

## Malachite Green Removal by Zn/Al-citrate LDHs in Aqueous Solution

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### Abstract

Zn/Al-citrate LDHs was synthesized using co precipitation method at basic condition and the material were applied as adsorbent of malachite green (MG) dye in aqueous medium using batch system. Adsorption of MG onto Zn/Al-citrate was investigated through kinetic, isotherm adsorption and thermodynamic studies. Kinetic model was fitted PSO than PFO for MG adsorption. The rate of adsorption  $k_2$  for Zn/Al LDHs was  $0.000692 \text{ g.mg}^{-1} \text{ min}^{-1}$  and  $0.000371 \text{ g}$  for Zn/Al-citrate LDHs. $\text{mg}^{-1} \text{ min}^{-1}$ . Adsorption of malachite green onto Zn/Al LDHs and Zn/Al citrate LDHs was investigated and following Langmuir adsorption isotherm model shows chemical adsorption process. The adsorption capacity maximum of Zn/Al-citrate is  $333 \text{ mg/g}$  from Zn/Al LDHs is only  $111 \text{ mg/g}$ . Thermodynamic parameters of Zn/Al-citrate confirmed adsorption process was endothermic and spontaneous.

### Keywords

LDHs, citric acid, intercalation, adsorption, malachite green

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## 1. INTRODUCTION

Various industries are widely applied dyes to colour their product. Disposal of dye wastewater from the dyestuff manufacturing, printing, dyeing and textile industry represent a serious problem all over the world, because in wastewater dyes undergo chemical changes and destroy aquatic life and they even endangers human health (Song et al., 2013). Cationic reactive dyes are widely used in the tannery, paper, textile industries, distilleries, food beverage etc. Malachite green is a cationic base dye used in manufacturing of paints and printing inks. It also most commonly used for dyeing silk, cotton, paper and leather (Hameed and El-Khaiary, 2008). Malachite green has reported to affect the immune and reproductive system of animal due to its carcinogenic properties (Song et al., 2020). Malachite green also represents adverse effect on reproductive and immune system (Yildirim and Bulut, 2020). Therefore an increased interest has been focused on removing of such dyes from wastewater.

Many methods have been used to decolorize dye wastewater including adsorption, membrane filtration, coagulation, electrochemical methods, oxidation and biological technology. Of these techniques due to its effective and economical, adsorption is a common method for dye removal (Palapa et al., 2019). Layered double hydroxide (LDH) is a type of anionic clay having a hydrotalcite crystal structure, that are formed by two kinds of metal ions, usually a divalent and trivalent one, together with hydroxyl group, an interlayer anion and water

molecules (Pan et al., 2020). The general formula of LDH is  $[M_{1-x}^{+2}M_x^{+3}(OH)_2]^{+3}[A_{x/n}] \cdot mH_2O$ , where x is the molar ratio  $M^{+3}/(M^{+2} + M^{+3})$  ranging from 0.20 to 0.30 in order to avoid the formation of undesirable phase (Lesbani et al., 2020). To improve of LDH sorption properties some researchers conducted intercalation in the layer space using anion such as hexacyanoferrat (II) anion (Puzyrnaya et al., 2016) and ethylenediaminetetraacetic acid (Kameda et al., 2013).

The aim of this study was to examine the feasibility of using Zn/Al-citrate for the removal of MG dyes from aqueous solution. The effect of different parameters including contact time, dye concentration and temperature were studied to optimize the sorption process. Descriptions of the adsorption process were explored through kinetic parameter, adsorption isotherm and thermodynamic parameter.

## 2. EXPERIMENTAL SECTION

### 2.1 Material and instrumentation

All the chemical used in this study were of analytical grade (p.a)  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$ ,  $N_2$  gas, NaOH, malachite green and aquadest. The instrument spectrophotometer UV-Vis (EMC-61-PC Spektrofotometer) used for measuring concentration of MG.

## 2.2 Methods

### 2.2.1 Synthesis of Zn/Al-citrate

Zn/Al LDHs was synthesized by coprecipitation method according to Palapa et al. (2019). As much as the solution containing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  0.3M and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  0.1M with molar ratio Zn/Al 3:1 was added one drop at a time to a vigorously stirred solution of NaOH and 1 M at a constant solution pH of 10. The resulting precipitate dried hydrothermally at  $80^\circ\text{C}$  for 18 h. Preparation of Zn/Al-citrate was conducted under nitrogen atmosphere, 2 gs of Zn/Al LDH gel was diluted by 50 mL deionized water whereas in another beaker 10 gs of citric acid was diluted by 50 mL deionized water. The solution of LDH added dropwise into citric acid with continuous stirring for 24 hours. Wash and dried obtained materials in room temperature.

### 2.2.2 Adsorption experiments

MG adsorption were determined using effect of contact time, initial concentration and temperature adsorption. As much as 0.02 g Zn/Al LDHs and Zn/Al-citrate LDHs were contacted with 25 mL of 100 mg/L MG solution for effect of adsorption time contact experiments by varying time ranging 5 to 180 minutes. The effect of initial concentration and temperature were determined by 140 and 190 mg/L for Zn/Al LDHs and Zn/Al-citrate LDHs, respectively, and the various temperature from 30 –  $60^\circ\text{C}$  after each adsorption experiment completed, samples were filtrated to separate supernatant and precipitate. Supernatants were analyzed using spectrophotometer at 617 nm.

## 3. RESULTS AND DISCUSSION

### 3.1 Kinetic Models

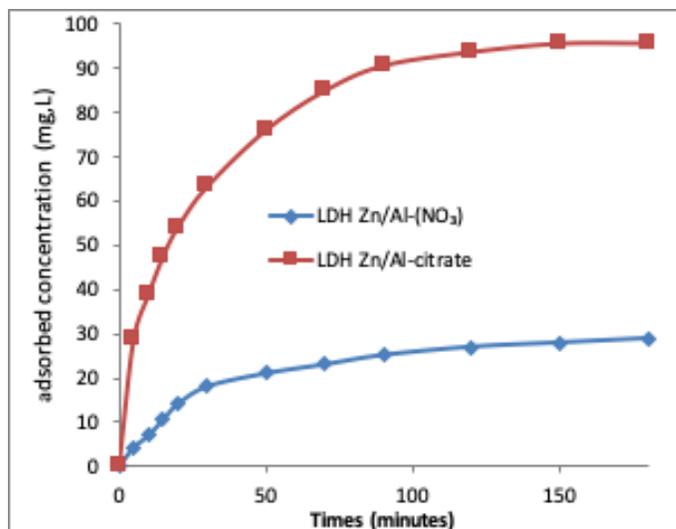
Successful application of malachite green removal by LDHs, can be achieved through high adsorption for malachite green in a short time. Fig 1 shows malachite green adsorption on LDHs as function of contact time. The rate of malachite Green removal by LDHs was sharp at initial time followed by a long slow decline. The adsorption equilibrium was fully established after 120 minutes for both of LDHs. The result show that adsorption of Zn/Al-citrate LDHs was higher than Zn/Al LDH.

The adsorption rate constant ( $k$ ) and malachite green adsorbed at equilibrium time were determined from the slope and intercept of linear plot of pseudo first order and pseudo second order according to Song et al. (2020). Table 1 showed mathematical form and parameter of both models.

Based on Table 1, both material were fitted in pseudo second order than pseudo first order according to coefficient correlation was closed to one. this phenomena were supported by adsorption rate of Zn/Al-citrate for was bigger than pristine. The adsorption capacity of both material indicated that the experimental adsorption capacity in pseudo second order better fitted by calculation adsorption capacity.

### 3.2 Isotherm Adsorption

The adsorption isotherms were obtained according Freundlich and Langmuir isotherm. The isotherm model parameters were listed in Table 2. Table 2 shows the values of the constants



**Figure 1.** Effect of time contact on malachite green adsorption onto Zn/Al LDHs

**Table 1.** Kinetics parameter for MG adsorption onto Zn/Al and Zn/Al-citrate

| Kinetic Model | Parameters                            | Zn/Al LDH | Zn/Al-citrate |
|---------------|---------------------------------------|-----------|---------------|
| PFO           | $q_{e_{exp}}$ ( $\text{mg/g}^{-1}$ )  | 36.181    | 119.636       |
|               | $q_{e_{calc}}$ ( $\text{mg/g}^{-1}$ ) | 31.9154   | 130.617       |
|               | $k_1$ ( $\text{min}^{-1}$ )           | 0.021     | 0.03915       |
|               | $R^2$                                 | 0.992     | 0.935         |
| PSO           | $q_{e_{exp}}$ ( $\text{mg/g}^{-1}$ )  | 36.181    | 119.636       |
|               | $q_{e_{calc}}$ ( $\text{mg/g}^{-1}$ ) | 43.4783   | 142.657       |
|               | $k_2$ ( $\text{g/mgmin}$ )            | 0.000692  | 0.000371      |
|               | $R^2$                                 | 0.997     | 0.998         |

obtained for the two models. Adsorption isotherm data using Freundlich and Langmuir adsorption isotherm of malachite green on Zn/Al LDHs showed that Langmuir isotherm adjusted best the experimental isotherm with  $R^2$  value 0.897-0.9935. It indicated homogeneity of adsorbent and formation monolayer of dye covering the surface of the adsorbent (dos Santos et al., 2017).

Table 2 also showed that the  $q_{max}$  of Zn/Al-citrate is better at lower temperature which amount of adsorption capacity maximum is 333 mg/g from Zn/Al LDHs is only 111 mg/g. This phenom indicated the intercalation process of Zn/Al LDHs was better adsorbed than pristine. However, the favorable of MG adsorption onto Zn/Al-citrate also denotes by  $K_L$  which is the value ranging  $0 < K_L < 1$  (Ahmad and Kumar, 2010)

### 3.3 Thermodynamic parameters for MG adsorption

The thermodynamic parameters which determined in the adsorption of malachite green dye on the synthesized LDHs including enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibbs free energy ( $\Delta G$ ). The value of Gibbs free energy ( $\Delta G$ ) is calculated from the enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) at various temperature. Thermodynamic

**Table 2.** Langmuir and Freundlich parameters for MG adsorption onto Zn/Al and ZnAl-citrate LDHs

| LDH           | Temperature (K) | Freundlich isotherm |       |        | Langmuir isotherm |              |        |
|---------------|-----------------|---------------------|-------|--------|-------------------|--------------|--------|
|               |                 | $K_F$               | N     | $R^2$  | $K_L$             | $q_m$ (mg/g) | $R^2$  |
| Zn/Al         | 303             | 2.559               | 1.437 | 0.9182 | 0.013             | 111.111      | 0.9753 |
|               | 313             | 7.328               | 2.146 | 0.9158 | 0.014             | 111.111      | 0.9474 |
|               | 323             | 13.868              | 3.058 | 0.9162 | 0.025             | 90.909       | 0.9843 |
|               | 333             | 20.137              | 4.032 | 0.9206 | 0.038             | 83.333       | 0.9935 |
| Zn/Al citrate | 303             | 20.417              | 2.183 | 0.8395 | 0.014             | 333.333      | 0.897  |
|               | 313             | 27.606              | 2.558 | 0.803  | 0.023             | 250          | 0.9231 |
|               | 323             | 33.729              | 2.89  | 0.8369 | 0.027             | 250          | 0.9579 |
|               | 333             | 36.475              | 3.021 | 0.7731 | 0.029             | 250          | 0.945  |

adsorption data parameters can be seen in Table 3.

**Table 3.** Thermodynamic parameters for MG adsorption onto Zn/Al and ZnAl-citrate LDHs

| T   | LDH           | $Q_e$<br>( $\text{mg}\cdot\text{g}^{-1}$ ) | $\Delta H$<br>( $\text{kJ}\cdot\text{mol}^{-1}$ ) | $\Delta S$<br>( $\text{J}\cdot\text{mol}^{-1}$ ) | $\Delta G$<br>( $\text{kJ}\cdot\text{mol}^{-1}$ ) |
|-----|---------------|--|---|--|---|
| 303 | Zn/Al         | 34.23                                      | 9.653   | 0.025  | 1.997   |
| 313 |               | 37.605                                     |   |  | 1.744   |
| 323 |               | 40.506                                     |   |  | 1.492   |
| 333 |               | 43.671                                     |   |  | 1.239   |
| 303 | Zn/Al-citrate | 118.776                                    | 4.904   | 0.23   | -1.95   |
| 313 |               | 121.308                                    |   |  | -2.176  |
| 323 |               | 123.734                                    |   |  | -2.403  |
| 333 |               | 126.213                                    |   |  | -2.629  |

Table 3 showed that the adsorption capacity of malachite green by Zn/Al LDH and Zn/Al-citrate increases with increasing temperatures. Enthalpy ( $\Delta H$ ) has a positive value so it can be seen that the reaction is endothermic. Gibbs free energy ( $\Delta G$ ) has a negative for Zn/Al-citrate denotes that the value MG adsorption process was spontaneity.

#### 4. CONCLUSIONS

Kinetics experiment showed adsorption of malachite green on Zn/Al-citrate LDHs fitted best to pseudo second order showing that process is controlled by chemical adsorption. The adsorption isotherm fitted best to the Langmuir model indicate that homogeneity of adsorbent and formation monolayer of dye covering the surface of the adsorbent. Thermodynamic parameters for Zn/Al-citrate confirmed that endothermic nature of adsorption process, increasing disorder process and spontaneous of adsorption process

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