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# Degradation of Metaldehyde in Aqueous Solution by Nano-Sized Photocatalysts and Granular Activated Carbon.

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Metaldehyde, has been detected in drinking water system in relatively high concentration which has exceeded European water quality standard. In order to address this problem, the aim of this project was to treat metaldehyde aqueous solution by advanced oxidation processes (AOPs) and granular activated carbon (GAC) column. Ten novel materials were tested for degradation rates of metaldehyde under ultraviolet light in the C spectrum (UVC). For treatment of 1 mg/L metaldehyde solution by AOPs, the highest degradation rate is 16.59% under UVC light with the aid of nitrogen doped titanium dioxide coated graphene ($NTiO_2$/ Gr). Furthermore, the effect of metaldehyde concentration was investigated, 0.5 mg/L is the optimal concentration for degradation of metaldehyde with N-$TiO_2$/Gr under UVC light. Apart from that, the lifetime of GAC column could be elongated on condition that metaldehyde has been treated by AOPs previously. Hence, the method, combination of AOPs and GAC column is promising in treating water containing metaldehyde.

**Keywords**: Metaldehyde, Photocatalyst, Semi-conductor, Granular Activated Carbon, AOPs

## 1. INTRODUCTION

Metaldehyde has been detected in drinking water system in relatively high concentration which has exceeded European water quality standard[1]. In the UK, the range of metaldehyde concentration is from 0.4 μg/L to 0.6 μg/L (up to 2.7μg/L also detected)[1] which exceeds the European regulatory limit for pesticides in drinking water (0.1μg/L)[2]. It is crucial to decrease the concentration of metaldehyde in order to satisfy the requirement of dringking water quality standards. The potential of activated carbon modified to adsorb metaldehyde has drawn attention. Phenolic resin-derived activated carbons have higher adsorption and capacity compared with conventional GAC, but this absorbent is costly and not chemical free[2]. Advanced oxidation processes (AOPs) are also promising methods in metaldehyde reduction[3]. It has shown that 95% metaldehyde can be degraded through AOPs, but this system requires the dosage of $H_2O_2$ or increase of UV intensity. None of these methods alone can remove metaldehyde ideally[3]. Thus, combinations of different methods may be the solution. Therefore, the aim of this study is to treat metaldehyde aqueous solution by AOP and granular activated carbon (GAC) column.

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## 2. MATERIALS AND METHODS

### 2.1 Materials

Ten types of nanomaterials tested for degradation of metaldehyde and characteristics results of them

are described in Table 1. The largest surface area is 219.98 $m^2/g$ from the materials of N-doped $TiO_2$/Graphene. G3 (Germanate glass doped with CdSe nanoparticles) has the lowest band gap (1.68 eV) which means G3 can be easiest to be activated by light.

### 2.2 Methods

There was 1L solution with 1 mg/L metaldehyde concentration prepared, and 500 mL of it was measured and added to the reaction chamber. Furthermore, about 20 mL solution was taken and stored in a clean and dry glass bottle[2]. Before reacting, the UVC light should be turned on for at least 15 minutes to obtain the stable intensity of light during the photocatalysis. Photocatalyst with the mass of 0.1 g was added to the reaction chamber with the UVC light insertion. After two hours of reaction, the UVC light and magnetic stirring apparatus were turned off[2]. Then photocatalyst was settled for 3 minutes before the sample with the volume of 20 mL was taken out with a single syringe. Then the sample was filtered by a syringe driven membrane (MILLEX 0.22 μm produced by Millipore Express) and was put in a clean and dry glass bottle with the label (120 minutes). These two samples were stored in the refrigerator before testing the concentration of them. All the ten photocatalysts were tested in the same manner. After photocatalytic treatment, GAC column test was performed. The mass of GAC particles was reduced to 1g with the height of 14.5 mm were packed in column. Two hundred milliliter initial solution (0.5 mg/L) was added in the GAC column, after that, the solution was taken and stored in a glass bottle with the label (200 mL filtered volume). Then another 200 mL solution was passed through the GAC column. This procedure was repeated until the total solution treated by GAC column was 1800 mL. The contact time for each treatment was approximate 3 minutes. After that, the initial solution was replaced to the samples which had already treated by AOPs, and every 200 mL solution was added in GAC column until the total solution passed through GAC was 1800 mL. In order to obtain the rate of degradation and

Table 1. Ten photocatalysts used in the AOP

| Sample | Doping and composite (%) | Band gap (eV) | Particle size (nm) | Surface area ($m^2/g$) |
|---|---|---|---|---|
| N-doped ZnO* | Nitrogen is doped in ZnO | 2.3 | 50–100nm sized nanocubes as the primary growth and 4–5 nm size nanoparticles as a secondary growth | 45.26 |
| N-doped $TiO_2$* | Nitrogen is doped in $TiO_2$ | 2.9 | ~10 | 157.70 |
| N-doped ZnO/Graphene* | Nitrogen is doped in ZnO and its graphene composite (Graphene 2%) | 2.1 | ~5 | 81.90 |
| N-doped $TiO_2$/Graphene* | Nitrogen is doped in $TiO_2$ and its graphene composite (Graphene 2%) | 2.4 | ~7-10 | 219.98 |
| G1 (Germanate glass doped with Bi nanoparticles)* | Germanate glass doped with spherical Bi nanoparticles | 2.00 | 1-2 | - |
| G2 (Germanate glass doped with $CdS_{.5}Se_{.5}$ nanoparticles)* | Germanate glass doped with spherical $CdS_{.5}Se_{.5}$ nanoparticles | 2.12 | 5-7 | - |
| G3 (Germanate glass doped with CdSe nanoparticles)* | Germanate glass doped with spherical CdSe nanoparticles | 1.68 | 5-6 | - |
| G4 (Germanate glass doped with CdSe nanoparticles)* | Germanate glass doped with spherical CdSe nanoparticles | 2.37 | 2-3 | - |
| Cu/Cr:0.5** | The ratio of nanosized Cu to Cr equal to 0.5 | 2.58 | 5-10 | 38.20 |
| Cu/Cr:1.0** | The ratio of nanosized Cu to Cr equal to 1.0 | 2.58 | 5-10 | 51.63 |

*Catalysts developed by the Centre for Materials for Electronics Technology (C-MET), India; **Catalysts developed by the National Chemical Laboratory (NCL), India.

adsorption, the concentration of all samples were obtained by GC-MS (Perkin Elmer precisely Clarus 500) with SPE.

## 3. RESULTS AND DISCUSSION

The degradation rates of metaldehyde under UVC light are shown in Figure 1. N-$TiO_2$/Gr showed the highest effectiveness on metaldehyde degradation. From the Table 1, this material has the largest surface area resulting the highest degradation rate (16.59%). Besides, the figure for N-ZnO/Gr were also relatively high (16.40%). However, the figure for N-ZnO was lowest, ranking after the degradation rates of Cu-Cr (1.0) and Cu-Cr (0.5). That is because the surface area of N-ZnO was smaller than Cu-Cr (0.5) and Cu-Cr (1).

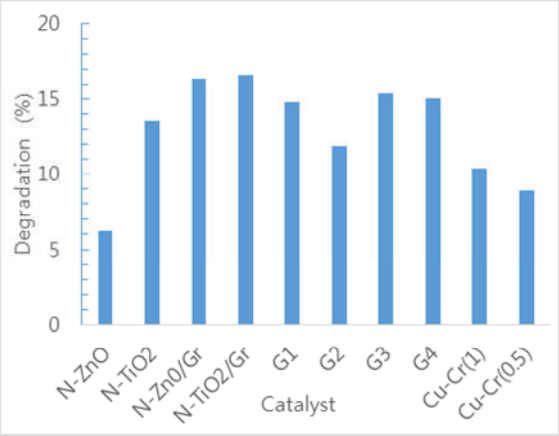


Fig 1. Degradation of metaldehyde by 10 photocatalysts under UVC light

The other materials had similar rates which were in the range of 10%-16%. There were 1800mL metaldehyde samples treated by AOP (initial solution of 0.5 mg/L in AOP). According to Tao and Fletcher (2016), 1 g of GAC column can adsorb about 0.84 mg metaldehyde. To obtain the breakthrough curve of GAC, 10 g GAC was replaced by 1 g GAC. Every 200 mL sample from photocatalytic reactor was added to the GAC column. Afterwards, metaldehyde solution of 0.5 mg/L was passed through GAC column directly. Comparing the results from these two experiments, the curves are shown in Figure 2.

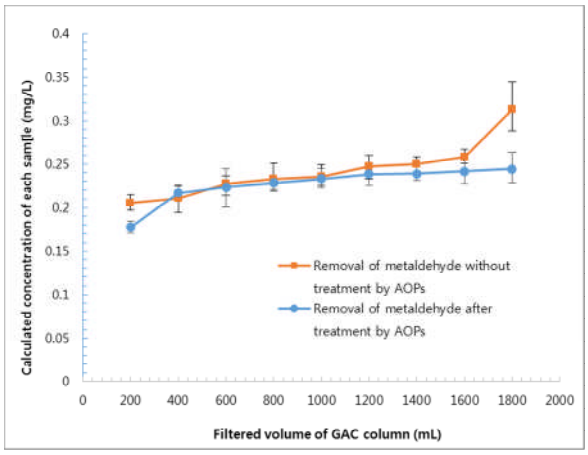


Fig. 2 Removal of metaldehyde through GAC column with and without pre-AOP

From Figure 2, the calculated concentrations of samples after treatment by GAC column along with their error bars are presented. Overall, the average removal rate of each sample was 50% which was similar to the results of 30-50% from Li et al.[2]. However, the GAC column was not saturated by metaldehyde in both methods so this means more samples should be added to the GAC column. Hence, there were no kinetic models due to unclear trends, so the adsorption capacity of GAC in this study could not be calculated. On average, the concentration values on the blue line (with pre-AOP) were lower than the ones on the orange line (without pre-AOP), which means the concentrations of solutions treated by AOP and GAC column were lower than the ones treated only by GAC filtration. The concertation for 200mL on the orange line was higher than that on the blue line. This is because the initial solution concentration for blue line (0.408 mg/L) was lower than concentration for orange line (0.504 mg/L). The difference of concentration was caused by metaldehyde degradation in pre-AOP. After that, there were increasing trends in both orange and blue line with the similar figures. After 1600 mL of treated solution, the orange line showed a significantly increasing trend. This means the GAC column may be saturated whereas the blue line was almost stable, which illustrates for treatment without pre-AOP, the GAC column

was saturated more quickly. Hence, the treatment of AOPs can prolong the lifetime of GAC. Therefore, the combination of nano-sized photocatalysts and GAC can be a cost-effective method to remove metaldehyde.

## 4. CONCLUSION

Metaldehyde with relative high concentration has been detected in drinking water system, which brings adverse impacts on human health. In this work, metaldehyde with concentration of 1 mg/L was degraded using ten novel materials under UVC light. Among 10 different types of photocatalysts, N-$TiO_2$/Gr and N-ZnO/Gr had the highest degradation rate and it can be concluded that the higher surface area of catalysts holds the key to the effectiveness of photodegradation. The GAC column was used to adsorb metaldehyde in samples after treatment by AOP and the average removal rate for samples was 50%. Compared with concentrations of solutions only treated by GAC column, pre-AOP can prolong the lifetime of GAC column, which means the GAC column can be used for longer time. Hence, combination of nano-sized photocatalysts and GAC is a promising method to reduce metaldehyde concentration in drinking water.

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