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## Introduction

#### In the past few decades, various useful methodologies have been successfully developed for the generation of allyl metals and the exploitation of the metal-carbon bond reactivity for the synthesis of various important molecules.<sup>1</sup> In particular, the addition of allyl metals to carbonyl compounds leads to synthetically important homoallylic alcohols, which can participate in various synthetically useful transformations: cycloaddition, dihydroxylation, epoxidation, hydroboration, hydroformylation, hydrogenation, hydration, olefin metathesis, ozonolysis, etc.<sup>2</sup> The corresponding allyl metals may be generated either via the oxidative addition of an allyl electrophile to a main group or transition metal through a Grignard-like protocol or via the oxidative addition of an allyl electrophile to a transition metal followed by coupling with a main group metal salt in tandem.<sup>3</sup> Although allyl metals are considered to be important reagents in many aspects, their metal counterparts are treated as waste materials after the completion of the reaction. Amongst the various metal mediated Grignard type allylation reactions, we were particularly interested in Zn(0) promoted allylation<sup>4</sup> because we wanted to utilize the corresponding waste zinc as a

# Waste management in zinc promoted allylation of aldehyde<sup>†</sup>

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By using an efficient, sustainable and green procedure, the waste zinc material in Zn(0) promoted Grignard–Barbier type allylation of aldehydes has been successfully utilized as a reusable material for the adsorption of various dyes and also converted into the corresponding hexagonal wurtzite phase of ZnO. The need for aqueous  $NH_4Cl$  was justified by experimental and theoretical evidence, which suggests that the probable coordination of  $H_2O$  or  $NH_3$  to the Zn center in both the intermediate and transition states is responsible for a lower activation energy and consecutively higher yield of products in both the cases. The conversion of the corresponding Zn(0) to its hydroxide or ZnO was studied by XRD analysis, which showed the facile conversion of Zn(OH)<sub>2</sub> to its corresponding ZnO after calcination of the sample at 300 °C. The reported method is a cost-effective chemical route for producing the ZnO nanomaterial at the gram level. The as-obtained zinc waste from allylation reaction shows an excellent ability as a reusable material for the adsorption of Congo red, methyl red and methylene blue and is expected to be useful in many other applications. The easy synthesis, effortless separation, efficient recycling and good adsorption capability of the waste zinc nanomaterial toward various dye molecules make it a competent candidate for wastewater treatment.

useful material. Amongst the various metal oxides, zinc oxide provides one of the greatest assortments of varying particle structures and is widely used in numerous materials and products including plastics, ceramics, glass, ointments, *etc.*<sup>5</sup> ZnO is present in the earth's crust as the mineral zincite; however most of the commercial ZnO is produced synthetically.<sup>6</sup> In the past few decades, various synthetic methods have been established based on solvothermal, precipitation, chemical vapour deposition, hydrothermal, sol–gel, and mechanochemical techniques.<sup>7</sup> In this work, the utilization of the corresponding zinc waste in zinc(0) promoted allylation of aldehydes was shown to produce a ZnO nanomaterial. The role of water, additives, and aldehydes in zinc(0) promoted allylation of aldehydes was investigated from experimental and theoretical evidence (Fig. 1).



Fig. 1 Conversion of waste zinc in zinc promoted Barbier-type allylation reaction to a useful zinc oxide nanomaterial.



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The conversion of the waste zinc material to the corresponding ZnO nanomaterial was monitored by XRD analysis, which showed the facile conversion of the  $Zn(OH)_2$  waste to the corresponding ZnO nanomaterial after calcination of the sample at 300 °C. The reported method is a cost-effective chemical route for producing the ZnO nanomaterial at the gram level with a band gap of 3.15 eV. The as-obtained zinc waste from the Zn(0) promoted allylation of aldehydes is found to be active for the adsorption of dyes like Congo red, methyl red and methylene blue with good adsorption capacity.

## Results and discussion

#### Role of additives and water

In most of the zinc promoted Barbier type allylation reactions, the corresponding zinc salts were thrown away as waste products after the isolation of the corresponding homoallylic alcohols from aldehydes (Scheme 1).

As an important contribution, Luche et al. showed the zinc mediated effective allylation of aldehydes and ketones in aqueous media using THF as a cosolvent under magnetic stirring or sonication conditions.8 They observed enhanced efficiency in zinc mediated allylation of aldehydes in the case of replacing water by an aqueous saturated ammonium chloride solution.9 On the other hand, the replacement of ammonium chloride with sodium chloride (NaCl) does not show any product formation. So, the higher efficiency in the case of aqueous saturated ammonium chloride solution is due to both the increased acidity of the media and the formation of complexes between the metal ion and ammonia. Recently, by using the Hammett plot, kinetic isotope effects, and theoretical studies, Madsen et al. showed that Zn(0) promoted Barbier type allylation is feasible through a sixmembered transition state between allyl zinc and aldehydes.<sup>10</sup> For the model studies, zinc promoted room temperature allylation of 4-chlorobenzaldehyde was chosen as a model reaction in the THF/water solvent system. To investigate the effect of pH on the model reaction, the model reaction was performed in the presence of NH<sub>4</sub>Cl, HCl, and NH<sub>4</sub>OH (Table 1). The allylation reaction proceeds smoothly in NH<sub>4</sub>Cl, while a low yield of the corresponding homoallylic alcohol (1a) was achieved under both acidic and basic conditions. The oxidative addition of allyl bromide to Zn(0) leads to an allyl zinc reagent, which further reacts with the aldehyde to give the corresponding homoallylic alcohol (1a) with the release of the corresponding Zn(OH)Br (Scheme 2). Under acidic conditions, there is a chance of probable

 $\begin{array}{c} \swarrow X + \underset{R}{\overset{O}{\longrightarrow}} \underset{R'}{\overset{O}{\longrightarrow}} \\ & \xrightarrow{\text{additive}} \\ & \xrightarrow{\text{organic solvent/H_2O}} \\ & \swarrow X + \underset{R}{\overset{O}{\longrightarrow}} \underset{R'}{\overset{O}{\longrightarrow}} \\ & \xrightarrow{\text{additive}} \\ & \xrightarrow{\text{additive}} \\ & \xrightarrow{\text{additive}} \\ & \xrightarrow{\text{r}} \underset{R'}{\overset{O}{\longrightarrow}} \\ & \xrightarrow{R'} \underset{R'}{\overset{O}{\longrightarrow} } \\ & \xrightarrow{R'} \underset{R'}{\overset{O}{\longrightarrow} } \\ & \xrightarrow{R'} \underset{R'}{\overset{O}{\longrightarrow} } \\ & \xrightarrow{R'} \underset{R'}{\overset{O}{\longrightarrow} \\ & \xrightarrow{R'} \underset{R'}{\overset{O}{\overset{O}{\longrightarrow}} \\ & \xrightarrow{R'} \underset{R'}{\overset{R'}{\overset{R'}{\longrightarrow}} \\ & \xrightarrow{R'} \underset{R'}{\overset{R'}{\overset{R$ 

Scheme 1 Conversion of waste Zn to useful ZnO and its utilization.

 Table 1
 Effect of different additives on Zn(0) promoted allylation reaction



Reaction condition: 1 mmol aldehyde, 0.4 ml of allyl bromide,  $Zn^0$  (70 mg), and additive (3 mmol) were added to 2 ml of THF and 3 ml of water and stirred at room temperature.



Scheme 2 Probable mechanism of Zn(0) promoted allylation reaction of aldehydes.

oxidation of Zn(0) to  $Zn(\pi)$ , which will inhibit the first step of the reaction by decreasing the available Zn(0).

On the other hand, the presence of an acid will promote step-3 of the allylation reaction. So, a slightly acidic pH in  $NH_4Cl$  medium (4.6 to 6) promotes the overall allylation process. The role of water and  $NH_4Cl$  was further studied from theoretical analysis.

We have also optimized the probable intermediate and sixmembered transition states between allyl zinc bromide and aldehydes at the B3LYP level of theory using the effective core potential (ECP) along with valence basis sets (LANL2DZ) for zinc and the 6-31G\* basic set for other atoms.<sup>11</sup> The free energy of activation of zinc promoted allylation of benzaldehyde is found to be 6.2 kcal mol<sup>-1</sup>. The probable coordination of water or ammonia with the intermediate and transition states will facilitate the reaction. In fact, the calculated free energy of activation is found to be lower in both the cases, which justifies the requirement of aqueous reaction medium and saturated ammonium chloride in zinc promoted allylation reactions. The activation energy in both the gas phase and THF solvent shows similar results.

#### Effect of aldehydes

Further to check the substituent effect on the allylation reaction, the Zn(0) promoted allylation reaction was performed with different aldehydes. The Zn(0) promoted allylation reaction in the case of electron withdrawing aldehydes like 4-chlorobenzaldehyde and 4-(trifluoromethyl)benzaldehyde leads to the corresponding homoallylic alcohols in 72 and 86% yield,



Fig. 2 Gibbs free energy (in kcal  $mol^{-1}$ ) profile for Zn(0) promoted allylation of benzaldehyde under different reaction conditions in gas phase and in tetrahydrofuran (in parentheses).

respectively, after 6 h. On the other hand, the yield of the corresponding homoallylic alcohols in the case of electron rich aldehydes like 4-methylbenzaldehyde and 4-methoxybenzaldehyde is found to be 58 and 52% after 12 and 14 h, respectively (Fig. 2).

In terms of yield, electron withdrawing aldehydes are better substrates compared to electron rich aldehydes because the higher electrophilicity at the carbonyl centre in the former case will facilitate the formation of a six-membered transition state (Table 2). For better understanding, we have optimized both the intermediate and transition states of three different *para* substituted aldehydes. In fact, the calculated free energy of activation ( $\Delta G^{\#}$ ) in the case of electron withdrawing aldehydes like 4-chlorobenzaldehyde is found to be lower compared to benzaldehyde in both gas phase and THF (Fig. 3). On the other hand, the highest  $\Delta G^{\#}$  was achieved in the case of 4-methoxy benzaldehyde, which also explains the lower yield of the corresponding homoallylic alcohol in this case (Table 2).



Reaction condition: 1 mmol aldehyde, 0.4 ml of allyl bromide,  $Zn^0$  (70 mg), and 300 mg of NH<sub>4</sub>Cl were added to 2 ml of THF and 3 ml of water and stirred at room temperature.



**Fig. 3** Gibbs free energy (in kcal  $mol^{-1}$ ) profile for Zn(0) promoted allylation of three different *para* substituted benzaldehydes in gas phase and in tetrahydrofuran (in parentheses).

#### Synthesis and characterization of waste zinc

Now, we are interested in checking the fate of the Zn metal after the reaction. For this, we isolated the corresponding white zinc material after the completion of the Zn(0) promoted allylation reaction and washed it with water and methanol several times. The as-prepared white material was calcined at 100 °C for different time intervals and the samples were collected for XRD analysis. Most of the peaks in XRD analysis of the freshly prepared white material match with Zn(OH)<sub>2</sub> (JCPDS 38-385), which indicates the formation of Zn(OH)<sub>2</sub> after hydrolysis of the corresponding allyl zinc reagent (Fig. 4).

When the white material was calcined at 100  $^\circ C$  for 6 h, the transformation of  $Zn(OH)_2$  to ZnO (JCPDS 36-1451) was



Fig. 4 The XRD pattern of the zinc material after the Zn(0) promoted allylation reaction, (a) as-prepared white material; (b) white material after calcination at 100 °C for 6 h; white material after calcination at 100 °C for 24 h.

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Fig. 5 The XRD pattern of the as-obtained white material (ZnO-1) after calcination at 300  $^\circ\text{C}$  for 6 h.

observed as the XRD peaks matched well with the standard XRD pattern of both the samples. Interestingly, higher conversion of Zn(OH)<sub>2</sub> to ZnO was achieved by heating the sample for a longer time. Although we successfully utilized the waste zinc material in the allylation reaction as a useful ZnO material, we failed to obtain a good crystalline ZnO material even after calcination of the white material at 100 °C for a prolonged time (Fig. 4). So, the white waste material was further calcined at 300 °C to obtain a good crystalline ZnO material. Gratifyingly, the XRD analysis of the white material after calcination at 300 °C for 6 h reveals the hexagonal wurtzite structure of ZnO as all the diffraction peaks match with the standard data for the hexagonal wurtzite phase of ZnO (JCPDS 36-1451). Finally, we were successfully able to convert the corresponding waste material of Zn(0) promoted allylation reaction to a useful hexagonal wurtzite phase of ZnO. The XRD data show the presence of both Zn(OH)<sub>2</sub> and ZnO in the material as most of the peaks matched well with the standard XRD pattern of both the samples (Fig. 5).

The as-obtained waste Zn material after heating at 100 °C for 24 h (hereafter ZnO-1) and after calcination at 300 °C (hereafter ZnO-2) was used for further characterization and application. The HR-TEM images of the synthesized ZnO-1 at different magnifications revealed fibrous morphology with several nanorods wedged into a bundle. We also analyzed the lattice fringes of the nanocrystal (Fig. 6); the lattice spacing between two planes was observed to be 0.28 nm, corresponding to the distance of two (100) planes of ZnO. The optical properties of both the nanomaterials were investigated by DRS experiments. The band gap calculation of the synthesized materials was done using the plot of  $(\alpha E_p)^2$  *versus*  $E_p$  based on the direct transition and the extrapolated value of  $E_p$  at  $\alpha = 0$ .

The observed band gap values of ZnO-1 and ZnO-2 nanomaterials are found to be 3.22 and 3.15 eV, which are slightly smaller compared to bulk ZnO (3.3 eV), maybe due to the oxygen vacancies or crystal lattice defects in the synthesized materials.<sup>12</sup> The nanomaterials have large surface to volume ratios, and their surface may consist of several uncompensated



Fig. 6 TEM/HR-TEM image of ZnO-1

hanging bonds and charged ions/groups. Generation of enhanced surface charge is possible after dispersion in an aqueous medium due to the possible surface ionization and adsorption of ions. To obtain insight into the surface charge of the synthesized ZnO nanomaterials, the zeta potentials of the powdered samples suspended in nanopure water were measured. The zeta potential of the ZnO-1 material is found to be +10.6 mV, which suggests a slightly positive charge at the ZnO surface. Based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) model, agglomeration of uncapped nanocrystals depends upon the repulsive interaction arising from electrostatic force and the van der Waals force of attraction.13 As the surface charge of the nanoparticles (NPs) mainly influences the electrostatic repulsive force, NPs with a larger zeta potential will generally reduce the hydrodynamic size. In this case, a slightly positive charge on the ZnO surface will contribute less to the electrostatic repulsive force, so a larger hydrodynamic size of the synthesized ZnO-1 material is expected. In fact, the measured average hydrodynamic size of the ZnO samples suspended in nanopure water is found to be 600 nm. On the other hand, the zeta potential of the ZnO-2 material is found to be +1.2 mV, which suggests a



Fig. 7 Nitrogen adsorption-desorption isotherm of ZnO-1.



slightly positive charge at the ZnO surface. The nitrogen adsorption–desorption isotherm and the pore size distribution of ZnO-1 and ZnO-2 nanomaterials are shown in Fig. 7 and 8.<sup>14</sup> ZnO-1 is found to be more porous compared to ZnO-2 because high temperature calcinations transform the amorphous ZnO-1 to more crystalline ZnO-2 with a reduced surface area and pore volume. Next, the adsorption activity of both the materials was investigated using various dyes.

#### Application of waste zinc for adsorption of dye molecules

The textile, paper, plastic, tannery, and paint industries consume large quantities of water and produce large volumes of wastewater in different steps of the dyeing and finishing processes.<sup>15</sup> The wastewater is often rich in color, contains various dyes and chemicals, and poses a direct threat to water bodies and the ecosystem by causing non-aesthetic pollution and eutrophication.<sup>16</sup> In addition, dyes are commonly toxic and some are carcinogenic and mutagenic and if discharged into water, they can cause deterioration in water quality and sometimes food chain contamination resulting in adverse effects on



Fig. 9 ZnO-1 promoted adsorption of Congo red (CR) at room temperature.



Fig. 10 ZnO-1 promoted adsorption of methyl red (MR) at room temperature.

biodiversity. Therefore, understanding and developing effective technologies for wastewater treatment is environmentally important. To date, various physical and chemical paths including adsorption on activated carbon, reverse osmosis, coagulation by chemical agents, visible or UV light photocatalysis, chlorination, ozonolysis, and oxidation processes for wastewater treatment have been reported.<sup>17</sup> Towards the search for a cost effective route for the removal of dyes from wastewater, the waste ZnO-1 nanomaterial was successfully utilized for the color dye removal.<sup>18</sup> The as-obtained ZnO-1 nanomaterial was found to be active towards the adsorption of methylene blue (MB), Congo red (CR), and methyl red (MR). The aqueous solution of Congo red shows three peaks at 495, 340, and 237 nm with extinction coefficients ( $\epsilon$ , mol<sup>-1</sup> L cm<sup>-1</sup>) of 20 300, 14 000, and 17000, respectively. Upon addition of waste ZnO-1 in aqueous solution of CR, a gradual decrease in the absorbance of all the three peaks was observed, which indicates the adsorption of CR on the surface of the ZnO-1 nanomaterial.

Although we observed faster adsorption initially, over time the adsorption process became slower, which may be due to the low availability of the active pores and repulsion between adsorbed CR and incoming CR. The deep red color CR solution faded away with time and the colorless ZnO-1 adsorbent turned



**Fig. 11** Digital images of Congo red (CR), methyl red (MR), and methylene blue (MB) with increasing adsorption time and the color of the ZnO-1 nanomaterial after adsorbing different dyes.

 Table 3
 Adsorption activity of both ZnO and Zn(OH)<sub>n</sub> for various dyes

#	Congo	Methyl	Methylene
	red	red	blue
Adsorption capacity (mg $g^{-1}$ ) of ZnO-1	53.7	45.5	29.0
Adsorption capacity (mg $g^{-1}$ ) of ZnO-2	38.7	30.7	21.2



**Fig. 12** Plot of percentage of adsorption *versus* number of cycles for ZnO-1 and ZnO-2 for the adsorption of CR.

deep red, which also indicates the complete adsorption of negatively charged CR molecules on the slightly positive surface of the synthesized ZnO-2 nanomaterial (Fig. 9).<sup>19</sup> The adsorption activity of the synthesized ZnO-1 for MR was found to be slightly sluggish, maybe due to the less electrostatic interaction between neutral MR (Fig. 10) and the slightly positively charged ZnO-1 surface compared to CR and ZnO-1. On the other hand, it took almost 20 days for complete adsorption of aqueous MB solution on the ZnO-1 surface. This negligible adsorption activity of ZnO-1 for MB is due to the electrostatic repulsion between cationic MB and positively charged ZnO-1 (Fig. 11). The adsorption capacities of both the synthesized ZnO-1 and ZnO-2 nanomaterials for various dyes were calculated and are summarized in Table 3. The observed adsorption capacity of ZnO nanomaterials for anionic CR is found to be higher compared to that for neutral MR and cationic MB, which also justifies the more electrostatic attraction between two oppositely charged CR and ZnO surfaces. On the other hand, the adsorption activity of the as-obtained waste ZnO-1 nanomaterial is found to be higher compared to ZnO-2. The higher adsorption activity of ZnO-1 compared to ZnO-2 is attributed to the larger surface area and surface volume and the slightly more positive charge in the former case, which make it feasible for more attraction between ZnO-1 and dye molecules. Both the nanomaterials were



Fig. 13 Linear plot for the adsorption of CR onto ZnO-1: (a) pseudo-first-order kinetic plot and (b) pseudo-second-order kinetic plot for the adsorption of CR onto ZnO-1, (c) Langmuir and (d) Freundlich isotherms.

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Fig. 14 Non-linear plot for the adsorption of CR onto ZnO-1: (a) pseudo-first-order kinetic plot and (b) pseudo-second-order kinetic plot for the adsorption of CR onto ZnO-1, (c) Langmuir and (d) Freundlich isotherms.

found to be inactive for the adsorption of other dyes like rhodamine B, crystal violet, and methyl green. For practical applications of such heterogeneous ZnO nanomaterials for wastewater treatment, the lifetime of the materials and their reusability are very important factors. For this, the adsorption of aqueous CR solution promoted by the as-obtained ZnO-1 nanomaterial was studied. After the completion of the first reaction, the ZnO nanomaterial was carefully separated through centrifugation, washed with acetone and methanol 3–4 times to remove the adsorbed dye from the ZnO surface and dried for reutilization as an adsorbent. A new reaction was then performed using a fresh CR solution under optimized reaction conditions.

In terms of adsorption activity, the ZnO-1 nanomaterial could be reused at least 6 times without any change in activity. However, a slight drop in the activity of the ZnO-1 nanomaterial was observed in cycles 7–9. The XRD analysis of the used ZnO nanomaterial after the 7th cycle was performed. No appreciable change was observed in the XRD spectrum, which suggests the robustness of the material and it can be used potentially for wastewater treatment as an adsorbent.<sup>20</sup> On the other hand, in terms of reusability, ZnO-2 is found to be less suitable for the

Table 4	Linear and non-linear	adsorption kinetics	narameters	of 7nO-1 with	Congo red (	(CR)
	Linear and non linear	ausorption kinetics	parameters		Congo reu (	

		Linear		Non-linear	
Model		Value	Standard error	Value	Standard error
Pseudo first order	$K_1 ({\rm min}^{-1})$	$9.4 imes10^{-4}$	0.03769	1.56	3.33753
	$q_{\rm e}  ({\rm mg g}^{-1})  [{\rm cal}]$	49.76	0.30746	52.16	1.28528
	$R^2$	0.9977	—	0.999	—
Pseudo second order	$K_2 (\min^{-1})$	$6.62\times10^{-4}$	0.58784	0.341	0.68867
	$q_e^{\tilde{i}}$ (mg g <sup>-1</sup> ) [cal]	38.85	0.27761	43.15	0.29636
	$R^2$	0.9797	—	0.9802	—
Experimental $q_e$	53.72 mg $g^{-1}$				

Table 5 Comparison between two isotherm models for Congo red (CR) adsorption onto ZnO-1 using linear and non-linear fits

		Linear		Non-linear	
Model		Value	S.E.	Value	S.E.
Langmuir isotherm	$b~(\mathrm{L~mg^{-1}}) \ q_{\mathrm{m}}~(\mathrm{mg~g^{-1}}) \ R^2$	0.171 74 0.9950	0.20655 0.00344 —	0.2202 28.8 0.9917	0.32466 0.00765 —
Freundlich isotherm	$egin{array}{l} K_{ m F}\left(\left({ m mg}^{1-n}\;{ m L}^n ight){ m g}^{-1} ight)\ N\ R^2 \end{array}$	0.894 7.02 0.9764	0.00833 0.455252 —	2.3125 7.02 0.98044	0.02065 0.89521 —

adsorption of CR. Further to know the reaction mechanism, the kinetics of ZnO-1 nanomaterial promoted dye adsorption was studied using CR (Fig. 12).

#### Kinetics of dye adsorption

Both the pseudo-first-order (1) and pseudo-second-order (2) kinetic models were employed to study the adsorption kinetics of the ZnO promoted CR removal process. In the following equations,  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the amount of the adsorbate adsorbed at equilibrium and at any time t (min), respectively, whereas  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are the pseudo-first-order and pseudo-second-order adsorption rate constants (Fig. 13):

$$\ln(q_e - q_t) = \ln q_t - k_1 t \tag{1}$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e$$
 (2)

The adsorption kinetics of CR with the ZnO nanomaterial was monitored in 5 ml aqueous solution with varying amounts of CR and ZnO at different time intervals by UV-vis spectroscopy. The linear analysis of isotherm data in isotherm models is an alternative mathematical approach to predict the overall adsorption behaviour. However, linear analysis for modelling of isotherm data might cause inconsistency between the predictions and experimental data. So, to obtain a better set of results, both the linear and non-linear isotherm models have been studied for describing the number of adsorption parameters. The collected data were fitted in both the pseudo-first-order and pseudo-second-order kinetic models using both linear and nonlinear methods (Fig. 14).<sup>21</sup> When judged in terms of correlation coefficient  $(R^2)$ , a better correlation has been found in the pseudofirst-order (1) model in both linear and non-linear fittings (Table 4). However, the calculated  $q_e$  from the non-linear pseudofirst-order model is found to be closer to the experimentally observed  $q_{e}$ , which also indicates that the adsorption process of CR follows the pseudo-first-order model (Table 4). Further, to study the interaction between adsorbates and adsorbents and the mechanism involved in the process both the Langmuir (3) and Freundlich (4) adsorption models are employed (Fig. 14).<sup>22</sup>

$$1/q_{\rm e} = 1/q_{\rm m} + 1/C_{\rm e}q_{\rm m}b$$
 (3)

$$\ln q_{\rm e} = \ln K_{\rm f} + (1/n) \ln C_{\rm e} \tag{4}$$

In the above equations,  $q_{\rm m} \,({\rm mg g}^{-1})$  is the maximum adsorption capacity corresponding to a complete monolayer coverage,  $C_{\rm e}$  and  $q_{\rm e}$  are the equilibrium concentration and the amount adsorbed at equilibrium (mg g<sup>-1</sup>), *b* is the equilibrium constant (L mg<sup>-1</sup>) and it

is related to binding strength,  $K_{\rm F}$  is a rough indicator of the adsorption capacity, and *n* is the adsorption intensity. The accuracy of adsorption parameters is compared in both linear and non-linear isotherm models to establish a suitable equilibrium correlation. All the fitting parameters derived from both the Langmuir and Freundlich adsorption isotherms are shown in Table 5. The standard errors and correlation coefficient ( $R^2$ ) of each plot were used to measure the goodness-of-fit (Table 5 and Fig. 14). When judged in terms of correlation coefficient ( $R^2$ ) and standard error of each plot, a better correlation was found in the Langmuir model compared to the Freundlich model in both non-linear and linear analyses, possibly confirming the occurrence of monolayer adsorption of CR molecules onto the internal and external surfaces of ZnO-1.

## Conclusions

In summary, the reaction mechanism and the effect of water, reaction pH, additives, and aldehydes in zinc(0) promoted Barbier type allylation of aldehydes were investigated from suitable experimental and theoretical studies, which suggested that (i) a slightly acidic pH in saturated aqueous NH4Cl and probable coordination of water or ammonia with the intermediate and transition states will facilitate the reaction by lowering the free energy of activation ( $\Delta G^{\#}$ ) and (ii)  $\Delta G^{\#}$  in electron withdrawing aldehydes is found to be lower compared to electron rich aldehydes. The as-obtained waste Zn material from the allylation reaction was successfully utilized as a reusable material for the adsorption of dyes like Congo red, methyl red, and methylene blue. At the same time, the conversion of the as-obtained waste Zn material to the hexagonal wurtzite phase of ZnO at the gram scale was performed using a cost effective, sustainable, and green procedure. The kinetic study on waste Zn promoted dye adsorption shows monolayer adsorption of CR molecules onto the internal and external surfaces of waste Zn. The as-obtained waste Zn nanomaterial is a competent candidate for wastewater treatment because of its easy synthesis, effortless separation, efficient recycling and good adsorption capability for various dye molecules.

### Experimental section

# Typical procedure of Zn(0) promoted allylation reaction of aldehydes and isolation of the ZnO-1 material

In a 25 ml round bottom flask, 4 mmol 4-chlorobenzaldehyde, zinc dust (260 mg), and 0.8 ml of allyl bromide are taken in a

mixture of 5 ml of water and 5 ml of THF. To this, 350 mg of ammonium chloride is added and the mixture is subjected to vigorous stirring overnight at room temperature. The gray color zinc metal turns into a milky white material after stirring overnight. The milky white precipitate is washed with distilled water and THF 4–5 times under centrifugation, and dried in an oven for 24 h at 100  $^{\circ}$ C and collected for further study.

# General procedure of Zn(0) promoted allylation reaction with different aldehydes

In a 25 ml round bottom flask, 1 mmol concentration of an appropriate aldehyde, zinc dust (70 mg), and 0.4 ml of allyl bromide are taken in 2 ml of THF. To this, 3 ml of aqueous ammonium chloride solution is added and stirred vigorously at room temperature for the required time. After completion of the reaction (vide TLC monitoring), the product is isolated with 10 ml of ethyl acetate and the conversion of the desired product is analyzed by the GC-MS study.

#### **Kinetics** experiment

Standard solutions of 100, 50, 30, 20 and 10  $\mu$ M methylene blue (MB) in distilled water are prepared from a 1000  $\mu$ M stock solution. The absorbance of all the standard solutions is recorded from the wavelength scan using a UV Visible spectrophotometer. After that, 5 different known weights of adsorbents are added to 5 ml of 100  $\mu$ M MB solution in five different vials and the time is recorded. From each flask, a 4 ml sample is taken every 10 minutes and analyzed using a UV-spectrophotometer by reading the absorbance values for the determined wavelength until the equilibrium concentration is reached. The time and data are recorded accordingly.

# Computational details

All the calculations were performed using the Gaussian 09 suite of programs.<sup>23</sup> The geometries of all the reactants and transition states (TSs) were optimized at the B3LYP level of theory employing the effective core potential (ECP) along with valence basis sets (LANL2DZ) for the Lewis acidic transition or main group metal and the 6-31G\* basic set for other atoms. The free energy of activation of all the reactions was calculated at the same level of theory with zero-point energies (ZPE) and thermal corrections at 298 K. The free energy of activation in tetrahydrofuran (THF) was determined by frequency calculations in a single point run of the optimized gas phase geometry in solution phase using a polarized continuum model (PCM)<sup>24</sup> employing THF as the solvent.

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