of Cr(VI) from aqueous solution: an optimization study. Appl. Water Sci. 9, 116 (2019).
43. Schaff, H. Mithteilungen aus dem Universitats-laboratorium in Pisa (A report from the University Laboratory in Pisa). Justus Liebig Ann. Chem. 131, 118–119 (1864).
44. Mishra N., Gound S.S., Mondal R., Yadav R., Pandey R., Synthesis, characterization and antimicrobial activities of bemothiazole-imino-benzoic acid ligand and their Co(II), Ni, Cu (II), Zn (II), and Cd (II) complexes. Results Chem. 100006 (2019).
45. Ali, S. M. M. et al. In vivo anticancer activity of vanillin semicarbazone. Asian Pac. J. Trop. Biomed. 2, 438–442 (2012).
46. Omomentya, F. K., Nyawade, E. A., Andala, D. M. & Kinyua, J. Synthesis, Characterization and Antibacterial Activity of Schiff Base, 4-Chloro-2-(E)-[(4-Fluorophenyl) imino ] methyl phenol Metal (II) Complexes. J. Chem. 8, 2020 (2020).
47. Kumar, S., Dhar, D. N. & Saxena, P. N. Applications of metal complexes of Schiff bases-A review. J. Sci. Ind. Res. 72, 1599–1609 (2008).
48. Gupta, K. C. & Sutar, A. K. Catalytic activities of Schiff base transition metal complexes. Coord. Chem. Rev. 252, 1420–1450 (2008).
49. Patil, S., Jadhav, S. D. & Shinde, S. K. CES as an efficient natural catalyst for synthesis of Schiff bases under solvent-free conditions: an innovati ve green approach. Org. Chem. Int. 2012, 1–5 (2012).
50. Varma, R. S., Daihya, R. & Kumar, S. Clay catalyzed synthesis of imines and enamines under solvent-free conditions using microwave radiation. Tetrahedron Lett. 38, 2039–2042 (1997).
51. Vibhute A.Y., Mokle S.S., Malwar Y.S., Vibhute Y.R., & Gurav V.M., An efficient and operationally simple synthesis of some new Schiff base using grinding technique. Bulletin of the Catalysis Society of India. 8, 164–168 (2009).
52. Chakraborti, A. K., Bhagat, S. & Rudrawar, S. Magnesium perchlorate as an efficient catalyst for the synthesis of imines and phenylydrazones. Tetrahedron Lett. 45, 7641–7644 (2004).
53. Naeimi, H., Salimi, F. & Rabiei, K. Mild and convenient one pot synthesis of Schiff bases in the presence of P2O5/Al2O3 as new catalyst under solvent-free conditions. J. Mol. Catal. A Chem. 260, 100–104 (2006).
54. Ravishankar, L., Patwe, S. A., Gosarani, N. & Roy, A. Cerium(III)-catalyzed synthesis of Schiff bases: a green approach. Synth. Commun. 40, 3177–3180 (2010).
55. Naeimi, H. & Rabeie, K. Montmorillonite as a heterogeneous catalyst in the efficient, mild and one pot synthesis of Schiff bases under solvent-free conditions. J. Chin. Chem. Soc. 59, 208–212 (2012).
56. Muzzammil, M., Trivedi, P. & Khetani, D. R. Synthesis and Characterization of Schiff base m-nitro aniline and their complexes. Res. J. Chem. Sci. Res. 5, 2231–2606 (2015).
57. Shukla, M., Kulshrahashta, H. & Seth, D. S. Comparative study of the Schiff bases by conventional and green method and antimicrobial activity. Int. J. Mater. Sci. 12, 71–76 (2017).
58. Fonkui, T. Y., Ikhide, M. L., Njohbeh, P. B. & Ndintoh, D. T. Benzimidazole Schiff base derivatives: synthesis, characterization and antimicrobial activity. BMC Chem. 13, 1–11 (2019).
59. Look G. C., Murphy M., Campbell D. A., & Gallop A. Trimethylorthoformate: a mild and effective dehydrating reagent for solution and solid phase imine formation. Tetrahedron Letters, 17, 2937–2940 (1995).
60. Boullot, F. A. simple, convenient and mild of imines on alumina surface without solvent. Synthesis 6–7, 679–681 (1985).
61. Wadher, S. J., Puranik, M. P., Karande, N. A. & Yeole, P. G. Synthesis and biological evaluation of Schiff base of dapsone and their derivative as antimicrobial agents. Int. J. PharmTech Res. 4, 22–33 (2009).
62. Silva, P. J. New insights into the mechanism of Schiff base synthesis from aromatic amines in the absence of acid catalyst or polar solvents. Peer J Organs. Chem. 2 (2020).
63. Cordes E. H. & Jencks W. P. On the Mechanism of Schiff Base Formation and Hydrolysis. J. Am. Chem. Soc. 84, 832–837 (1962).

Acknowledgements
We are highly thankful to Amity University, Jaipur, and Rajasthan for providing us laboratory facilities. The authors thank the Department of Science and Technology, Government of India, New Delhi for providing FIST grant (SR/FST/LS-II/2017/56) to Amity Institute of Biotechnology, Amity University Jaipur (Rajasthan).

Author contributions
Renu Verma wrote manuscript text, N.P. Lamba and K. Modi prepared figure and edited the manuscript, M.S. Chauhan and J.Prasad designed, guided and monitored the whole research experiments. Anshu Dandia has given expert comments and technical suggestions to improve the data. Anamika Srivastava has done characterizations or reported material.

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to M.S.C. or J.P.
Reprints and permissions information is available at www.nature.com/reprints.
Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
