DECOLORIZATON OF METHYLENE BLUE DYE USING MAGNETIC *ANANAS COMOSUS* LEAF

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Abstract

The study was conducted to investigate the feasibility of using magnetic *Ananas comosus* leaf (MACL) as adsorbent for the removal of Methylene Blue (MB) dye. *Ananas comosus* leaf (ACL) was chosen due the availability of this waste material.The ACL was first pretreated with different concentration of nitric acid, HNO_3 to compare its surface area before modification process. Following that, ACL with the highest surface area was selected to produce MACL by precipitation of iron oxide on the surface of ACL. Both adsorbents, ACL and MACL were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), Scanning Electron microscopy (SEM) and Energy Dispersive X-Ray (EDX). The BET surface area of ACL and MACL recorded are 35.20 m^2/g and 81.42 m^2/g respectively. Equilibrium and kinetic studies were carried out under different pH of MB solution, adsorbent dosage, contact time and initial MB concentration. The equilibrium data were fitted to Langmuir and Freundlich isotherms. The equilibrium adsorption for both ACL and MACL were best described by the Langmuir isotherm, with MACL exhibiting a larger adsorption capacity compared to ACL. The sorption data was also analysed using pseudo-first-order and pseudo-second-order kinetic model. The experimental data obtained was found to follow pseudo-second-order with correlation coefficient R^2 of 0.9889 and 0.9998 for ACL and MACL respectively.

Keywords: Ananas comosus leaf, methylene blue, kinetic model, equilibrium study

INTRODUCTION

Discharge of untreated or partially treated dye from industrial wastewater into the environment poses a serious threat and danger to life, not only by retarding the physicochemical and biological properties of environmental components but also from the toxicological point of view.Hence, the removal of synthetic dyes such as methylene blue is of great concern since some dyes and their degradation products may be carcinogens and toxic [1]. Methylene blue (MB), is a heterocyclic aromatic chemical compound, also known as Swiss blue [2]. Among the available technologies for dye removal from aqueous media, adsorption is widely studied because it is efficient, easy to operate, environment-friendly, and easy to disseminate. Adsorption technique is preferredcompared to othertechniques such as biodegradation, electrochemical degradation, photochemical degradation, coagulation/flocculation, sonicated degradation, membrane filtration, among others because adsorption has been found to be an efficient and economical process for the removal of pigments and other colorants and also to control the bio-chemical oxygen demand. However, of late, attention has been geared towards the application of magnetic particle technology to overcome environmental problems. The magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and can be easily separated from the medium by a simple magnetic process after adsorption [4].

Adsorbent for the removal of MB from aqueous media was prepared from *Ananas comosus* leaf (ACL) or pineapple.The pineapple leaf is used in this study due to its availability in the pineapple industry. The production of magnetic *Ananas comosus* leaf (MACL) was carried out by precipitating iron oxide onto pretreated ACL. The characteristic of MB removal by ACL and MACL was analyzed by Langmuir and Freundlich adsorption isotherm through batch sorption experiment.

MATERIALS AND METHODS

Materials

The materials used for the study is ACL obtained from Pekan Nenas, Johor.Analytical grade sodium hydroxide pellet from Merck (99.5% purity), analytical grade Ferric chloridеferrous sulphate from Merck), nitric acid (Merck), ethanol and Methylene Blue from Sigma-Aldrich (M). The general chemical structure of Methyene Blue is illustrated in Figure 1.

Preparation and Characterization of ACL and MACL

The ACL were pre-treated by drying in an oven (80^0C), ground and sieved (<75 μm) until fine powder was obtained. The ground ACL was treated using different concentration of nitric acid (HNO_3) i.e. 0.1 M, 0.5 M and

 ISBN 978-967-0194-52-3

1.0 M for 24 hours. The magnetic ACL (MACL) was prepared by suspending 1.0 g ACL in 20 mL distilled water. A ferric chloride solution ($FeCl_3$) of 0.09 M was freshly prepared by adding 0.72 g of $FeCl_3$ into 52 mL distilled water. A ferrous sulphate solution, ($FeSO_4$) of 0.88 M was also prepared by adding 0.8 g $FeSO_4$ into 6 mL distilled water. Both solution were combined and vigorously stirred at 60-70^{0}C. The suspension formed was added into an aqueous solution of ACL at room temperature and stirred slowly for 30 min. After mixing, 10 M NaOH was added dropwise into the suspension until the pH raised to 10-11. After mixing for 60 min, the suspension was aged at room temperature for 24 hours and then repeatedly washed with distilled water followed by ethanol. The MACL was vacuum filtered and dried overnight at 50^{0}C in a hot air oven.The prepared ACL and MACL were characterized using BET Single Point Surface Analyzer, FTIR, XRD, XRF, FESEM-EDX, and SEM-EDX.

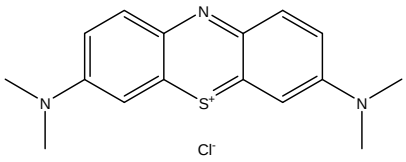

Figure 1: Chemical structure of MB dye

Batch Equilibrium Adsorption Study

Stock solution of MB was prepared by dissolving 0.1 g of MB into 1 L volumetric flask. The test solutions were prepared by diluting 1 mL, 1.5 mL, 2.0 mL, 2.5 mL and 3.0 mL are transferred into 100 mL volumetric flasks and diluted to series of 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L. A calibration curve was plotted using absorbance versus concentration of the solution to identify the concentration of MB solution after adsorption process.

The effect of ACL and MACL dose on the amount of MB adsorbed was obtained by contacting 100 mL of 50 mg/L MB solution with different amount of adsorbent. The amount of ACL and MACL used are in range of 0.1 to 1.0 g to see the effect of adsorbent dosage toward removal of MB.

The effect of pH on the removal of MB was analyzed under pH range 3-11. Experiments were conducted at 50 mg/L initial MB concentration for both 0.50 g ACL and MACL at 30 ^{o}C to observe whether pH is significant to the adsorption process.

A series of an appropriate concentration of 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L MB were prepared for quantifying the effect of initial MB concentration on adsorption rate with known amount of 0.50 g ACL and at a temperature of 30 ^{o}C.

RESULTS AND DISCUSSION

Characterization ACL and MACL

The FTIR spectra obtained revealed various functional groups on the surface of ACL and MACL. Based on the Table 1, some peaks were shifted or disappeared and new peaks were also detected. Iron oxide appeared at 473.17 cm^{-1} and 590.56 cm^{-1}at MACL indicates thepresence of iron oxide onto ACL.

Table 1: FTIR data of ACL and MACL

Functional group	ACL	MACL
O-H (stretching)	3367.10	3402.67
C-H (stretching)	2918.43	2920.05
C=O	1737.83	-
C=C (aromatic)	1638.76, 1459.34	1633.17, 1419.95
N=O	1516.61, 1383.81	-
C-N	1338.22	1341.01
Iron oxide	-	473.17, 590.56

Absorbance in cm^{-1}

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Surface area analysis (BET)

The surface areas of ACL and MACL treated with different concentration of nitric acid are shown in Table 2.The surface area analysis of ACL (35.20 m^2/g) and MACL (81.42 m^2/g) pretreated with 0.5 M HNO_3 shows the highest surface area .

Table 2: BET analysis of ACL and MACL

Sample	Surface area (m^2/g)
Raw ACL	7.69
ACL 0.1M HNO_3	31.70
ACL 0.5M HNO_3	35.20
ACL 1.0M HNO_3	32.02
MACL 0.1M HNO_3	69.80
MACL 0.5M HNO_3	81.42
MACL 1.0M HNO_3	65.52

Surface Morphology Analysis

Figure 1 (A-D) and Figure 1 (E-H) show the SEM micrograph of ACL and MACL at different magnification respectively. The ACL appears fibrouswith the presence of agglomerates. The MACL surface shows the presence of pores..Precipitation of of iron oxide onto surface of ACL plump out the agglomerated surface into a porous texture with iron oxide particles covering the pores. The distribution of pores are uniform. Pore development during iron oxide formation process enhanced the surface area of MACL compared to ACL.

Elemental Analysis

The elemental analysis of ACL and MACL are shown in Table 3. Elemental analysis of MACL shows the presence of iron attributed to the precipitationof iron oxide, confirming the precipitation of iron oxide on the ACL.

Table 3: Elemental analysis of ACL and MACL

Sample	Weight (%)				
	Carbon(C)	Oxygen(O)	Aluminium(Al)	Phosporus (P)	Iron (Fe)
ACL	59.78	40.22	-	-	-
MACL	34.44	38.76	1.04	1.07	29.66

Adsorption Isotherm Study

Effect of dosage

The effect of adsorbent dosage on adsorption of MB onto ACL and MACL is illustrated in Figure 2. From the graph of ACL, the percent removal of MB increased from 48.63% to 85.07% from an increased in ACL dosage from 0.10 to 0.80 g. It was observed that the percent removal MB increased with increasing adsorbent dosage until to 0.80g ACL and gradually remains unchanged. The highest percentage removal of MB achieved using ACL was 85.07% and the optimum dose was found to be 0.80g for 100 mL of MB solution.

MACL displayed highest percent removal of MB up to 95.92%. The percent removal of MB using MACL increased rapidly using varies amount of MACL of 0.10 to 0.50 g which showed the percent removal of 90.56% to 95.92%. The graphs concluded that MACL promoted higher MB removal compared to ACL. These may be associated to the presence of iron oxide. For MACL, the optimum dose was 0.50 g with percentage removal of 95.92%.

Effect of solution pH

The effect of pH on the adsorption capacity of MB on ACL and MACL was studied by performing equilibrium adsorption experiments at different pH. Based onFigure 3, ACL shows the highest adsorption capacity at higher pH and achieve equilibrium at minimum pH 7. The adsorption capacity of MB increased up to pH 8 and remained nearly constant at pH 9 and above. Lower adsorption capacity of MB at acidic pH is due to the presence of excess H^+ ions in the adsorbate which competes with cation groups on MB for adsorption site. A similar result was reported for adsorption of MB onto ACL and rejected tea [2][5].

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Similarly, MACL also shows equilibrium adsorption capacity at a minimum pH 7. However, MACL displayed higher adsorption capacity compared to ACL. Both graphs exhibited increase in adsorption capacity at increase pH.

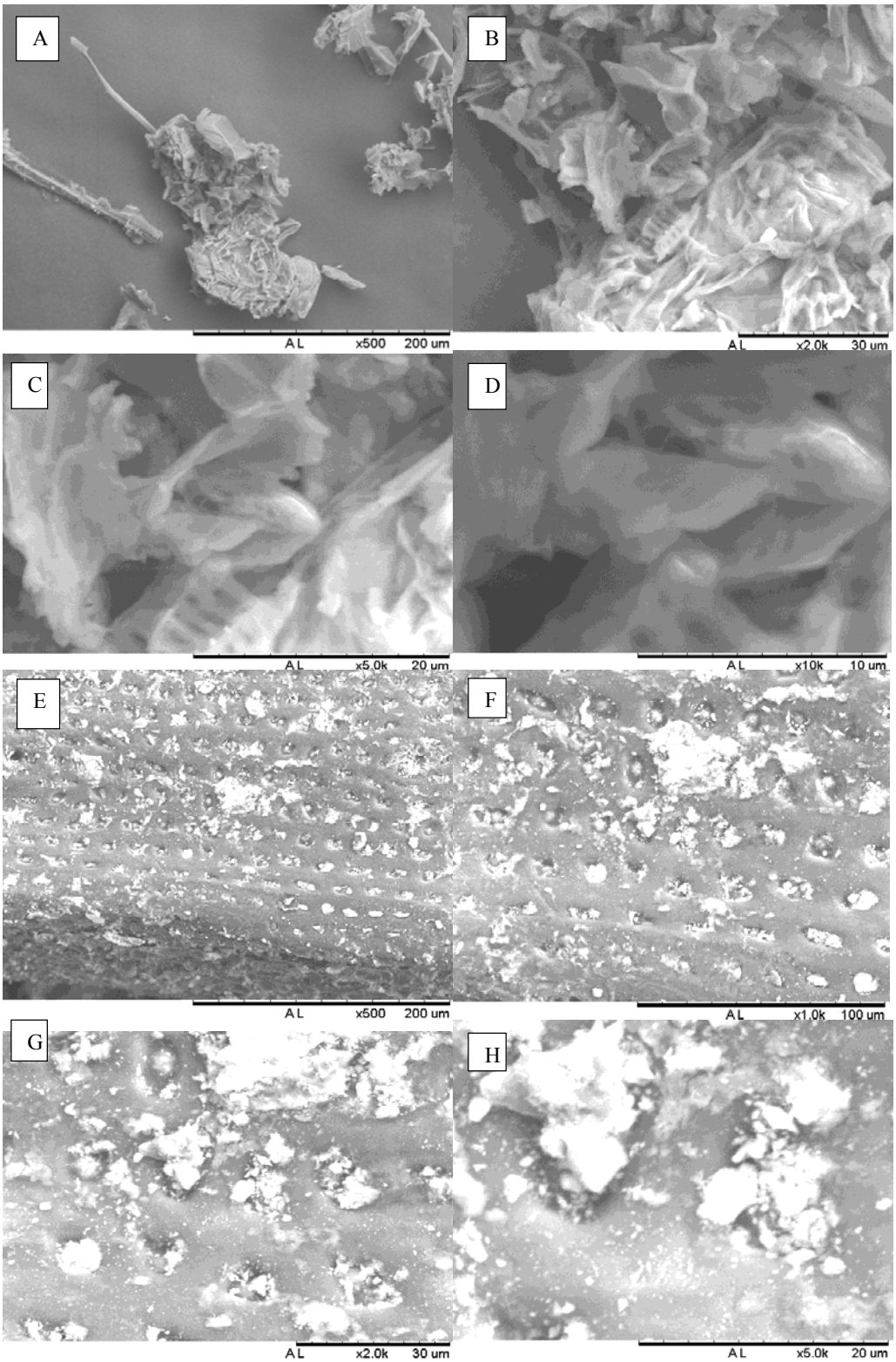

Figure 1 : SEM of ACL (A) x 500, (B) x 2.0k, (C) x 5.0k, (D) x 10.0k and MACL (E) x 500, (F) x 1.0k, (G) x 2.0k, (H) x 5.0k

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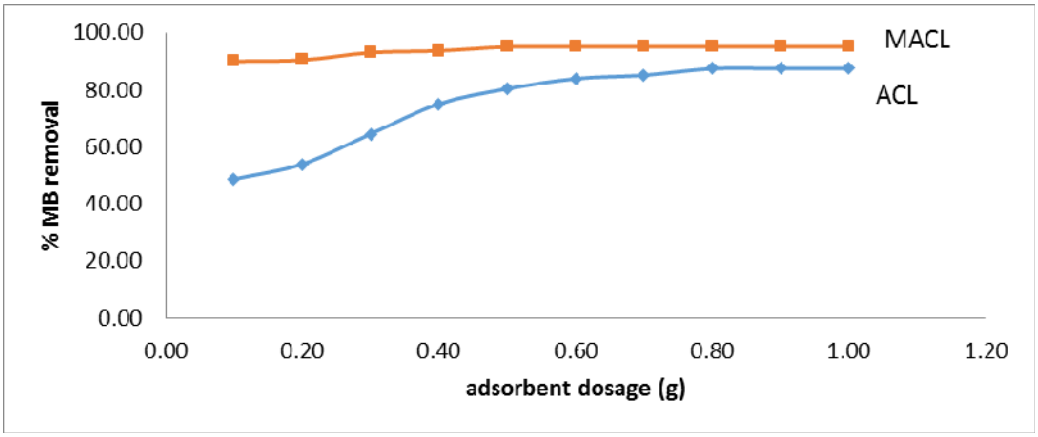

Figure 2: Effect of adsorbent dosage

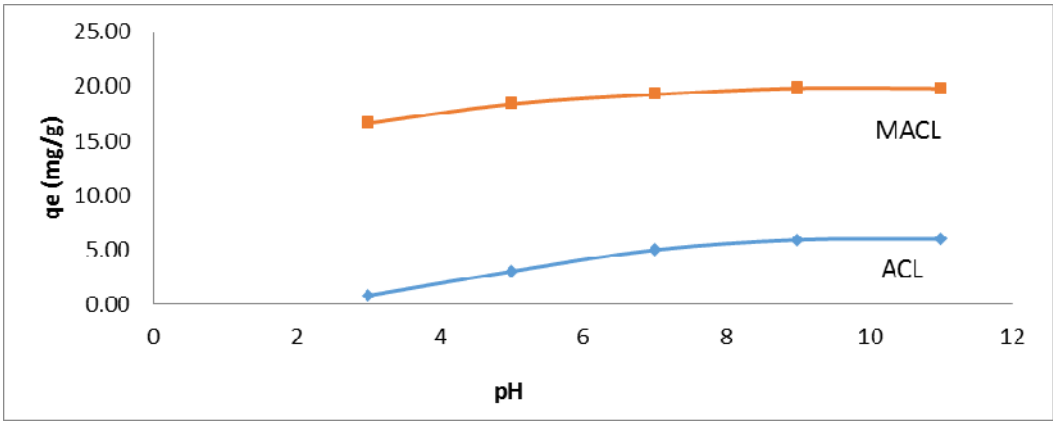

Figure 3: Effect of solution pH on adsorption of MB

Effect of initial concentration and contact time

Figure 4shows the effect of initial dye concentration (50-250 mg/L) on the adsorption of MB. For ACL, it was observed that amount of MB adsorbed was rapid for the first 40 minutes and proceeded gradually at slower rate and finally reached saturation at 90 minutes for 50 mg/L. The equilibrium adsorption increases from 5.90 to 21.3 mg/g with concentration of 50 to 250 mg/L. It was found out that equilibrium removal of MB decreased from 88.0% to 68.4% as concentration increased from 50 to 250 mg/L. MACL shows rapid adsorption for the first 25 minutes and reached equilibrium at 30 minutes for 100 mg/L.

Equilibrium Study

Based on the Table 4, value of q_{max} for ACL is lower compared to MACL. MACL shows higher maximum adsorption capacity of 70.92 mg/g. This results fromthe higher surface area of MACL compared to ACL. Moreover, iron oxide also plays an important part as active site in MB removal. R^2 value is an indication to determine the favourability of adsorption. From the value of coefficient correlation R^2, both ACL and MACL exhibit $R^2 > 0.99$. This means that Langmuir isotherm is more favourable.

Table 4: Langmuir isotherm parameter

Sample	q_{max} (mg/g)	K_a (dm^3/mg)	R^2
ACL	30.769	0.034	0.9937
MACL	70.92	0.091	0.9942

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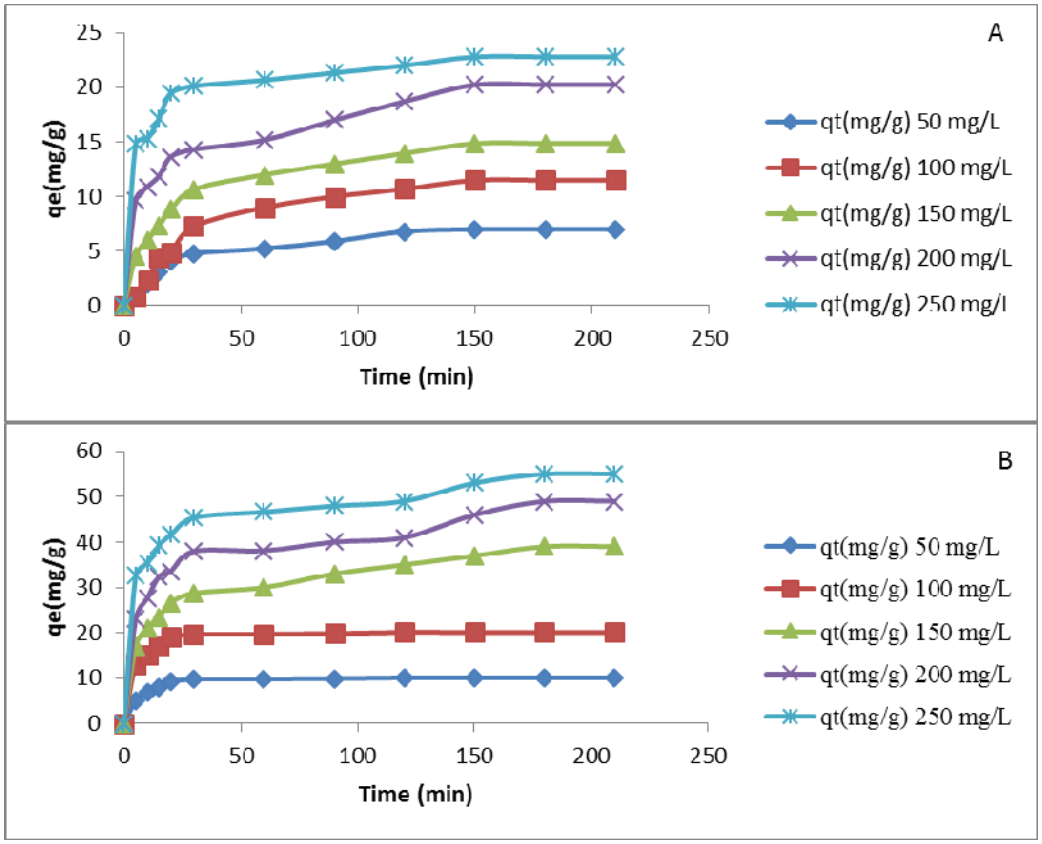

Figure 4: Effect of contact time and initial concentration on the adsorption of MB on (A) ACL and (B) MACL

Table 5: Freundlich isotherm parameter

Sample	K_F	1/*n*	R^2
ACL	1.090	0.8614	0.8957
MACL	4.500	1.0471	0.9566

Multilayer adsorption is best described by Freundlich isotherms where only employed onto heterogeneous surface. The Freundlich isotherm for ACL and MACL parameters were tabulated in Table 5. There are two Freundlich constants which are K_F and n. K_F is known as adsorption or distribution coefficient that show the quantity of dye adsorbed for a unit equilibrium concentration. 1/*n* indicates the surface heterogeneity. The adsorption is said heterogeneous when value of n closer to zero [6]. From the 1/*n* values above, the adsorption of ACL and MACL are homogeneous as the 1/*n* values are further than zero. R^2 value for both ACL and MACL are 0.8957 and 0.9566.

Thus, in brief the adsorption follows Langmuir isotherms as R^2 value higher than Freundlich. It can be concluding that the adsorption involved only monolayer coverage which focusing on chemical adsorption.

Kinetic study

Table 6 indicated that the kinetic data did not fit well with pseudo-first-order. The R^2 results from pseudo-first-order are rather low which are 0.6353 and 0.9156 for ACL and MACL. The q_e experimental and q_e calculated gave a big different hence the adsorption of MB onto ACL and MACL does not follow pseudo-first-order kinetic.

The plot of t/q_t against t as in Figure 6 shows that the intercept are very close to zero. This means that the pseudo-second-order is more applicable and favourable. The coefficient correlation, R^2 for pseudo-second-order is $R^2 > 0.98$ for both ACL and MACL. Since the q_e calculated and q_e experimental of pseudo-second-order displayed the almost same value, the kinetic studied is more suitable and applicable to pseudo-second-order.

Table 6: Kinetic parameters

Sample	Pseudo-first-order				Pseudo-second-order		
	q_e exp (mg/g)	q_e cal (mg/g)	k_1 (1/min)	R^2	q_e cal (mg/g)	k_2 (1/min)	R^2
ACL	30.76	14.64	0.030	0.6353	25.19	0.005	0.9889
MACL	70.92	24.15	0.023	0.9156	76.92	0.006	0.9998

CONCLUSION

Based on adsorption study, the adsorption capacity obtained for ACL and MACL are 30.77 mg/g and 70.92 mg/g respectively. Based on R^2values which are 0.9937 for ACL and 0.9942 for MACL, the adsorption could be fitted to the Langmuir isotherm. Kinetic studiesshows that the adsorption is pseudo-second-order with R^2 values for ACL is 0.9889 and MACL 0.9998.

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