

## Supporting Information for

### Efficient Decomposition of Melamine-formaldehyde Foam into Melamine via Selective Disconnection of Bond

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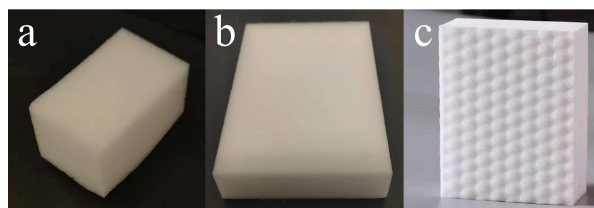
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## 1. Materials

Three different types of melamine formaldehyde resin foam were used (as shown in **Fig. S1**). The first one (sound absorption melamine foam) that is mainly used for sound absorption and noise reduction (**Fig. S1a**) was purchased from Henan province Puyang Greencos New Material Technology Co., Ltd., the second one (the flame-retardant melamine compression foam) that is mainly applied as flame retardant heat insulation (**Fig. S1b**) was purchased from Shanghai Zhenmo New Material Technology Co., Ltd., while the third one (the cleaning type melamine foam) that is mainly used for cleaning stains (**Fig. S1c**) was purchased from Henan province Langcui Science and Technology Co., Ltd.



**Fig. S1** Three types of melamine formaldehyde resin foam: (a) sound absorption melamine foam, (b) the flame-retardant melamine compression foam, (c) the cleaning type melamine foam.

## 2. Experimental

### 2.1 Degradation of MFF and products separation

0.15 g of Melamine-formaldehyde resin foam (MFF) ( $1.5\text{cm} \times 1.5\text{cm} \times 1.5\text{cm}$ ) and 0.15 g of ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) (25 wt%~29 wt%, with a ca. average concentration of 27wt%) were added into a Teflon-lined autoclave with a volume of 10 ml. The Teflon-lined autoclave was then sealed tightly, and heated in a homogeneous reactor at  $170\text{ }^\circ\text{C}$  for 12 h. After the degradation reaction, the autoclave was cooled down to room temperature (R. T.), and the melamine product precipitated from the degradation solution as light yellow transparent crystals. The crystals were removed from the solution, washed with ethyl alcohol for several times until the ethyl alcohol after washing was clear, and then dried at  $80\text{ }^\circ\text{C}$  for 12 h to obtain melamine product.

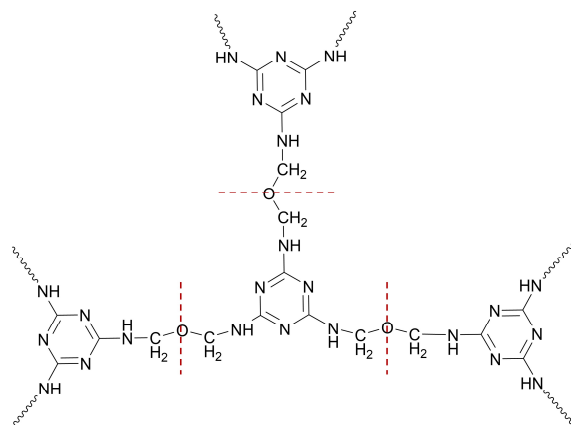
### 2.2 Calculation of MFF degradation rate and melamine yield

The degradation rate was calculated by the following equation 1 (eq. 1). In eq. 1,  $m_0$  is the mass of MFF added before the reaction and  $m_1$  is the mass of MFF remained after the reaction. The melamine yield was calculated by the following equation 2 (eq. 2). In eq. 2, 0.65 is the theoretical mass (unit: g) of melamine contained in 1 g of MFF. The value of 0.65 was calculated as following: in the typical structure unit of MFF (as shown in **Fig. S2**), each melamine rings were connected to the others via three dimethyl ether bonds. The structure can be separated into four melamine units when the three dimethyl ether bonds were disconnected by the red dotted lines in **Fig. S2**. In such case, besides the melamine ring (the six-member ring  $\text{N}_3\text{C}_3$  with the three -NH- groups on it), every melamine unit has three methylene (- $\text{CH}_2$ -) groups and 1.5 oxygen atoms (0.5

oxygen atom was obtained after disconnecting each dimethyl ether bond). So, melamine product has a molecular weight of 126 g/mol, while the total molecular weight of per melamine unit should be 192 g/mol (melamine product: 126 g/mol, the three -CH<sub>2</sub>-groups: 42 g/mol, and 1.5 oxygen atoms: 24 g/mol). The melamine mass ratio in per MFF structure unit should be 126/ (126+42+24) ( $\approx 0.65$ ). After the reaction between NH<sub>3</sub>·H<sub>2</sub>O and MFF, the degradation system was dried to remove NH<sub>3</sub>·H<sub>2</sub>O, and the quality of remaining solid after drying was denoted as m<sub>2</sub>; the remaining solid was then dissolved in excess DMSO solvent, and the melamine product in the remaining solid can completely dissolve in DMSO. The DMSO with dissolved melamine were collected after centrifugation and filtration. Ethanol was added into the DMSO solution, by which melamine can precipitate from the whole solution as solid. The melamine solid was washed with ethanol for several times and then weighed as m<sub>3</sub>.

$$\text{Degradation rate (R}_d, \%) = \frac{m_0 - m_1}{m_0} \times 100\% \quad (1)$$

$$\text{Melamine yield (Y}_{ma}, \%) = \frac{m_2 - m_3}{m_0 \times 0.65} \times 100\% \quad (2)$$



**Fig. S2** The typical structure unit of MFF.

### 2.3 Calculation of melamine purity

After the reaction of MFF in NH<sub>3</sub>·H<sub>2</sub>O, the melamine product was washed ethanol for several times until the ethanol after washing was clear, followed by the drying of melamine product via evaporation. NMR characterization was applied to determine the purity of dried melamine product with piperazine as the internal standard. The purity of melamine was determined using the following equation 3 (eq. 3). Specifically, the parameters of m, MW, P, nH, and I in eq. 3 represented the mass (unit: g), the molecular weight (unit: g/mol), the purity, the number of moles of protons generating the selected signals for integration (unit: mol), and the integral for the selected NMR peaks of the substance, respectively; meanwhile, the subscript x and std in each parameter

represented melamine product and piperazine internal standard, respectively.

$$m_{(x)} = P_{(std)} \times \frac{MW_{(x)}}{MW_{(std)}} \times \frac{nH_{(std)}}{nH_{(x)}} \times \frac{m_{(std)}}{P_{(x)}} \times \frac{I_{(x)}}{I_{(std)}} \quad (3)$$

## 2.4 Exploration of the pathway for melamine formaldehyde (MF) resin degradation

### 2.4.1 Stability test of melamine in $NH_3 \cdot H_2O$

Melamine standard and 27wt%  $NH_3 \cdot H_2O$  were added into a Teflon-lined autoclave with a volume of 10 ml. The Teflon-lined autoclave was then sealed tightly, and heated in a homogeneous reactor to 170 °C and maintained at 170 °C for 12 h. After the reaction, the autoclave was cooled down to R. T., and the solid product were collected and dried at 80 °C for 24 h, and then analyzed by the quantitative  $^1H$ -NMR analysis. The NMR result showed that >99% of melamine maintained stable in  $NH_3 \cdot H_2O$  solution.

### 2.4.2 Reaction of ammelide, ammeline and cyanic acid in $NH_3 \cdot H_2O$

Ammelide and ammeline were chosen as the model reactants to react with 27wt%  $NH_3 \cdot H_2O$  at 170 °C for 12 h, respectively. No melamine was produced after the two reaction tests. Cyanic acid was also reacted with 27wt%  $NH_3 \cdot H_2O$  at the same conditions, in which the formation of melamine was not observed. These results indicated that ammelide, ammeline and cyanic acid cannot convert to melamine in  $NH_3 \cdot H_2O$ . Hence, MF resin decomposed directly to melamine without the reaction intermediate(s) of ammelide, ammeline and/or cyanic acid.

### 2.4.3 Reaction of ethylenediamine in $NH_3 \cdot H_2O$

Ethylenediamine was utilized as the model substitute for  $NH_3$  in  $NH_3 \cdot H_2O$  solution to cleave the C-N bond of MFF. An aqueous solution of ethylenediamine, with a mass concentration equivalent to that of  $NH_3 \cdot H_2O$  (27wt%  $NH_3$ ) was prepared for use 3.00 g of the ethylenediamine solution and 0.15 g of MFF were added into a Teflon-lined autoclave. The autoclave was then sealed tightly and heated in a homogeneous reactor at a temperature of 170 °C of 12 h. After the reaction, the autoclave was cooled down to R. T. The resulting degradation solution was further dried at 120 °C for 12 h to remove ethylenediamine and  $H_2O$ , by which the solid product was collected and analyzed by  $^1H$ -NMR.

## 3.Characterization methods

To explore chemical structure of degradation products, NMR analysis was performed using an AVANCE III 400 (Bruker, Germany) spectrometer(400MHz). To analyze the functional groups of MFF and the degradation products, IR spectra were collected on a Vertex 80V (VBUKER, Germany) spectrometer in the change of 4000-400 $cm^{-1}$  wavenumber. Elemental analysis was performed using an Vario EL Cube, Germany.

## 4. Computational details

All calculations were performed using the density functional theory (DFT) method implemented in the commercial Gaussian 16 program package. Molecular geometries of the model complexes were optimized applying the B3LYP functional. For all atoms,

the 6-31G Pople basis set was used. As soon as the convergences of optimizations were reached, frequency calculations at the same level were performed to identify all the stationary points as minima. The intrinsic reaction coordinate (IRC) calculations were carried out to confirm that the transition structures can indeed connect the related reactant and product. All the optimized geometries mentioned were built by Gaussview 6.0.

## 5. Green metrics analysis

Environmental impact factor (E-factor, EF), proposed by R. A. Sheldon, has been extensively used as a metric to quantify the sustainability of a process.<sup>1,2</sup> The traditional calculation of E-factor is performed by eqn1. Besides, for comparison, two new metrics simple E-factor (sE-factor, sEF) by eqn2 and complete E-factor (cE-factor, cEF) by eqn3 are also proposed. The amount of waste generated in recycling a certain amount of MF resin was calculated by the eqn 4. A lower EF means less waste production and is more positive to the environment. Process Mass Intensity (PMI) introduced by the EPA and ACS GCI, assesses efficiency by considering all materials as well as water used in a process (eqn 5).<sup>3</sup> A lower PMI means greater efficiency and economy. Here we introduce in detail the green index analysis of the technology of recovering MF resin in this work and the previous recovery method of MF resin (Table S2 and S3).

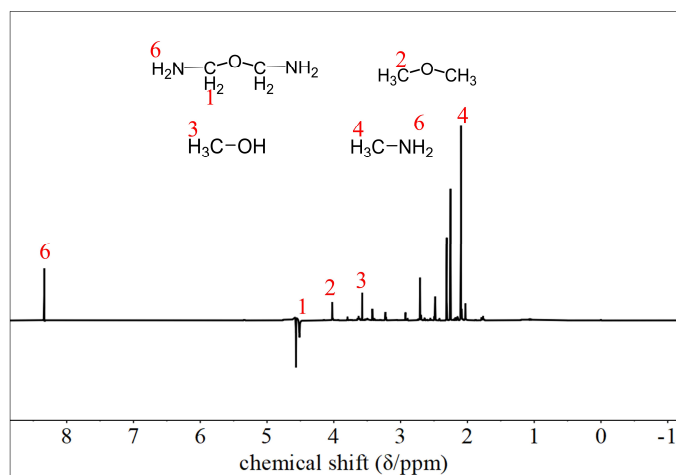
$$EF = \frac{\sum m(\text{raw materials}) + \sum m(\text{catalysts}) + \sum m(\text{solvents}) * 10\% - \sum m(\text{products})}{\sum m(\text{products})} \quad (1)$$

$$cEF = \frac{\sum m(\text{raw materials}) + \sum m(\text{catalysts}) + \sum m(\text{solvents}) - \sum m(\text{products})}{\sum m(\text{products})} \quad (2)$$

$$sEF = \frac{\sum m(\text{raw materials}) + \sum m(\text{catalysts}) - \sum m(\text{products})}{\sum m(\text{products})} \quad (3)$$

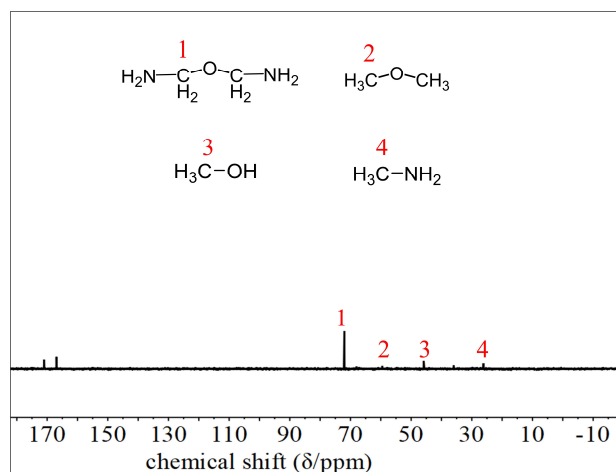
$$\text{Waste amount} = \frac{EF * \sum m(\text{products})}{\sum m(\text{MF resin})} \quad (4)$$

$$PMI = \frac{\sum m(\text{input materias incl. process water})}{\sum m(\text{products})} \quad (5)$$



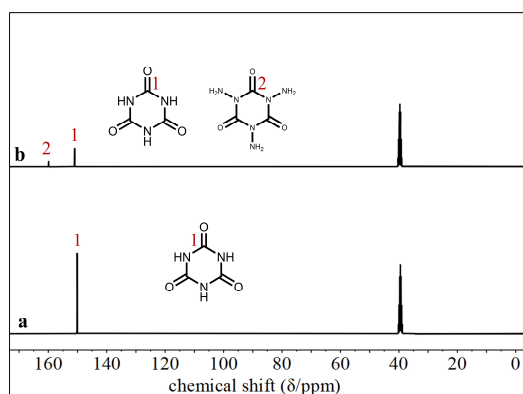
**Fig. S3**  $^1\text{H}$  NMR spectrum of degradation solution after 3g  $\text{NH}_3 \cdot \text{H}_2\text{O}$  degrade 0.15g MFf at 170 °C for 12h.

Diamine methyl ether ( $\text{NH}_2\text{-CH}_2\text{-O-CH}_2\text{-NH}_2$ ) chemical shift as 4.5ppm ( $\text{-CH}_2\text{-}$ ) and 8.47ppm( $\text{-NH}_2$ ). dimethyl ether chemical shift is 4.02ppm( $\text{-CH}_3$ ), chemical shift of methanol is 3.57ppm ( $\text{CH}_3\text{-}$ ), methylamine has chemical shift of 2.11ppm ( $\text{CH}_3\text{-}$ ) and 8.47ppm( $\text{-NH}_2$ ).



**Fig. S4**  $^{13}\text{C}$  NMR spectrum of degradation solution after 3g  $\text{NH}_3 \cdot \text{H}_2\text{O}$  degrade 0.15g MFF at 170 °C for 6h.

Diamine methyl ether ( $\text{NH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{NH}_2$ ) chemical shift as 72.0ppm, it has same chemical shift with Tr-NH- $\text{CH}_2$ -O- $\text{CH}_2$ -NH-Tr groups of MFF. dimethyl ether chemical shift is 59.5ppm, chemical shift of methanol is 48.6ppm, methylamine has chemical shift of 26.2ppm.

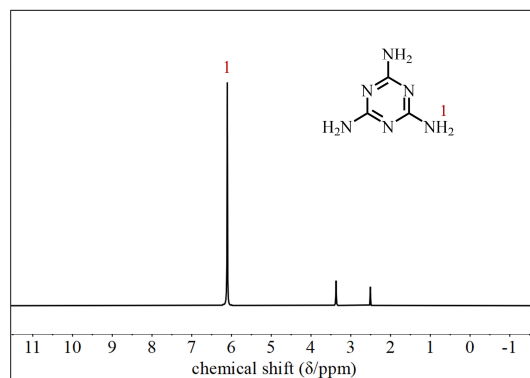


**Fig. S5** <sup>1</sup>H-NMR spectra of: cyanuric acid standard (a), and the reaction product of cyanuric acid standard and NH<sub>3</sub>·H<sub>2</sub>O (b).

0.15g of cyanic acid was added into 0.15 g of 27wt% NH<sub>3</sub>·H<sub>2</sub>O in a teflon-lined autoclave with a volume of 10 ml. The autoclave was sealed tightly and heated in a homogeneous reactor at 170 °C for 12 h.

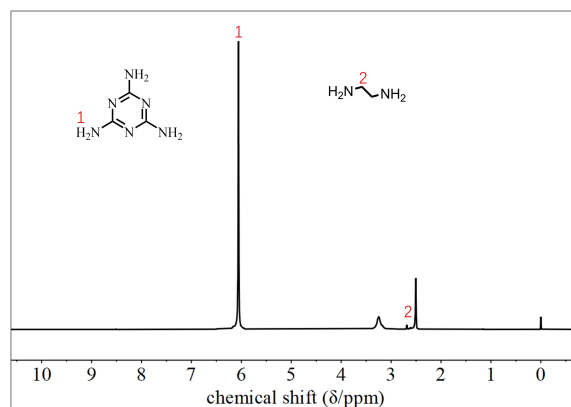
The chemical shift of melamine is commonly located at ca. 167.5 ppm, while the solid collected after the reaction of cyanic acid with NH<sub>3</sub>·H<sub>2</sub>O showed a chemical shift at 160.5 ppm, clearly excluding it as melamine.





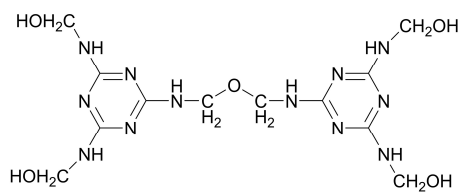
**Fig. S6** <sup>1</sup>H NMR spectrum of melamine after treating in NH<sub>3</sub>·H<sub>2</sub>O at 170 °C for 12h.

0.15 g of melamine standard was mixed with 0.15 g of 27wt% NH<sub>3</sub>·H<sub>2</sub>O in a teflon-lined autoclave with a volume of 10 ml. Then, the Teflon-lined autoclave was sealed tightly and heated in a homogeneous reactor at 170 °C for 12 h.

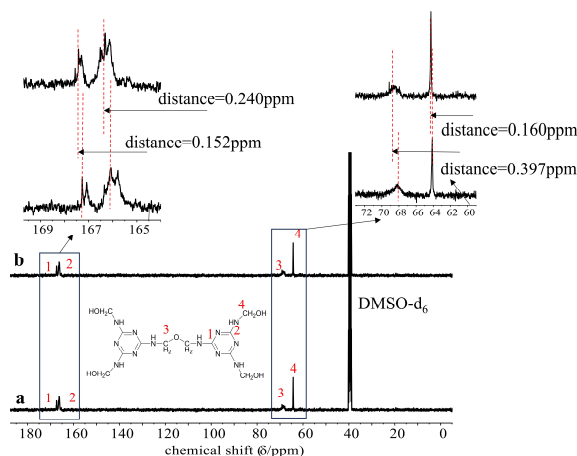


**Fig. S7** The  $^1\text{H}$  NMR spectrum of reaction products of 27wt%ethanediamine- $\text{H}_2\text{O}$  and MF (170 $^\circ\text{C}$ , 12h).

0.15 g of MF and 3 g of 27wt% ethanediamine- $\text{H}_2\text{O}$  were added into a Teflon-lined autoclave with a volume of 10 ml. The autoclave was sealed tightly and heated in a homogeneous reactor at 170  $^\circ\text{C}$  for 12 h.  $^1\text{H}$ -NMR result proved the solid product as melamine.

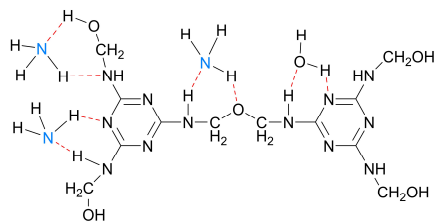


**Fig. S8** The chemical structure of MF resin prepolymer.



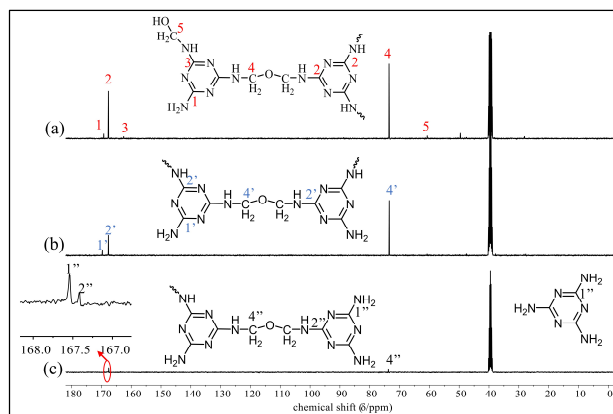
**Fig. S9**  $^{13}\text{C}$ -NMR spectra of: (a) MF resin prepolymer and (b) mixture of MF resin prepolymer with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (with  $\text{DMSO-d}_6$  as the deuterium reagent).

10mg MF resin prepolymer and 400 $\mu\text{l}$   $\text{DMSO-d}_6$  (a), 10mg MF resin prepolymer, 400 $\mu\text{l}$   $\text{DMSO-d}_6$  and 100 $\mu\text{l}$   $\text{NH}_3 \cdot \text{H}_2\text{O}$  (b). MFF prepolymer contains 1,3,5-triazine (Tr) ring-NH- $\text{CH}_2$ -OH and Tr-NH- $\text{CH}_2$ -O- $\text{CH}_2$ -NH-Tr main groups. (a)For Tr-NH- $\text{CH}_2$ -OH, C atoms chemical shift in the Tr was 166.3ppm, 2, and C atoms chemical shift out of Tr was 64.3ppm, 4. For Tr-NH- $\text{CH}_2$ -O- $\text{CH}_2$ -NH-Tr, C atoms chemical shift in the Tr was 167.4ppm, 1, and C atoms chemical shift out of Tr was 69.1ppm, 3. (a)For Tr-NH- $\text{CH}_2$ -OH, C atoms chemical shift in the Tr was 166.5ppm, 2, and C atoms chemical shift out of Tr was 64.4ppm, 4. For Tr-NH- $\text{CH}_2$ -O- $\text{CH}_2$ -NH-Tr, C atoms chemical shift in the Tr was 167.5ppm, 1, and C atoms chemical shift out of Tr was 69.5ppm, 3.



**Fig. S10** Possible interaction of MF resin prepolymer with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  via forming hydrogen bonds.

The possible hydrogen bonds forming between MF resin prepolymer with  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in  $\text{NH}_3 \cdot \text{H}_2\text{O}$  were illustrated as the red dotted lines.



**Fig. S11**  $^{13}\text{C}$ -NMR spectra of the products obtained from degradation of MF resin prepolymer at: (a) 170 °C for 3 h, (b) 150 °C for 6 h and (c) 160 °C for 9 h (with  $\text{DMSO-d}_6$  as the deuterium reagent).

0.15 g of MFF and 3 g of 27wt%  $\text{NH}_3\text{-H}_2\text{O}$  were added into a Teflon-lined autoclave with a volume of 10 ml. After the reaction, the degradation solution was removed, centrifuged, and 200  $\mu\text{L}$  of the upper transparent degradation solution was taken and mixed with 400  $\mu\text{L}$   $\text{DMSO-d}_6$  for  $^{13}\text{C}$ -NMR analysis. The use of 3g 27wt%  $\text{NH}_3\text{-H}_2\text{O}$  is due to the fact that the oligomer produced by MFF is not completely depolymerized will be dissolved in 27wt%  $\text{NH}_3\text{-H}_2\text{O}$  under reaction condition (170°C), and the single oligomer is insoluble in most organic solvents at room temperature, and the direct dissolution during the reaction process is convenient for analysis of the degradation process.

(a) 169.2ppm, 1, was C atoms of 1,3,5-triazine (Tr) ring- $\text{NH}_2$  structure chemical shift. For  $\text{Tr-NH-CH}_2\text{-O-CH}_2\text{-NH-Tr}$ , C atoms chemical shift in the Tr was 167.6ppm, 2, and C atoms chemical shift out of Tr was 73.5ppm, 4. For  $\text{Tr-NH-CH}_2\text{-OH}$ , C atoms chemical shift in the Tr was 162.5ppm, 3, and C atoms chemical shift out of Tr was 60.7ppm, 5. (b) Compared with (a), the  $\text{Tr-NH-CH}_2\text{-OH}$  chemical group disappeared (3',5'), the content of  $\text{Tr-NH-CH}_2\text{-O-CH}_2\text{-NH-Tr}$  chemical groups decreased (2',4'), and  $\text{Tr-NH}_2$  chemical groups increased (1'). The chemical shift of (c) has a significant shift, 1'' shift close to 2'' and two chemical shift peaks appear at 167.5ppm and 167.4ppm, and it can be clearly seen that the height of 1'' has exceeded 2'' and 4'', which indicates the continuous generation of  $\text{Tr-NH}_2$ . (c) All chemical shifts were significantly reduced because the concentration of the degradation solution was reduced as a result of the precipitation of melamine solids.

**Table S1** Comparison of different melamine-formaldehyde (MF) resin chemical degradation technology.

Works	<sup>4</sup> Previous work 1	<sup>5</sup> Previous work 2	This work
Solvent	THF-H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O
Catalyst	CH <sub>4</sub> O <sub>3</sub> S	NaOH	NH <sub>3</sub>
Products	mixture of ammelide, ammeline and cyanuric acid	mixture of ammelide and ammeline	melamine
Solid-to-liquid ratio	1:33	1:33	1:1
Post-treatment	spin evaporation, neutralization, filtration, washing, dissolution and precipitation	neutralization, filtration, washing	washing

Reaction condition: mass of MF resin is 0.15g.

Work 1 uses toxic tetrahydrofuran (THF) and a small amount of H<sub>2</sub>O as solvent, both work 2 and this work use H<sub>2</sub>O as green solvent. Work 1 and work 2 use methane sulfonic acid (MSA) and sodium hydroxide (NaOH) as catalysts respectively, and this work use NH<sub>3</sub> which is greener than the first two catalysts. MSA is a strong organic acid with high boiling point (167 °C), which is difficult to remove and has certain toxicity, it's relatively expensive. NaOH and NH<sub>3</sub> are very cheap, but NaOH as a strong base, has a strong corrosion, NH<sub>3</sub> although there is a bad smell, but its ecological environment is still more friendly, can be used as fertilizer, can also be absorbed by plants, so NH<sub>3</sub> is more greenly. In work 1, mixture of ammelide, ammeline and cyanuric acid are generated, all of which are slightly soluble in MSA-THF-H<sub>2</sub>O system, and the three substances are difficult to separate separately, the substances dissolved in the system need to go through the process of distillation, alkali neutralization, washing and other processes to obtain, and is also a mixture, difficult to directly reuse. Work 2 degradation reaction to produce a mixture of ammelide and ammeline, and dissolved in NaOH-H<sub>2</sub>O system, through the acid neutralization, washing, drying and other processes to obtained the product, besides, ammelide and ammeline are difficult to separate separately, difficult to use directly. In this work, monomer melamine was generated, NH<sub>3</sub> and H<sub>2</sub>O are easily volatilized and removed. Due to melamine not dissolve in H<sub>2</sub>O, the product treatment only requires simple washing to remove impurities on the surface of the product to obtain melamine products. Compared with the previous two works, in this work, no acid or base is consumed to neutralize the system in the post-treatment process, and melamine is widely used and can be directly used, while the mixed product of ammelide and ammeline is difficult to achieve common reuse, so our degradation reaction system and post-treatment process are more greenly. The Solid-to-liquid ratio in work 1 and 2 is 1:33, and the degradation effect

will become worse if it is reused for more than five times, The solid-to-liquid 1:1 is used in this work, the processing capacity is much higher than the previous two works, and we can recycle the ammonia gas after the reaction, similarly, MF resin was degraded using MSA-THF-H<sub>2</sub>O system and NaOH-H<sub>2</sub>O system at solid-to-liquid 1:1, which did not have degradation effects at 200°C. Work 1 and 2 required a large amount of solvent to meet the contact between catalyst and MF resin, while ammonia as a gas was easy to contact with MF resin. In summary, this work relative to the work 1 and work 2 systems, use NH<sub>3</sub>-H<sub>2</sub>O system to degrade MF resin is a greener choice.



**Table S2** Element analysis results of melamine standard and MF resin degradation product melamine

Sample	C (%)	H (%)	N (%)
melamine standard	28.58	4.80	66.55
product melamine	28.57	4.83	65.94

The content of each element in the product obtained by  $\text{NH}_3\text{-H}_2\text{O}$  degradation is very close to the content of the standard melamine. Only N content is slightly high, which may be due to the presence of trace nitrogen impurities in the crystallization products.

**Table S3** Material input-output table for the recycling of MF resin in different recycle technology

Works	Input material	Input type	Output material	Input weight/g	Output weight/g	Yield /%	
<sup>a</sup> Work 1 <sup>4</sup> cycle 7 times	MF resin	Raw material		1.0500			
	THF	Solvent		3.5000			
	H <sub>2</sub> O			0.5000			
	MSA	Catalyst		1.0000			
						0.3100 50.6	
			Ammelide, ammeline Cyanuric acid		0.3000	49.4	
<sup>b</sup> Work 2 <sup>5</sup> cycle 5 times	MF resin	Raw material		0.7500			
	H <sub>2</sub> O	Solvent		4.5000			
	NaOH	Catalyst		0.5000			
						0.4700	
				Ammelide, ammeline			97.2
<sup>c</sup> This work no cycle	MF resin	Raw material		0.1509			
	H <sub>2</sub> O	Solvent		0.1132			
	NH <sub>3</sub>	Catalyst		0.0419			
						0.0935	
				Melamine			95.3

<sup>a</sup> Reaction conditions: 0.15g MF resin, 4.5g MSA-THF-H<sub>2</sub>O, 180°C for 12h, the degradation solution was reused directly by simply adding 0.15 g fresh MF resin at the end of each run. <sup>b</sup> Reaction conditions: 0.15g MF resin, 5g NaOH-H<sub>2</sub>O, 160°C for 4h, the degradation solution was reused directly by simply adding 0.15 g fresh MF resin at the end of each run. <sup>c</sup> Reaction conditions: 0.15g MF resin, 0.15g NaOH-H<sub>2</sub>O, 170°C for 12h.

**Table S4** Green metrics for the recycling of MF resin in different recycle technology

System	sEF (kg/kg)	cEF (kg/kg)	EF (kg/kg)	Waste amount (kg/kg MF resin)	PMI (kg/kg)
MSA-THF-H <sub>2</sub> O <sup>4</sup>	2.36	8.92	2.93	1.70	9.92
NaOH-H <sub>2</sub> O <sup>5</sup>	1.65	11.23	1.65	1.03	12.23
NH <sub>3</sub> -H <sub>2</sub> O	1.06	2.27	1.06	0.66	3.27

A lower E-factor means less waste production and is more positive to the environment. Compared with the previous recovery methods, the values of sEF, cEF, and EF of our MF resin recovery technology are the smallest, which means that our system is more positive to the environment. As same time, the waste amount and PMI value of the ammonia system are the smallest, which means greater efficiency and economy.

## References

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