Photocatalytic activity investigation

The photocatalytic activity of the modified samples was investigated by the determination of the remaining concentration of the nominated pollutant, acetaldehyde, over various time intervals. Figures. 5 and 6 show the photodecomposition activity of different modified TiOâ,, nanoparticles under 8w visible light irradiation in the continuous flow reactor with a flow rate of 95 ml/min.

According to Figures. 5 and 6, all the modified samples show much higher photocatalytic activity than the pure TiOâ,,, confirming that N and Co doping is an effective way of improving the photocatalytic activity. The highest activity was observed for 1%Co-N-TiOâ,, sample, and the 50 min irradiation by visible light resulted in 44. 2% of acetaldehyde degradation for this sample.

The increased visible light absorption and specific surface area are key factors that influenced the photoactivity of the different modified samples under visible light irradiation compared to pure TiO $_2$.

The decrease in the particle size and increase in the BET surface area (Table 1) contribute to the improvement of the acetaldehyde degradation. Table 1 shows that the crystallite size of samples decreases from 21. 9 to 14. 7 nm; this decrease may be beneficial for the photocatalytic activity. Compared with the N-TiO $_2$ sample, Co-N/TiO $_2$ photocatalysts have a larger surface area, which increases the photoactivity rate because of the large amounts of acetaldehyde molecules being adsorbed on the photocatalytic surface and easily reacted by photogenerated oxidizing species.

The light absorption characteristics of the modified samples are extended towards the visible light region after N and Co doping, which implies that the formation of photogenerated charge carriers will be increased under visible light irradiation. Also, cobalt doping with a low cobalt content can act as a charge trap to prevent electron-hole recombination and improve the interfacial charge transfer to degrade acetaldehyde. After the optimal doping ratio of cobalt was exceeded (1wt % Co-N-TiO$_2$), reduced photocatalytic activity was observed. This result can be due to the coverage of the surface of photocatalyst with increased cobalt ions (Co^{2+}) which inhibited interfacial charge transfer due to inadequate amount of light energy available for activation of all the photocatalyst particles. Also due to excessive concentration, Co particles acting as recombination centers for photogenerated electrons and holes .

Based on the acetaldehyde degradation results in this study, it is therefore evident that photocatalytic activity is strongly dependent on the doping ratio rather than the band gap of the samples and activities of the Co-N-TiO$_2$ co-doped samples are higher than those of N-TiO$_2$ or pure TiO$_2$.

**   Fig. 5**

**   Fig. 6**

Kinetic study

The Langmuir-Hinshelwood kinetic model has been extensively used to describe heterogeneous photocatalysis on titanium dioxide . This model successfully describes the kinetic of Eq. (3), which is the reaction between

hydroxyl radical and adsorbed acetaldehyde. When the photocatalytic reaction obeys a Langmuir-Hinshelwood model, the relationship between the rate of reaction r (μmol g^{-1} min^{-1}) and the acetaldehyde concentration C$_{act.}$ (μmol l^{-1}) can be described as follows in Eq. (4):

Where k is the rate constant (μmol g^{-1} min^{-1}) and K$_a$ is the adsorption constant (l μmol^{-1}).

Some assumptions were used in Eq. (4). Only acetaldehyde is adsorbed on the catalyst surface and all intermediates and products desorbed immediately after chemical reaction; therefore, they have not been detected in Eq. (4).

The mathematical modelling for the plug photoreactor at unsteady condition with the assumption of isothermal condition, ignored diffusion resistance and constant flow rate, the mass balance equation inside the continuous photoreactor would become as follows in Eq. (5):

Where Q is the volumetric flow rate (l min^{-1}), W is the weight of catalyst (g), V is the volume of the reactor (l), and t is the time of experiment (min).

Kinetic parameters (k, K) were calculated using the Nelder-Mead method, which was used through computer programming in MATLAB by minimization of sum of squared of relative error, the difference between the calculated and experimental outlet concentration results, as the following objective function:

By minimization of Eq. (6), kinetic parameters (k, K_a) are predicted and shown in Table 3. A good agreement among the predicted and experimental data were found that are shown in Fig. 7.