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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} (νN-O; nitrate), 347 cm^{-1} (νMg-O; layered double hydroxides), 586 cm^{-1} (νFe-O; layered double hydroxides) for Mg/Fe and 1381 cm^{-1} (νN-O; nitrate), 493 cm^{-1} (νNi-O; layered double hydroxides), 516 cm^{-1} (νFe-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 R ± 0.99 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.

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 ananionic 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 benzidineand metabolizes to carcinogenic product. It is aeye,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].

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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 $[M_{1-x}^{+2}M_x^{+3}(OH)_2]^{+3}[A_{x/n}].mH_2O$, where x is the molar ratio $M^{+3}/(M^{+2}+M^{+3})$. 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 gradeFe$(NO_3)_2.9H_2O$, $Mg(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, NaOH,Na_2CO_3, NaCl, HCl, Congo red and aquadest.

2.2. Instrumentation

The instrument used for characterization included Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu Prestige-21) for identifying the presence offunctional 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 $Ni(NO_3)_2.6H_2O$ 0,3M and $Fe(NO_3)_2.9H_2O$ 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_2CO_3 1 M at a constant solution pH of 10. The resulting precipitate dried hydrothermally at 80°C for18 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 $Mg(NO_3)_2.6H_2O$ 0,3M and $Fe(NO_3)_2.9H_2O$ 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_2CO_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 2Θ = 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 performedby 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} (νN-O; nitrate), 347 cm^{-1} (νMg-O; layered double hydroxides), 586 cm^{-1} (νFe-O; layered double hydroxides) for Mg/Fe and 1381 cm^{-1} (νN-O; nitrate), 493 cm^{-1} (νNi-O; layered double hydroxides), 516 cm^{-1} (νFe-O; layered double hydroxides) for Ni/Fe.

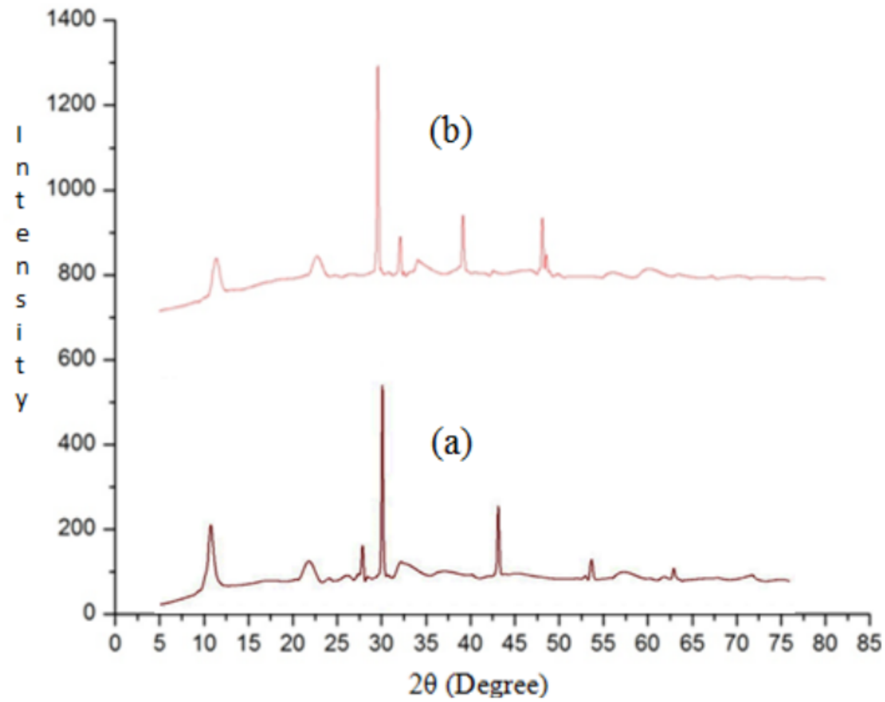

Figure 1. XRD patterns of Ni/Fe LDH (a) and (b) Mg/Fe LDH

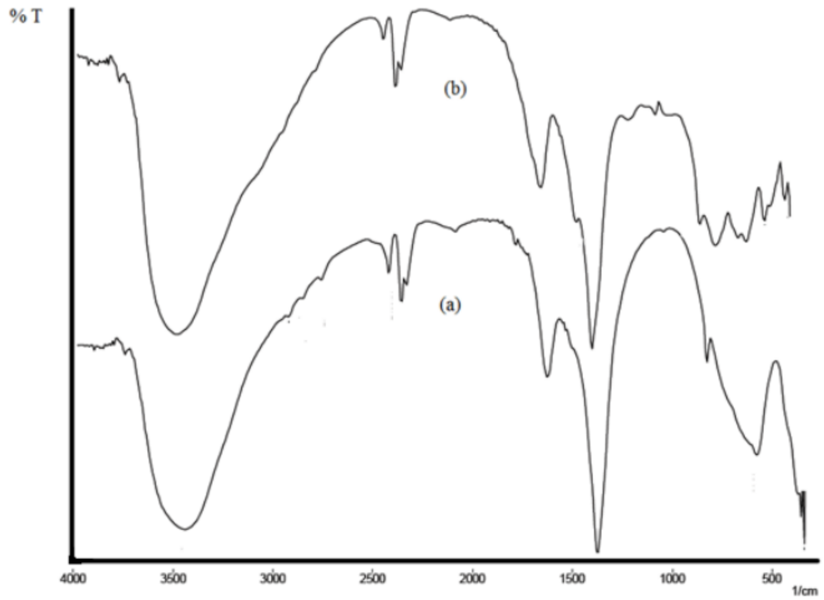

Figure 2. FTIR spectra of Mg/Fe LDH (a) and (b) Ni/Fe LDH

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 3shows 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 about66 % and 90 % of Congo red adsorptionoccurred 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.

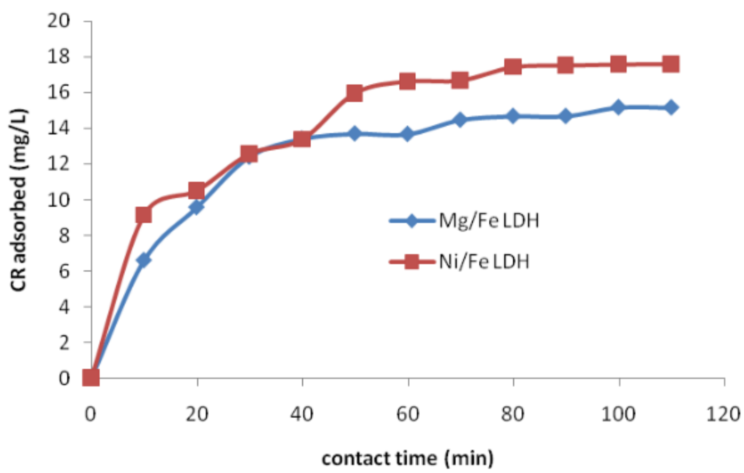

Figure 3. Congo red adsorption on LDHs as a function of time

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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 experiment (mg g^{-1})	10.2873	8.543
	k_2 (g/mg min)	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 isoterm 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 = Isoterm Freundlich constant
n = Degree of adsorption freedom

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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 calculatedas slope and interceptfromlnq_e/c_eversus 1/T whereas the Gibbs free energy (G) 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 indicatethose adsorptions Congo red on LDHs are spontaneous.

Table 3. Thermodynamic parameters for adsorption of Congo red on LDHs

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	-49.22	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	-54.42	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	-48.30	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	-36.10	14.4217	85.3765	-30.1241	-25.8992
	313	4.07			-36.64	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	-32.61	19.3197	87.4799	-31.4468	-26.5378
	313	4.35			-33.08	17.3469			-27.4126
	323	4.89			-33.55	16.5986			-28.2874
	333	5.39			-34.02	13.1972			-29.1622
	343	6.07			-34.50	10.9523			-30.0370
30	303	3.38	63.76	-24185	-43.50	23.0612	80.9417	-29.2045	-24.5546
	313	3.87			-44.14	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

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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 ofMg/Fe and Ni/Fe LDHs. Both of LDHs can adsorbCongo 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* 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.

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