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# Natural Fruit Waste used as Nano-green Catalysts in Schiff Base Reaction of Different Derivatives of Aromatic Amines and Benzaldehydes

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## Abstract

The existence of multifunctional groups in kinnow peel waste has led to a multitude of reported applications, despite its easy and inexpensive availability. As a result, we investigated its use in the current work to create N-benzylideneaniline and its derivatives via the Schiff base reaction. We have also developed salicylaldehyde based ligand and form the metal (Cu and Co) complexes of it. Kinnow peel powder's functional groups, shape, surface, elements, and thermal stability are assessed using transmission emission spectroscopy (TEM) and scanning electron microscopy (SEM).

## Keywords

Green catalyst, Schiff's base, Fruit waste utilization, Chemical free catalyst

## Introduction

Reducing chemical waste, reaction times, economically viable, and hazardous chemicals in organic transformations has emerged as a new issue for researchers in the modern era. The primary function of green chemistry in synthetic chemistry is to reduce environmental disturbance by optimizing reaction product yield and minimizing byproduct formation without the need for hazardous chemicals or reaction conditions. The green catalyst is the only way to address every one of these problems. When an azomethine or imine group is added to the carbonyl group of a ketone or aldehyde, chemical molecules known as Schiff bases. Hugo Schiff initially described the Schiff base compounds in 1864 [1]. The nitrogen in Schiff bases is linked to either an alkyl or an aryl group, forming a carbon-nitrogen double bond. $R^1R^2C = NR^3$, where $R^3$ is an alkyl or phenyl group, is the general molecular formula for Schiff bases. Many substances have been used to create Schiff bases, including isatin, aminothiazoles, pyrazolone, 2-hydroxy-1-naphthalaniline, amino sugars, aromatic aldehydes, triazole ring, and thiosemicarbazides [2-4]. These substances function like Flexi-dentate ligands and have an azomethine group (-HC=N-). Schiff bases are widely used in a variety of biological activities, including industrial uses and antibacterial [5], anticancer [6], antioxidant [7], anti-inflammatory [8], and antifungal [9] properties. Because Schiff base ligands may form complexes with metal ions, they are frequently employed in the development of inorganic and coordination chemistry. At elevated temperatures, some of the Schiff base exhibits good catalytic performance [10]. Different kinds of chemical catalysts are used to catalyze the synthesis of Schiff base. But these triggers can be bad for both the environment and people. Some eco-friendly catalysts were created and reported to address these problems. Different kinds of

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Biomass is an excellent catalytic support material because it has a lot of oxygen functional groups and other components at its surface [11]. Nevertheless, several biomass-based catalysts derived from fruit peels have been described and discovered to be ineffective for catalytic purposes [12, 13]. One such catalyst was created from the residual pulp of *Citrus limetta* (Mausambi), a waste product [14, 15]. Consequently, the development of innovative biomass catalysts that are more dependable and stable for a wide range of applications is imperative. Recently, Dorsey et al. [16] reported the application of different parts including peel of pomegranate for the non-enzymatic glycation of proteins and investigate the investigates the effect of a phenolic whole pomegranate fruit extract and various parts (aril, peel, and membrane) of pomegranate fruit on the in vitro fructose-mediated glycation of albumin [16].

Furthermore, Verma et al. [17] also reported statistical study included biomass for Schiff base synthesis. We herein describe a an environmentally benign, efficient, and straightforward approach that furnished aromatic Schiff's bases high yields from aromatic aldehydes and aromatic amines in presence of kinnow peel powder as a biocatalyst. Herein, we reported the nano-sized peel particles for the Schiff base reaction in between derivatives of aromatic amines and benzaldehydes. Nanotechnology based investigations observed with important applications in various areas. Recently, Prabhu et al. [18], reviewed the applications of bio-nanocoating for extension of self-life of fruits.

## Materials and Methodology

Waste peels of kinnow mandarin were selected and used as a biocatalyst in this study. Kinnow peels were collected from local fruit stalls in Jaipur, Rajasthan. Genesis 90 thermo scientific ultraviolet-visible spectrophotometer Bruker Fourier transform infrared spectroscopy (FTIR), SEM, thermogravimetric analysis (TGA), energy dispersion X-ray spectroscopy (EDS), X-ray diffraction (XRD), TEM, thin layer chromatography (TLC) was used to characterize the kinnow peel powder. All chemicals and solvents were used without further purification: dimethyl sulfoxide, dichloro methane, acetonitrile, petroleum ether, diethyl ether, aniline, benzaldehyde, 95% ethanol, and distilled water.

### Preparation of catalyst

Kinnow peel waste was washed with deionized water to remove dirt particles and cleaned well. The peels were dried in an oven for 24 h at 70 ˚C to remove moisture content. The dried peel waste was converted into powder form and was stored for further experiment.

### Preparation of Schiff base and their derivatives

A mixture of benzaldehyde (1 mmol), aniline (1 mmol) and the kinnow peel powder (10 mg) as a catalyst was stirred for 3 min on the magnetic stirrer at room temperature to form the desired product. The performance of the reaction was monitored using TLC with mobile phase (9:1 ratio of hexane and ethyl acetate, respectively). After the completion of the reaction, the desired product was filtered and recrystallized using absolute ethanol. Similarly, Schiff base reaction is performed between derivatives of aniline and benzaldehyde, respectively (Figure 1).

### Synthesis of Schiff's base of salicylaldehyde

An ethanolic solution of salicylaldehyde 2 (2.44 g, 2.08 ml, 0.02 mol) was added to a mixture of catalyst and o-phenylene diamine 1 (1.08 g, 0.01 mol) in a minimum amount of absolute ethanol. The mixture was heated under reflux for 1 h and then kept overnight at room temperature. The orange color solid Schiff's base 3 formed was filtered off, washed with ethanol, and vacuum dried and 70% yield of relative Schiff base is obtained (Figure 2).

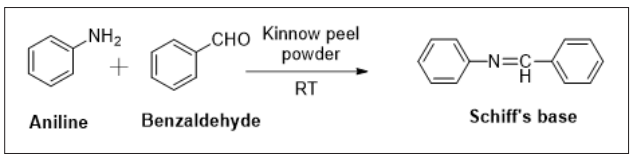



**Figure 1:** Schiff base reaction between benzaldehyde and aniline.

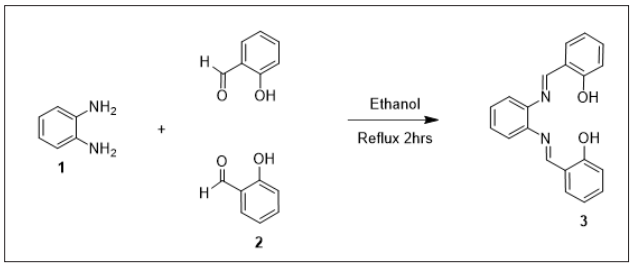



**Figure 2:** Synthesis of ligand by diamine and salicylaldehyde using kinnow peel as catalyst.

### Metal complexation of prepared Schiff base

A methanolic solution of Schiff's base 1 (0.316 g, 1 mmol) was added to methanolic solution of metal (Cu and Co) nitrate (1 mmol) and kept for stirring at room temperature for 30 min. The mixture was then kept overnight to form the desired metal complex (Table 1 and figure 3).

## Results and Discussion

The objective of this present work was to synthesize and obtain high yield of the Schiff base product using a green catalyst (organic material). This was achieved by adopting the green method for Schiff base reaction between benzaldehyde and aniline with kinnow peel powder. The resulting Schiff's base, N-benzylideneaniline was formed in 83% yield in 3 min (Figure 1).

### Schiff base reaction in between derivatives of benzaldehyde and aromatic amine

Derivatives of N-benzylideneaniline were also synthesized using an optimized experimental procedure. The different derivatives of benzaldehyde like 4-methoxy, 4-chloro,

**Table 1:** Synthesis of metal complex of prepared ligand.

| Metal complex | % Yield |
|---|---|
| Cu | 70 (brown color) |
| Co | 65 (brown color) |

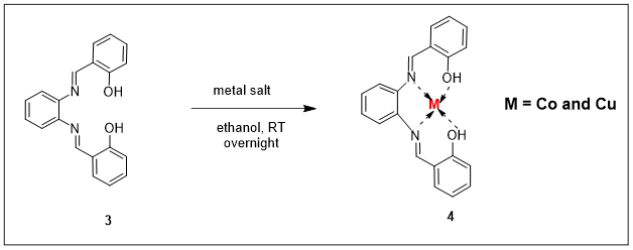



**Figure 3:** Synthesis of metal complex of prepared ligand.

4-methyl, 4-amino and 4-nitro with different derivatives of aromatic amine such as 4-nitro, and 4-methoxy aniline were used for Schiff base reaction by following optimized reaction conditions. Furthermore, it has also been observed that derivatives of aniline and benzaldehyde also affect the yield of relative Schiff base products (Figure 4). As shown in table 2, 4-nitro aniline provided low yield of relative N-benzylideneaniline (55% to 66%) than 4-methoxy aniline i.e., higher yield of N-benzylideneaniline obtained which is vary from 81% to 86%.

## Structural characterization of kinnow peel

Kinnow peel powder is characterized by SEM and TEM to observe the surface morphology and structure of powder particles. As shown in figure 5a kinnow peel powder's morphology is ascertained using a TEM. The particles in the samples are rod-shaped, measuring more than 50 nm in length, and spherical, which is equivalent to nanoparticle size i.e., ~100 nm and diameter of particles is more than 100 nm, according to TEM images. They are also mostly agglomerated at 200 nm. The TEM images show the larger and more varied-sized kinnow peel powder particle sizes. Figure 5b shows the SEM has been studied for morphology of kinnow peel powder particles. The particle core's spectra acquired in SEM. The irregular particles with varied morphology are seen in the SEM spectra. The particle's size, as determined by image J software, is 0.95 µm.

## Spectral analysis of ligand and its metal complexes

We obtained ligand of salicylaldehyde with orange color in solid form. This ligand synthesized by the reaction of salicylaldehyde and 1,2 diamine which is catalyzed by the kinnow peel powder. The prepared ligand characterized by the nuclear magnetic resonance (NMR) spectroscopy which is obtained as: H1-NMR (CDCl3): δ (ppm) = 13.057 (s, 2H, OH), 8.630 (s, 2H, N=CH), 7.387-6.907 (m, 12H, CHarom), C13-NMR (CDCl3): δ (ppm) = 117.54, 118.97, 119.22, 119.71, 127.70, 132.34, 133.36, 142.54, 161.34, 163.71 (Figure 6 and figure 7).

We have also compared the mentioned catalyst with previously reported catalysts which are explained in table 3.

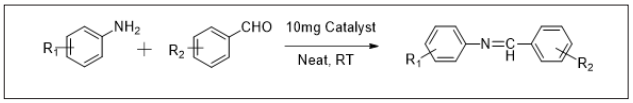



**Figure 4:** Schiff base reaction between substituted aromatic aldehyde and amines.

**Table 2:** Schiff base reaction in between derivatives of benzaldehyde and aromatic amine.

| Entry | $R^1$ | $R^2$ | % Yield |
|---|---|---|---|
| 1 | H | OH | 74 |
| 2 | H | OMe | 68 |
| 3 | H | $NO_2$ | 75 |
| 4 | H | Cl | 65 |
| 5 | H | $NH_2$ | 80 |
| 6 | OMe | OH | 82 |
| 7 | H | Ome | 81 |
| 8 | H | $NO_2$ | 86 |
| 9 | H | Cl | 80 |
| 10 | H | $NH_2$ | 85 |
| 11 | $NO_2$ | OH | 62 |
| 12 | H | Ome | 66 |
| 13 | H | $NO_2$ | 55 |
| 14 | H | Cl | 60 |
| 15 | H | $NH_2$ | 58 |

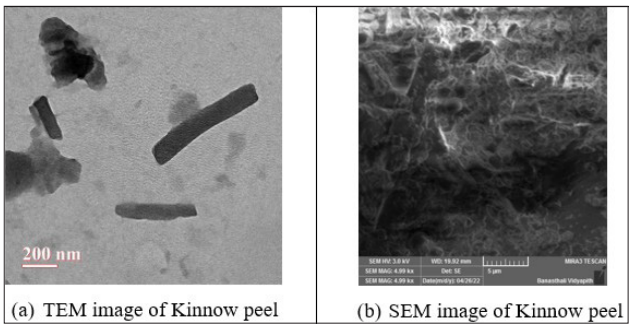



**Figure 5: (a)** TEM and **(b)** SEM analysis of kinnow peel powder.

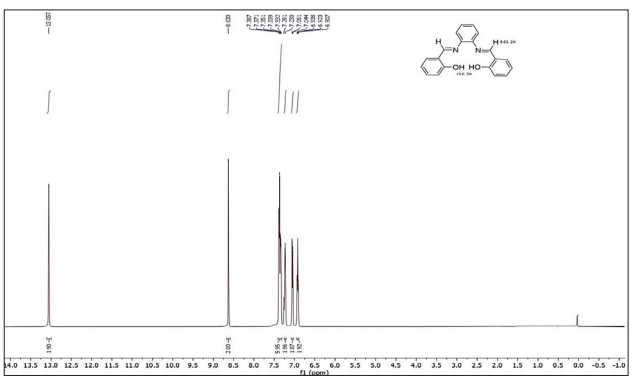


**Figure 6:** H1 NMR of ligand (3) of salicylaldehyde.

**Table 3:** Efficiency of the Schiff base reaction using various substrates and catalysts.

| Entry | Catalyst | Solvent | R (R-$NH_2$) | R' (R'-CHO) | Reaction condition | Time | Yield % |
|---|---|---|---|---|---|---|---|
| 1 | Calcined eggshell (CES) [19] | Solvent free | 4-$OCH_3$ | 4-OH | RT grinding | 10 - 15 min | 98 |
| 2 | Montmorillonite K-10 clay [20] | - | H | H | MW | 3 min | 98 |
| 3 | Acetic acid [21] | - | H | H | Grinding | 2 h | 89 |
| 4 | Glacial acetic acid [22] | Ethyl alcohol | 4-F-2-$CH_3$ | H | Reflux | 2 h | - |
| 5 | Hot ethanoic solution [23] | Ethanol | Substituted | (1,3-dihydrobenzoimidazole-2-ylidene) amide | Reflux | 4 h | 78 |
| 6 | Acid catalysis [24] | Trimethyl orthoformate | H | H | Stirring | 8 h | - |
| 7 | Alumina [25] | - | H | H | Stirring 20 °C | 2 h | 99 |
| 8 | Conc. $H_2SO_4$ [26] | Ethanol | - | - | Reflux | 1 h | 70 |
| 9 | Kinnow peel powder (present work) | Solvent free | H | H | Stirring | 3 - 10 min | 55 - 86 |

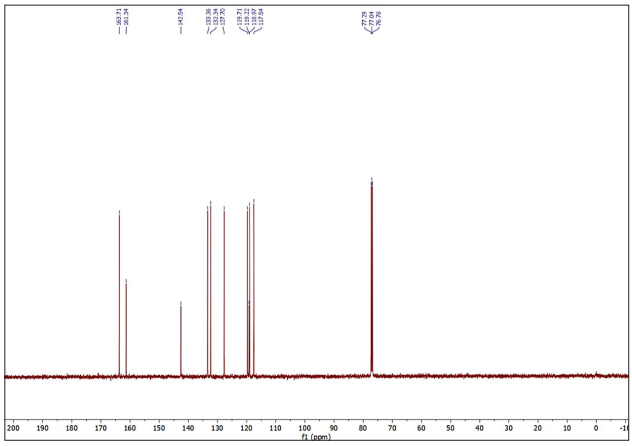


**Figure 7:** C13 NMR of ligand (3) of salicylaldehyde.

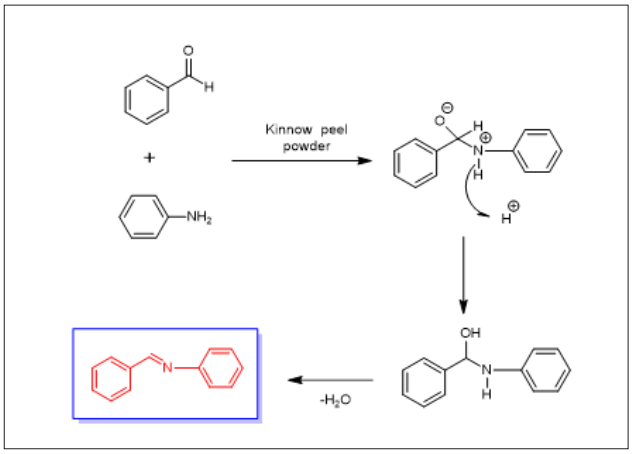



**Figure 8:** Mechanism of Schiff base formation.

Mechanisms of Schiff base formation from benzaldehyde and aniline via catalyst involves two steps (Figure 8). In first step one there is formation of carbinolamine intermediate while the second step involves dehydration of carbinolamine to give the final product imine. The catalyst (containing OH group) helps to proceed the protonation of the carbonyl group.

## Conclusion

N-benzylideneaniline and their derivatives were synthesized by using differently substituted benzaldehyde and aniline in presence of kinnow peel as an efficient and environmentally benign catalyst. This reaction resulted in 85% yield in neat condition. Comparisons of the yield of the six derivatives have also been done.

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## Conflict of Interest

None.

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