ANIONIC AND CATIONIC DYES REMOVAL FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO SYNTHETIC Mg/Al HYDROTALCITE-LIKE COMPOUND

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ABSTRACT

The current investigation reports an effective adsorption of both anionic species and cationic dyes on Mg/Al hydrotalcite-like compounds (Mg/Al HTlc) synthetic from brine water, as novel, inexpensive available alternative to the commercial hydrotalcite. The feasibility of the Mg/Al HTlc, for the adsorptive removal of both anionic (Eosin Yellow-EY and Methyl Orange-MO) and cationic (Methylene blue-MB) dyes from aqueous solution was evaluated in a batch process. Dyes adsorption process was thoroughly studied from both kinetic and equilibrium points of view for all adsorbents. The adsorption kinetics was tested for the pseudo-first order and pseudo-second order kinetic models at different experimental conditions. The dyes adsorption follows the pseudo-second order kinetics model, with correlation coefficients close to unity when experimental data were fitted in the model. The experimental isotherm data were analyzed using Langmuir and Freundlich isotherms. The results from Langmuir isotherm indicated that the capacity of Mg/Al HTlc for the adsorption of anionic dyes was higher than that for cationic dyes.

Keywords: *anionic dye; cationic dye; Mg/Al Hydrotalcite-like synthetic; commercial hydrotalcite*

ABSTRAK

Telah dilakukan adsorpsi zat warna anionik maupun kationik yang efektif dengan senyawa baru Mg/Al hydrotalcite-like (Mg/Al HTlc) sintetis dari brine water yang murah dengan dibandingkan hydrotalcite komersial. Adsorpsi dilakukan untuk menghilangkan senyawa warna anionik (Eosin Yellow-EY dan Methyl Orange-MO) dan senyawa kationik (Methylene blue-MB) dalam larutannya dengan proses batch. Untuk kedua adsorben dipelajari pula kinetika dan keadaan kesetimbangannya. Kinetika adsorpsi diuji dengan model kinetika pseudo-first order dan pseudo-second order. Hasilnya menunjukkan bahwa laju adsorpsi mengikuti model kinetika pseudo-second order yang koefisien korelasinya mendekati satu ketika dicocokkan dengan data eksperimen. Data isotherm penelitian dianalisis dengan isotherm Langmuir dan Freundlich. Hasilnya menunjukkan bahwa kapasitas Mg/Al HTlc untuk adsorpsi senyawa warna anionik lebih besar daripada senyawa warna kationik.

Kata Kunci: *senyawa warna anionik; senyawa warna kationik; Mg/Al Hydrotalcite-like sintetis; hydrotalcite komersial*

INTRODUCTION

An extensive application and large-scale production of synthetic dyes in textile, cosmetics, paper and pulp manufacturing, plastics, leather treatment, chemical, food, pharmaceutical industries and other industries can cause considerable environmental and wastewater pollution. Wastewater containing dye is usually difficult to treat due to their complex aromatic structures which provide them physicochemical, thermal and optical stability [1]. Further, due to the toxic, carcinogenic and mutagenic properties, the presence of even a small amount of synthetic dye into the natural aquatic streams is a serious health-risk factor [2]. In general, in terms of high efficiency and simplicity, adsorption was proven to be the superior technique for wastewater treatment than conventional physicochemical and biological processes including microbial biodegradation, photodegradation, coagulation and flocculation, chemical oxidation, membrane separation, reverse osmosis, etc. Currently activated carbon is the most widely used adsorbent for dye removal, but due to the expensive production and regeneration it is still considered uneconomical [2-3]. Therefore, in the past few years, there is a growing need to find low-cost, locally available, effective adsorbent for the removal of dyes. The extensive research has been undertaken to study the application

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of a number of natural resources including solid wastes such as natural and synthetic clay, as dye adsorbents have attracted interests [4-5].

Hydrotalcite-like compound (HTlc) also called layered double hydroxides (LDHs) are an interesting group of clay minerals which have been applied to the removal of numerous anionic pollutants from aqueous solution. Also known as anionic clays or hydrotalcite like materials LDHs consist of a layered structure similar to that of the mineral brucite ($Mg(OH)_2$)-like structure, as a class of anion layered compounds, have recently received considerable attention [6] because they can be widely used as catalysts, catalyst supports, stabilizers in polymer composites, drug delivery materials, adsorbents for wastewater treatment, etc. [7].

In LDHs a number of the divalent cations (M^{2+}) are substituted with a trivalent cation (M^{3+}) resulting in a layered structure which carries a net positive charge that is balanced by exchangeable anions intercalated into the interlayer regions. LDHs can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$, where M^{2+} is divalent cation, M^{3+} is trivalent cation, A^{n-} is the exchangeable anion (usually carbonate, chloride or nitrate) and $0.2 < x < 0.33$ [8-13].

In recent years, LDHs have been demonstrated as highly efficient adsorbents for removing anionic dyes from wastewater due to their high anionic exchange capacities and high layer charge densities. Both the features favor strong interaction with anion pollutants [14-16].

The aim of the present research is to explore the feasibility of utilizing brine water for Mg/Al HTlc synthetic as low-cost filter for dye removal in industrial wastewater. Brine water, also referred in the literature as concentrate or wastewater, is a by product of the desalination processes. The characteristic of brine water is almost same as seawater. They differ only in the concentration. Brine water discharge is more concentrated than seawater. In accordance Heraldy et al., 2012, the major chemical composition of sea water and brine water respectively are: sodium ion (Na^+) 16200 mg L^{-1}, 27054 mg L^{-1}; Chloride ion (Cl^-) 31800 mg L^{-1}, 53106 mg L^{-1}; magnesium ion (Mg^{2+}) 5395 mg L^{-1}, 9010 mg L^{-1}; Calcium ion (Ca^{2+}) 1205 mg L^{-1}, 2012 mg L^{-1}; sulphate ion (SO_4^{2-}) 2600 mg L^{-1}, 4342 mg L^{-1}; Potassium ion (K^+) 396 mg L^{-1}, 661 mg L^{-1} [17]. It is collected by grab sampling method from PT. Tanjung Jati B, Jepara, Central Java, Indonesia Coal Fire Power Plant. The present study focuses attention on the adsorption of three dyes (Eosin Yellow, Methyl Orange and Methylene Blue) on Mg/Al HTlc as adsorbent. In this study, two widely used adsorption isotherms, and two kinetic models were examined. Optimum conditions and kinetic study were evaluated to obtain highest dye removal capacity and certain constants related to the adsorption phenomena, respectively. In addition, a commercial hydrotalcite was used for further comparison.

EXPERIMENTAL SECTION

Materials

All reagents in analytical grade were obtained from Merck Co. Inc. (Germany) and used without further purification. In addition, commercial hydrotalcite characterized as well as comparison.

Instrumentation

Mac Science MXP3 X-ray Diffractometer was used for hydrotalcite structure identification, Horiba FT-720 spectrometer was used to functional group characterization in hydrotalcite, UV-vis spectrophotometer Hitachi 150-20 and Shimadzu AA 630-12 was used to analyze the brine water composition.

Procedure

Preparation of the adsorbent

Preparation of starting solution procedure. To a given volume (mL) brine water solution was added a number of a mixed of 0.001 M Na_2CO_3-0.002 M $NaHCO_3$ solution, stirring for 1 h at 95 °C and then the solution was filtrated.

Mg/Al HTlc procedure synthesis. Mg/Al hydrotalcite-like used in this study was prepared by a co-precipitation method following Kameda [18] with some modifications. Briefly, amount of as prepared 0.1 M Na_2CO_3 solution was added slowly to starting solution containing $AlCl_3.6H_2O$, with an initial Mg/Al molar ratio of 2.0 until pH 10.5 and then the solution was stirred for 1 h at 70 °C. The product was centrifuged to recover the white solid at a speed of 2000 rpm for 20 min. The wet cake was washed with distilled water until free of ion Chloride and dried overnight with oven.

Adsorption experiments

Stability test of Mg/Al HTlc. Fifty milligrams of Mg/Al HTlc was added to a series of 50 mL of aquabidest and the acidity was then adjusted to pH 3, 5, 7, 9, 11, and 13 using either HCl or NaOH solution. The mixture was stirred for 2 h. After separating supernatant from the solid, the remaining Mg/Al HTlc was dried by mean of heating in oven at 105 °C. The stability of Mg/Al HTlc was calculated based on the weight ratio of the remaining Mg/Al HTlc relative to its initial weight.

Effect of medium acidity. As conducted on the stability test of Mg/Al HTlc, a series of 50 mL of

5 mg L^{-1} dyes solutions were prepared and their acidity was adjusted to pH 3, 4, 6, 8, 10, 12, and 13 by using either HCl or NaOH solution. Into each dyes solution, 50 mg of Mg/Al HTlc was poured and then stirred for 2 h. After filtering, the concentrations of dyes solution in the supernatants were analyzed by using UV-vis spectrophotometer. Sample and blank solutions were analyzed under the same condition. The amount of dyes sorbed was determined from the difference between the initial and remaining amounts of dyes in the reacting solution each time the sample was analyzed.

Preparation of dyes solution. Every dyes solutions, Eosin Yellow (EY); Methyl Orange (MO) and Methylene Blue (MB) used as received without further purification. EY, MO and MB solutions were prepared by dissolving EY, MO and MB in aquabidest, respectively.

Adsorption kinetics. Batch adsorption kinetics studies of dyes onto hydrotalcite were carried out using a batch-type reactor of a 50 mL Erlenmeyer. The initial volume and dyes concentration were 50 mL and 5 mg L^{-1}, respectively. To each solution, 50 mg of hydrotalcite was added, the medium acidity was adjusted to pH 9.0, and stirred continuously. At selected time periods, a sample is immediately filtered. The concentration of the remaining dyes in the supernatant was analyzed by using UV–vis spectrophotometer. Sample and blank solutions were analyzed under the same conditions. The amount of dyes sorbed was calculated by the difference between the initial and remaining amounts of dyes in the reacting solution.

Capacity and energy adsorption. All batch adsorption experiments for the determination of capacity and energy of sorption were performed using a 50 mL Erlenmeyer. The initial volumes of the dyes solutions were 50 mL, and the concentrations of dyes in the solutions were varied from 0 to 30 mg L^{-1}. Into each dyes solution, 50 mg of hydrotalcite was added and followed by continuous stirring for 2 h. After stirring, the solutions were immediately filtered. The concentration of dyes remaining in the supernatant was analyzed by using UV–vis spectrometer. Sample and blank solutions were analyzed under the same conditions. The amount of each dyes adsorbed was calculated by the difference between the initial and the remaining amounts of dyes in the reacting solution.

RESULT AND DISCUSSION

Characterization of the Adsorbent

Representative XRD patterns of MgAl-HTlc are shown in Fig. 1 exhibit by the characteristic reflections of LDH materials [8,19]. It can be observed that a series of (*0 0 l*) peaks appear as sharp, intense and descending in order at low 2θ values and clear reflections at high 2θ values [20]. A number of small peaks at high 2θ values, indicating characteristic basal reflections of CO_3^{2-}HTlc materials were also observed. The three strong peaks about 11.59; 23.45 and 34.57° are characteristic of a layered structure and corresponds to the (*0 0 l*) reflections and the diffraction peak near 61.0° corresponds to the (*1 1 0*) crystal plane. Hence, the XRD pattern of the Mg/Al HTlc consists of both sharp and symmetrical peaks with some asymmetrical peaks at high angle, indicating good crystallinity [15]. It was thought that carbonate ion was intercalated into the product due to (*0 0 3*), (*0 0 6*) reflection of Mg/Al HTlc intercalated carbonate ion are around 7.58 and 3.80Å.

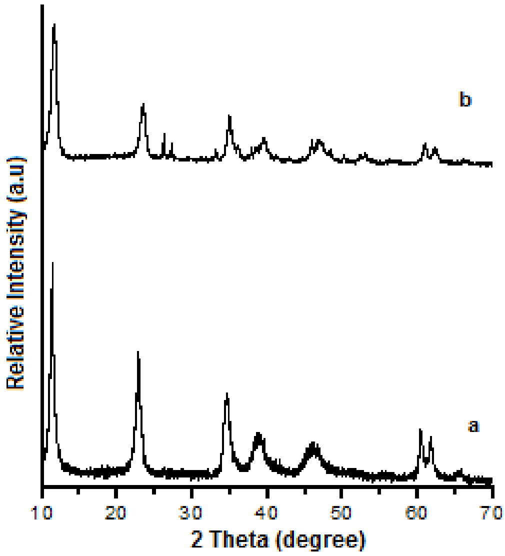

Fig 1. XRD patterns of the hydrotalcite samples: (a) Commercial, (b) Synthesis

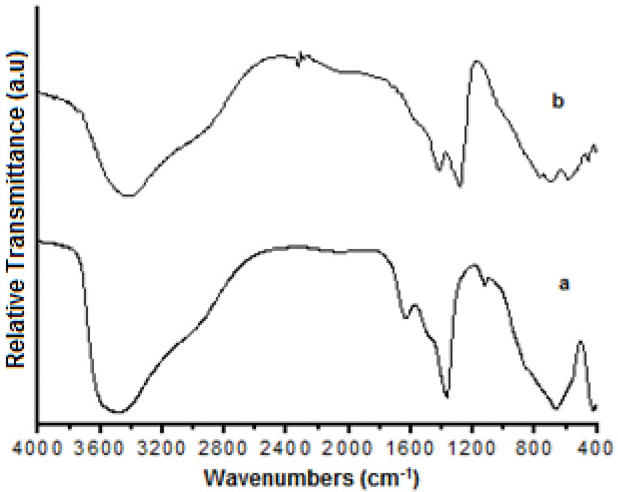

Fig 2. FTIR spectra of the hydrotalcite samples: (a) Commercial, (b) Synthesis

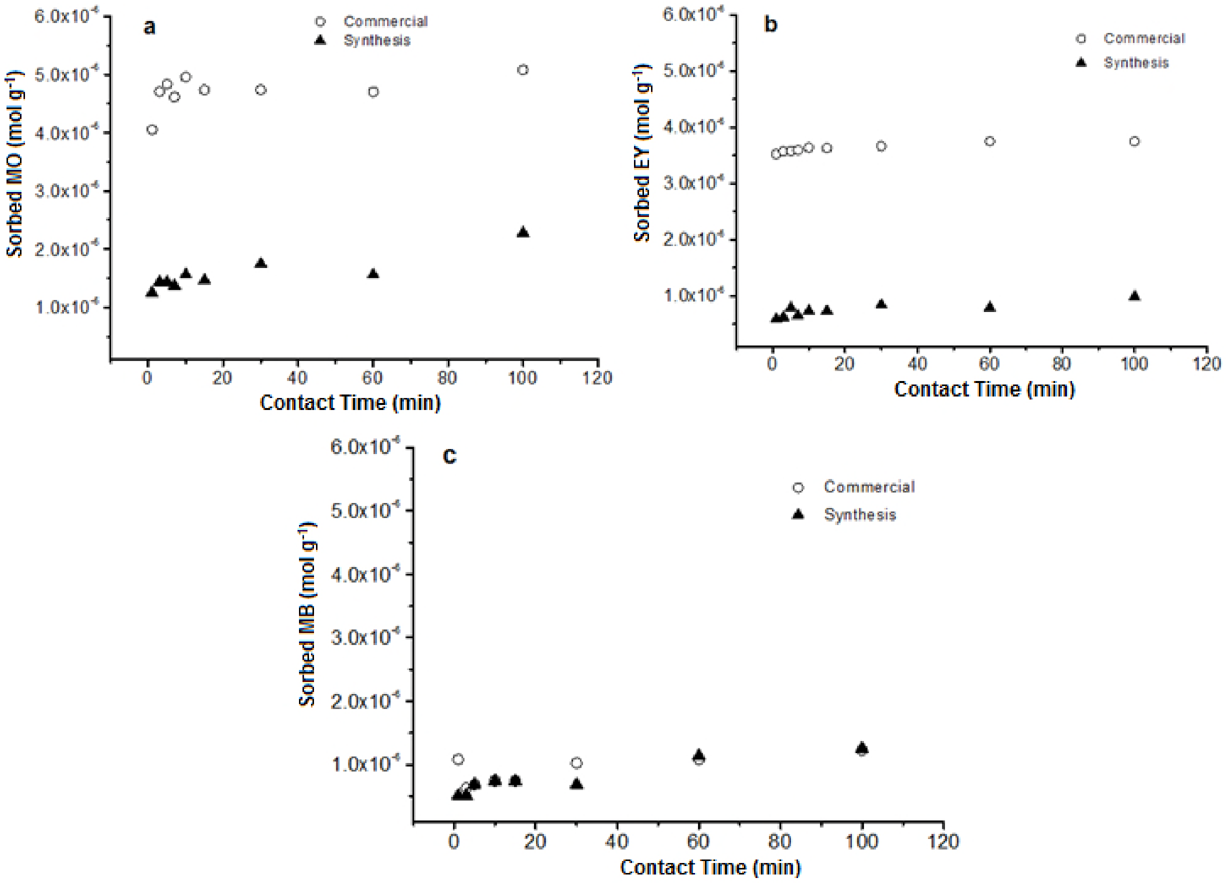

Fig 3. The effect of contact time on MO (a); EY (b) and MB (c) dyes adsorbed onto Mg/A hydrotalcite

Table 1. The specific surface areas and pore characteristics of the HTlc samples

Sample hydrotalcite	Average pore size (Å)	Pore volume (cm^{3}g^{-1})	Surface area (m^{2}g^{-1})
Commercial	13.923	50.76×10^{-3}	72.916
Synthetic	7.744	1.19×10^{-3}	30.823

FT-IR spectra of the hydrotalcite samples are shown in Fig. 2. It resembles that of other hydrotalcite-like phases with CO_3^{2-} as the counter anions [21]. There was strong and broad absorption band around 3440-3450 cm^{-1}, which was associated with a superposition of hydroxyl stretching band arising from metal-hydroxyl groups in the layers and hydrogen-bonded interlayer water molecules. The bending vibration of interlayer water is found at 1490-1500 cm^{-1}. The asymmetric vibration of carbonate anion appears around 1350 cm^{-1}. The peak below 1000 cm^{-1} is attributed to lattice vibration of Mg-O, Al-O and Mg-O-Al.

The porous structures of the hydrotalcite samples were characterized by N_2 adsorption–desorption analysis. The effect of changing the divalent metal cations on the pore structure and surface area of hydrotalcite were analyzed on the basis of nitrogen adsorption isotherms. The porous structure parameters of the hydrotalcites, such as the specific surface area, pore size and pore volume, are listed in Table 1. The results show that the hydrotalcites possess pore structure and surface area, which might be important for adsorption capacity in wastewater treatment.

Adsorption Kinetics

Effect of contact time

The effect of contact time on the adsorbed dyes onto Mg/Al hydrotalcites are shown in Fig. 3. The results reveal that the adsorption is fast in the initial 30 min; however it gradually becomes slower with passage of time reaching equilibrium in about 100 min. From this result, it can be said that kinetics of removal efficiency of both investigated dyes were formed in two phases: first, an initial rapid phase where the adsorption of dye molecules was fast and instantaneous, and the second phase was a slow stage in which the contribution to the total reactive dyes removal efficiency was relatively small, and finally the removal of both reactive dyes reached equilibrium [22]. The fastest adsorption, which occurred in the initial stage,

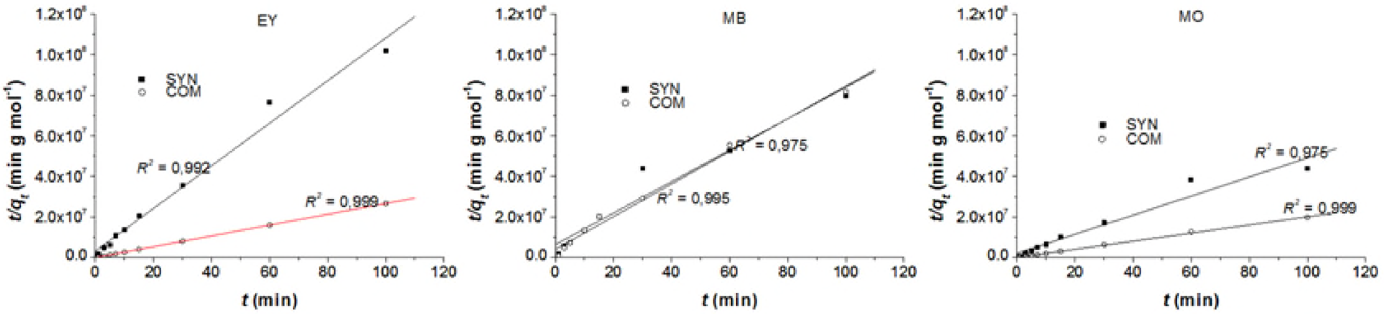

Fig 4. Plot of t/q_t against t in the kinetic model of pseudo second order adsorption reaching equilibrium dyes onto both Mg/Al HTlc

Table 2. Kinetic parameters of the dyes adsorption onto Mg/Al HTlc

Dyes	k_2 x 10^5 (g mol^{-1} min^{-1})		q_e x 10^{-7} (mol g^{-1})		R^2	
	Syn	Com	Syn	Com	Syn	Com
EY	3.37	8.43	9.53	37.64	0.992	0.999
MO	2.18	5.95	10.07	23.73	0.975	0.999
MB	1.71	2.86	6.98	6.73	0.975	0.995

may be associated with the existence of large numbers of vacant adsorption sites on the surface. However, fewer sites were available as the process continued, and the repulsive forces between the absorbed molecules and free molecules became stronger.

The kinetics is important for adsorption studies because it can describe the rate of adsorbate uptaken on HTlcs and control the equilibrium time. Fig. 3 results reveal that the adsorption is fast in the initial 30 min; however it gradually becomes slower with passage of time reaching equilibrium in about 100 min. From this result, it can be said that kinetics of removal efficiency three investigated dyes were formed in two phases: first, an initial rapid phase where the adsorption of dye molecules was fast and instantaneous, and the second phase was a slow stage in which the contribution to the total reactive dyes removal efficiency was relatively small, and finally the removal of both reactive dyes reached equilibrium [22]. The faster adsorption, which occurred in the initial stage, may be associated with the existence of large numbers of vacant adsorption sites on the surface. However, fewer sites were available as the process continued, and the repulsive forces between the absorbed molecules and free molecules became stronger.

Rate of sorption

To examine the mechanism of adsorption process, kinetics of dyes adsorption onto LDHs were analyzed using pseudo-second-order (Eq. (1)) that is in agreement with a chemisorption mechanism being the rate-determining step. The pseudo second-order kinetic model can be expressed as follows [23-24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (1)$$

where k_2 ($g^{-1}.mol^{-1}.min^{-1}$) and q_e, q_t are the pseudo second-order rate constant of adsorption and the adsorption capacity of dyes onto LDHs at equilibrium and time t. The q_e and k_2 can be obtained by linear plot of t/q_t versus t.

The correlation coefficients (R^2) for the model suggest a strong relationship between the parameters for both Mg/Al HTlc, which led conclusion that it is more suitable for describing the adsorption kinetics of MO, EY and MB dye. The parameters are presented in Table 2 showing that the commercial Mg/Al HTlc gives faster dye uptake rate and higher adsorption capacity than the synthetic one

Based on Fig. 4 summarized in Table 2 the adsorption rate constant (k_2) of commercial Mg/Al HTlc was higher 2.5; 2.7 and 1.6 times than that synthesis for EY, MO and MB, respectively. This condition indicates that HTlc commercial have larger pore size than HTlc synthetic and also have pore distribution of micropores to mesopores so that the diffusion from the outer surface to the inner surface is faster. The adsorption of dyes on the HTlc might be described as a four step process involving: (i) transport of the dyes in the bulk solution, (ii) sub-surface region diffusion, (iii) migration of adsorbate within the pores of the HTlc (intra-particle diffusion), and (iv) binding of the dyes on the active sites. The slowest one of these steps determines the overall rate of the adsorption process.

In addition, the adsorption capacity of Mg/Al HTlc commercial was larger 3.9 and 2.3 time than synthetic due to the specific surface area was 2.3 times larger than synthetic. With the big specific surface area, the adsorption rate of Mg/Al HTlc commercial to adsorption of dyes will be more. However, in case cationic dye,

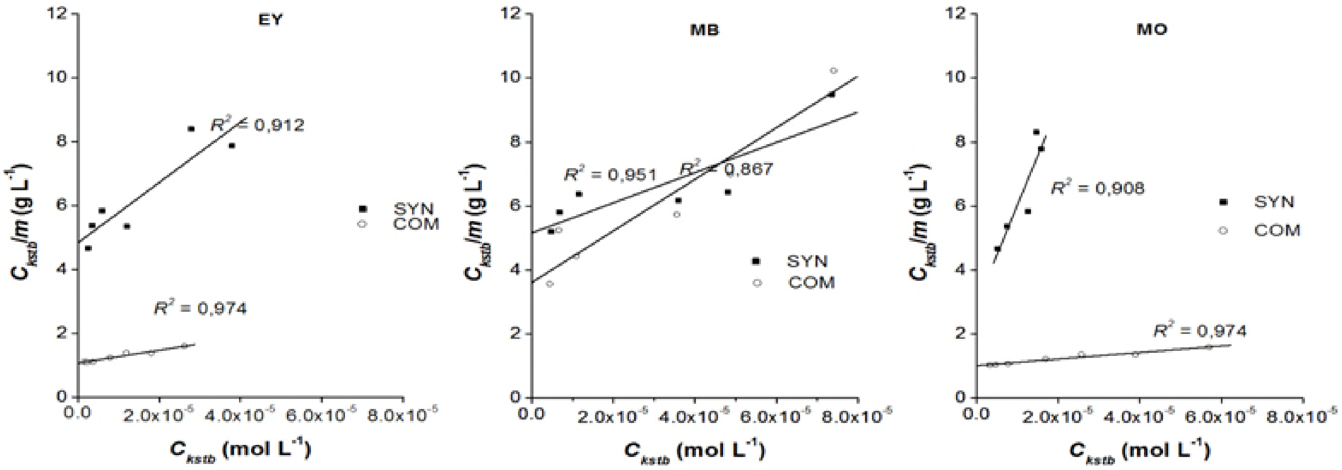

Fig 5. Profile of dyes sorption on Mg/Al HTlc a) synthesis and b) commercial in isotherm Langmuir model

the adsorption rate of both Mg/Al HTlc is similar. It is proven that for adsorption process of cationic dye (MB), the particle size or specific surface area of Mg/Al HTlc was not impact to adsorption rate of both adsorbent.

Adsorption isotherms

The equilibrium of adsorption is significant in describing the adsorption behavior. The parameters derived from the representing models provide important information on the adsorption mechanisms. Adsorption capacity at different aqueous equilibrium concentrations could be illustrated by the adsorption isotherm. In this research, in order to analyze the characteristics of the adsorption isotherms, two models including Langmuir, and Freundlich have been used to analyze the equilibrium adsorption data.

The non-linearized and linearized form of Langmuir isotherm model can be described as the following equation [25]:

$$q_e = \frac{q_m.K_L.C_e}{1+K_L.C_e} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L.q_m} \qquad (2)$$

where K_L (L.mol^{-1}) is the Langmuir adsorption constant related to the energy of adsorption, q_m and q_e (mol.g^{-1}) are the maximum and equilibrium adsorption capacity (mol.g^{-1}), respectively. The K_L indicates the affinity for the binding of reactive dyes. A high K_L value indicates a high affinity, while q_m represents the monolayer saturation at equilibrium when the surface is fully covered with dye molecules and assists in the explanation of adsorption performance. By plotting C_e/q_e against C_e, the values of q_m can be obtained from the 1/*slope*.

The linear plots of Langmuir model was showed in Fig. 5. From this plot of C_e/q_e against C_e, the obtained values of q_m for the adsorption of EY dye onto both commercial and synthetic Mg/Al HTlc were 4.99 and 1.06 $\times10^{-5}$ mol.g^{-1}; respectively. The linearity (R^2) of the plot were 0.974 and 0.912; respectively. Moreover, the obtained values of q_m and R^2 for the adsorption of MO dye and MB dye were presented in Table 3.

After obtaining q_m, the value of K_L is the able to be determined from the intercept of plot of C_e/q_e against C_e. The calculation yields K_L value for EY dye were 1.882 and 1.9552 $\times10^4$ (mol.L^{-1})$^{-1}$, respectively. Moreover, the calculation yields K_L value for the adsorption of MO dye and MB dye were presented in Table 3.

According to the equations $E_s = -G_s = RT \ln K_L$ [26], the adsorption energy (E_s) for EY dye adsorption onto Mg/Al HTlc are then obtained as high as 24.80 and 24.89 kJ.mol^{-1}, respectively. Moreover, the calculation yields E_s value for the adsorption of MO dye and MB dye were presented in Table 3.

Freundlich model applies to adsorption on heterogeneous surfaces with the interaction between the adsorbed molecules [27]. The non-linearized and linearized form of Freundlich isotherm model is given as the following equation [25]:

$$q_e = K_F C_e^{1/n} \qquad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (4)$$

while K_F (L.mol^{-1}) is the Freundlich constant, and 1/*n* is the heterogeneity factor. By plotting *ln* q_e versus *ln* C_e, the values of *n* and K_F can be obtained from the slope and the intercept of the linear plot. The values of 1/*n* imply the type of isotherm and can be classified as irreversible (1/*n* = 0), favorable (0 < 1/*n* < 1) and unfavorable (1/*n* > 1) [28-30]. The obtained values of 1/*n* (0.1 < 1/*n* < 1) showed the favorable nature of both investigated dyes and the heterogeneity of the adsorbent sites at temperatures studied.

The linear plots of Freundlich model was showed in Fig. 6. The fitted constants for the model along with regression coefficients were summarized in Table 3.

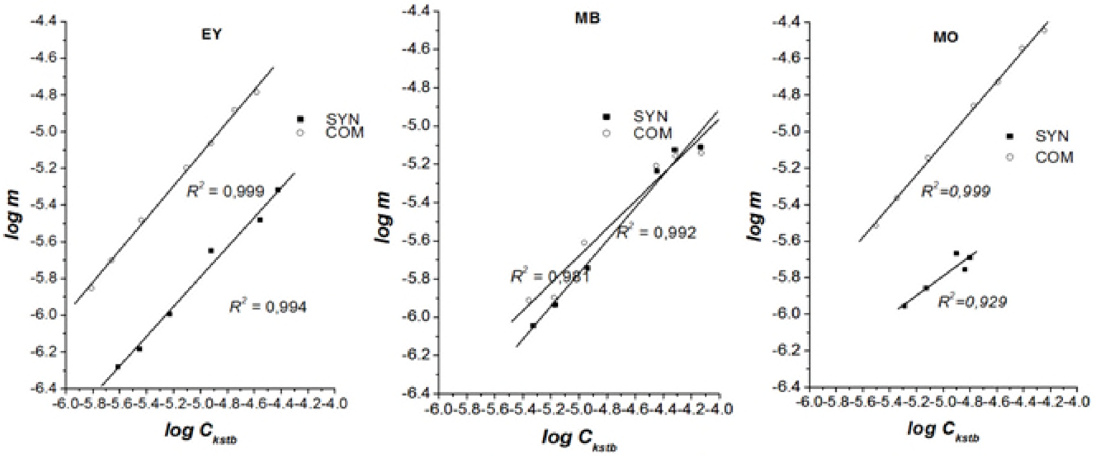

Fig 6. Profile of dyes sorption on Mg/Al HTlc a) synthesis and b) commercial in isotherm Freundlich model

Table 3. Adsorption capacity (q_m), energy (E), and affinity (K_L) were obtained from Langmuir isotherm and adsorption capacity (K_F) was obtained from Freundlich isotherm for sorption of dyes on Mg/Al HTlc

Adsorbent	Adsorption parameters						
	Langmuir				Freundlich		
	q_m (10^{-5}.mol.g^{-1})	K_L (mol.L^{-1})$^{-1}$	E^* (kJ.mol^{-1})	R^2	K_F (10^{-1}.mol.g^{-1})	n	R^2
EY dye							
Mg/Al HTlc-syn	1.06	19552	24.89	0.912	2.41	1.2	0.994
Mg/Al HTlc-com	4.99	18820	24.80	0.974	1.21	1.1	0.999
MO dye							
Mg/Al HTlc-syn	3.23	104989	29.13	0.908	4.93	1.9	0.929
Mg/Al HTlc-com	9.76	10100	23.22	0.974	0.99	1.2	0.999
MB dye							
Mg/Al HTlc-syn	2.12	9137	22.97	0.867	1.71	1.2	0.992
Mg/Al HTlc-com	1.32	18213	24.71	0.833	3.35	1.4	0.968

$*E = RT \ln K_L$

The R^2 values obtained for the Freundlich and Langmuir isotherms were all above 0.98, indicating a very good mathematical fit by both models. From Table 3, the calculated value of n (> 1) in the Freundlich equations indicated a favorable adsorption process [16]. This result showed that the adsorption process might be a heterogeneous adsorption.

CONCLUSION

The present study shows that the synthetic Mg/Al HTlc have been successfully used as an effective adsorbent for the removal of anionic and cationic dyes from aqueous solutions. The adsorption process obeyed the pseudo second-order model for the entire adsorption period. The adsorption is described by Freundlich-type isotherm due to the surface heterogeneity.

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