Adsorption of congo red using Mg/Fe and Ni/Fe layered double hydroxides

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Abstract. Layered double hydroxides with different divalent ions i.e. Mg/Fe and Ni/Fe were synthesized using coprecipitation method at basic condition. Materials were characterized using X-Ray diffraction and FTIR analyses. Furthermore, Mg/Fe and Ni/Fe layered double hydroxides were applied as adsorbent of Congo red dye in aqueous medium using batch system. Adsorption of Congo red on layered double hydroxides was investigated through kinetic and thermodynamic studies. X-ray diffraction analysis showed that unique diffraction of layered materials were identified at 2θ diffraction 11.33°, 29.55°, 59.66° (Mg/Fe) and 11.41°, 29.40°, 60.40° (Ni/Fe). Interlayer distance of Mg/Fe and Ni/Fe layered double hydroxides was 7.80 Å and 7.75 Å, respectively. IR spectrum of Mg/Fe and Ni/Fe layered double hydroxides showed that vibration of layered material was appeared at 1381 cm⁻¹ (vN-O; nitrate), 347 cm⁻¹ (vMg-O; layered double hydroxides), 586 cm⁻¹ (vFe-O; layered double hydroxides) for Mg/Fe and 1381 cm⁻¹ (vNi-O; nitrate), 493 cm⁻¹ (vNi-O; layered double hydroxides), 516 cm⁻¹ (vFe-O; layered double hydroxides) for Ni/Fe. Kinetic pseudo second order was fitted than pseudo first order kinetic model for adsorption of Congo red with R² = 0.99 for both Mg/Fe and Ni/Fe. The rate of adsorption k₂ for Mg/Fe and Ni/Fe layered double hydroxides was 0.008 g.mg⁻¹ min⁻¹ and 0.0058 g.mg⁻¹ min⁻¹. Adsorption of Congo red on Mg/Fe and Ni/Fe layered double hydroxides was well described and following Freundlich adsorption isotherm model shows physical adsorption process on layered double hydroxides.

1. Introduction

Dyes are widely applied in various industries to colour product. Wastewater from the dyestuff manufacturing, dyeing, printing and textile industry represent a serious problem all over the world, because dyes in wastewater undergo chemical changes and destroy aquatic life and they even endangers human health [1]. Anionic reactive dyes are widely used in the tannery, paper, textile industries, distilleries, food beverage etc. Congo red is an anionic acid dye with solubility 1g/30 mL in water. It is used as a laboratory aid in testing for free hydrochloric acid in gastric content, in the diagnosis of amyloidosis, as an indicator of pH and also as a histological stain for amyloid. Due to its strong affinity to cellulose fibre Congo red thus is used in textile industries. Congo red is derivative of napthoic acid and benzidine and metabolizes to carcinogenic product. It is a eye, skin, and gastrointestinal irritant. It may affect blood factor such as clotting and induce somnolence and respiratory problem. Therefore an increased interest has been focused on removing of such dyes from wastewater [2].
Many methods have been used to decolorize dye wastewater including membrane filtration, coagulation, electrochemical methods, oxidation, adsorption and biological technology. Of these techniques, adsorption is a common method for dye removal because it is effective and economical [3]. There are numerous studies using different low cost adsorbent such as activated carbon, nano material, and some agricultural by product to remove colour from dye wastewater [4-6].

Layered double hydroxide (LDHs) 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. LDH is formed following the general formula $[\text{M}^{1-\chi}\text{M}^{\chi+2}\text{M}^{\chi+3}(\text{OH})_{2}]^{\chi+3}[\text{A}_{x/n}.\text{mH}_2\text{O}]$, where $x$ is the molar ratio $\text{M}^{\chi+3}/(\text{M}^{\chi+2}+\text{M}^{\chi+3})$. Being similar to clay mineral LDH is mainly used as adsorbent, ion exchangers, photocatalystetc [7].

The aim of this study was to examine the feasibility of using Ni/Fe and Mg/Fe layered double hydroxides for the removal of Congo red 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 and thermodynamic parameter.

2. Materials and Methods

2.1. Materials
All the chemical used in this study were of analytical grade Fe(NO$_3$)$_2$.9H$_2$O, Mg(NO$_3$)$_2$.6H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O, NaOH, Na$_2$CO$_3$, NaCl, HCl, Congo red and aquades.

2.2. Instrumentation
The instrument used for characterization included Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu Prestige-21) for identifying the presence of functional group, XRD spectrophotometer (Shimadzu XRD-6000) for evaluating the crystallinity and UV-Vis spectrophotometer (EMC-61-PC Spectrophotometer) for measuring concentration of Congo red.

2.3. Methods

2.3.1. Synthesis of Ni/Fe layered double hydroxide [8]. Ni/Fe layered double hydroxide was synthesized by co-precipitation method. An aqueous solution containing Ni(NO$_3$)$_2$.6H$_2$O 0.3M and Fe(NO$_3$)$_2$.9H$_2$O 0.1M with molar ratio Ni/Fe 3:1 was added one drop at a time to a vigorously stirred solution of NaOH and Na$_2$CO$_3$ 1 M at a constant solution pH of 10. The resulting precipitate dried hydrothermally at 80°C for 18 h.

2.3.2. Synthesis of Mg/Fe layered double hydroxide [9]. Mg/Fe layered double hydroxide was synthesized by co-precipitation method. An aqueous solution containing Mg(NO$_3$)$_2$.6H$_2$O 0.3M and Fe(NO$_3$)$_2$.9H$_2$O 0.1M with molar ratio Mg/Fe 3:1 was added one drop at a time to a vigorously stirred solution of NaOH and Na$_2$CO$_3$ 1 M at a constant solution pH of 10. The resulting precipitate dried hydrothermally at 100°C for 10 h.

2.3.3. Characterization of Ni/Fe and Mg/Fe layered double hydroxides. X ray diffraction (XRD) pattern were recorded from 20 = 5 to 70° using X-Ray diffraction RigakuMinifex 600. FTIR spectra were collected on spectrophotometer FT-IR Shimadzu Prestige-21. Sample wasmixed with KBr and spectra were recorded in range 4000-400 cm$^{-1}$.

2.3.4. Adsorption experiments. Stock solution of 25g/L of Congo red was prepared by dissolving the appropriate amount of the dye in distilled water and the used concentration were obtained by dilution. Adsorption experiments were performed by batch methods in a series contact time from 10 to 120 minutes, the initial dyes concentration from 20 to 200 mg/L and temperature from 10-70°C. After each adsorption experiment completed, samples were filtrated to separate supernatant and precipitate. Supernatants were analyzed using spectrophotometer at 497 nm.
3. Result and Discussion

3.1. Characteristic of LDHs

The XRD pattern of LDHs sample is shown in fig 1. The sharp and symmetrical peak of the diffractogram for both Ni/Fe-LDH and Mg-Fe LDH indicated that these synthetic sample has ordered layered structure. X-ray diffraction analysis showed that unique diffraction of layered materials were identified at 2θ diffraction 11.33°, 29.55°, 59.66° (Mg/Fe) and 11.41°, 29.40°, 60.40° (Ni/Fe). Interlayer distance of Mg/Fe and Ni/Fe layered double hydroxides was 7.80 Å and 7.75 Å, respectively.

Fig. 2 shows the LDH infrared spectra in the 4000-400 cm\(^{-1}\) range. The adsorption peak at 3400 and 3400 were due to the overlapping stretching vibrations of the interlayer water and hydroxyl group. The observed peak at around 1632 cm\(^{-1}\) can be assigned to the bending vibration of the interlayer water. The band peaks in the 500-700 cm\(^{-1}\) region were the characteristic metal oxide absorption peak. FTIR spectrum of Mg/Fe and Ni/Fe layered double hydroxides showed that vibration of layered material was appeared at 1381 cm\(^{-1}\) (vN-O; nitrate), 347 cm\(^{-1}\) (vMg-O; layered double hydroxides), 586 cm\(^{-1}\) (vFe-O; layered double hydroxides) for Mg/Fe and 1381 cm\(^{-1}\) (vN-O; nitrate), 493 cm\(^{-1}\) (vNi-O; layered double hydroxides), 516 cm\(^{-1}\) (vFe-O; layered double hydroxides) for Ni/Fe.

![Figure 1. XRD patterns of Ni/Fe LDH (a) and (b) Mg/Fe LDH](image-url)
3.2. Adsorption kinetics
Successful application of Congo red removal by LDHs can be achieved through high adsorption for Congo red in a short time. Fig 3 shows Congo red adsorption on Ni/Fe and Mg/Fe LDHs as function of contact time. The rate of Congo red removal by LDHs increased rapidly in the initial 50 min followed by a long slow decline. At the first 10 minutes about 66% and 90% of Congo red adsorption occurred for Mg/Fe LDH and Ni/Fe LDH respectively. The equilibrium of adsorption process was fully established after 100 minutes for both of LDHs. The results showed that adsorption of Ni/Fe LDH were higher than Mg/Fe LDH.

Figure 2. FTIR spectra of Mg/Fe LDH (a) and (b) Ni/Fe LDH

Figure 3. Congo red adsorption on LDHs as a function of time
The rate constant (k) of adsorption and Congo red adsorbed (mg g\(^{-1}\)) at equilibrium time were determined through the intercept and slope of linear plot of pseudo first order and pseudo second order. Table 1 shows parameter of both models. Congo red adsorption on both LDHs fitted to pseudo second order as evidenced by the higher R\(^2\).

| Table 1. Kinetic parameters of Congo red adsorption by LDHs |
|-------------------------------------------------------------|
| Kinetic Model | Parameters | Ni/Fe LDH | Mg/Fe LDH |
| Pseudo-first-order | q\(_e\) experiment (mg g\(^{-1}\)) | 8.7959 | 7.612 |
|                  | q\(_e\) calculation (mg g\(^{-1}\)) | 16.8418 | 7.194 |
|                  | k\(_1\) (min\(^{-1}\)) | 0.0650 | 0.044 |
|                  | R\(^2\) | 0.9250 | 0.916 |
| Pseudo-Second-order | q\(_e\) experiment (mg g\(^{-1}\)) | 8.7959 | 7.612 |
|                  | q\(_e\) calculation (mg g\(^{-1}\)) | 10.2873 | 8.543 |
|                  | k\(_2\) (g/mg min\(^{-1}\)) | 0.0058 | 0.008 |
|                  | R\(^2\) | 0.9933 | 0.997 |

3.3. Adsorption isotherm
The characteristic of the adsorption equilibrium was analyzed through adsorption isotherm study. To analyze the equilibrium adsorption data some isotherm adsorption models used including Langmuir and Freundlich. Thermodynamic parameters for adsorption of Congo red on the synthesized LDHs were shown in Table 2.

The value of R\(^2\) indicated that Congo red adsorption on both LDHs was better fit to the Freundlich model. This result suggests that the adsorption Congo red on the LDHs is not limited by monolayer coverage. Freundlich adsorption isotherm model is widely used for multilayer adsorption on heterogeneous surface (X). Adsorption Congo red by the Mg/Fe and Ni/Fe LDHs however is not limited to the external surface and might be attributed to higher adsorption of Congo red onto internal surface.

| Table 2. Adsorption isotherm data using Freundlich adsorption isotherm on LDHs |
|-------------------------------------------------------------|
| Temperature | Parameter | Ni/Fe LDH | Mg/Fe LDH |
| 30 °C | K\(_F\) | 0.928 | 1.002 |
|       | N | 1.754 | 1.116 |
|       | R\(^2\) | 0.722 | 0.902 |
| 40 °C | K\(_F\) | 0.982 | 1.385 |
|       | N | 1.531 | 1.040 |
|       | R\(^2\) | 0.817 | 0.897 |
| 50 °C | K\(_F\) | 2.061 | 1.517 |
|       | N | 0.997 | 1.043 |
|       | R\(^2\) | 0.833 | 0.975 |
| 60 °C | K\(_F\) | 1.374 | 2.178 |
|       | N | 1.488 | 1.127 |
|       | R\(^2\) | 0.888 | 0.971 |
| 70 °C | K\(_F\) | 1.169 | 4.294 |
|       | N | 1.211 | 1.423 |
|       | R\(^2\) | 0.923 | 0.940 |

K\(_F\) = Isotherm Freundlich constant
n = Degree of adsorption freedom
3.4. Thermodynamic parameters for adsorption of Congo red

Thermodynamic parameter of Congo red adsorption on both Ni/Fe and Mg/Fe also were determined including enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG). Enthalpy (ΔH) and entropy (ΔS) were calculated as slope and intercept from lnq_e/c versus 1/T whereas the Gibbs free energy (ΔG) was calculated as follow ΔG = ΔH - TΔS. Thermodynamic parameters for adsorption of Congo red on the synthesized LDHs were shown in Table 3.

Negative enthalpy as shown in Table 3 shows that Congo red adsorption reaction on LDHs is exothermic reaction. Low enthalpy values indicate that Congo red dyes are adsorbed through physical interactions. The negative values of ΔG indicate that adsorptions Congo red on LDHs are spontaneous.

| Conc. (mg/L) | T (K) | Mg/Fe LDH | Ni/Fe LDH |
|--------------|-------|-----------|-----------|
| Q_e (mg.g⁻¹) | ΔS (kJ/mol) | ΔH (kJ/mol) | ΔG (kJ/mol) | Q_e (mg.g⁻¹) | ΔS (kJ/mol) | ΔH (kJ/mol) | ΔG (kJ/mol) |
| 5 | 303 | 0.74 | 74.44 | -26.663 | 1.1055 | 65.7629 | -22.1485 | -19.9483 |
| | 313 | 0.88 | -49.96 | 1.3436 | -20.6059 |
| | 323 | 1.02 | -50.71 | 1.4796 | -21.2636 |
| | 333 | 1.17 | -51.45 | 1.5817 | -21.9212 |
| | 343 | 1.53 | -52.19 | 1.7518 | -22.5788 |
| 10 | 303 | 1.35 | 82.65 | -29.382 | 5.9183 | 83.4559 | -28.2277 | -25.3154 |
| | 313 | 1.71 | -55.25 | 5.7142 | -26.1499 |
| | 323 | 2.05 | -56.08 | 4.3537 | -26.9845 |
| | 333 | 2.43 | -56.90 | 3.6734 | -27.8191 |
| | 343 | 3.01 | -57.73 | 2.9931 | -28.6536 |
| 15 | 303 | 2.00 | 72.63 | -26.297 | 10.2721 | 77.9046 | -27.2965 | -23.6324 |
| | 313 | 2.50 | -49.03 | 9.1156 | -24.4115 |
| | 323 | 3.13 | -49.76 | 7.6870 | -25.1905 |
| | 333 | 3.61 | -50.48 | 6.9387 | -25.9696 |
| | 343 | 4.12 | -51.21 | 5.6326 | -26.7486 |
| 20 | 303 | 3.56 | 54.04 | -19.721 | 14.4217 | 85.3765 | -30.1241 | -25.8992 |
| | 313 | 4.07 | -36.10 | 12.9251 | -26.7530 |
| | 323 | 4.46 | -37.18 | 11.8367 | -27.6067 |
| | 333 | 4.94 | -37.72 | 9.5918 | -28.4605 |
| | 343 | 5.95 | -38.26 | 7.7551 | -29.3143 |
| 25 | 303 | 3.52 | 47.17 | -18.316 | 19.3197 | 87.4799 | -31.4468 | -26.5378 |
| | 313 | 4.35 | -32.61 | 17.3469 | -27.4126 |
| | 323 | 4.89 | -33.08 | 16.5986 | -28.2874 |
| | 333 | 5.39 | -33.55 | 15.1972 | -29.1622 |
| | 343 | 6.07 | -34.02 | 13.9523 | -30.0370 |
| 30 | 303 | 3.38 | 63.76 | -24.185 | 23.0612 | 80.9417 | -29.2045 | -24.5546 |
| | 313 | 3.87 | -43.50 | 20.0068 | -25.3640 |
| | 323 | 5.73 | -44.78 | 18.5374 | -26.1734 |
| | 333 | 6.21 | -45.42 | 16.5306 | -26.9828 |
| | 343 | 6.76 | -46.06 | 13.1758 | -27.7922 |
4. Conclusions
Layered double hydroxides with different divalent ions i.e. Mg/Fe and Ni/Fe can be prepared by precipitation method at basic condition. X-ray diffraction and FTIR analysis confirmed the successful synthesis of Mg/Fe and Ni/Fe LDHs. Both of LDHs can adsorb Congo red in aqueous solution. Kinetic pseudo second order was fitted for adsorption of Congo red for both Mg/Fe and Ni/Fe. The rate of adsorption $K_2$ for Mg/Fe and Ni/Fe layered double hydroxides was 0.008 g.mg$^{-1}$min$^{-1}$ and 0.0058 g.mg$^{-1}$min$^{-1}$. Adsorption of Congo red on Mg/Fe and Ni/Fe layered double hydroxides was well described and following Freundlich adsorption isotherm model shows physical adsorption process on layered double hydroxides.

Acknowledgements
We gratefully acknowledge the financial support from DIPA Sriwijaya University through Hibah Profesi 2017-2018.

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