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To cite this article: Sri Hilma Siregar *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **509** 012136

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Kinetics adsorption of heavy oil spills in rivers on magnetite-(CTAB-montmorillonite) adsorbent

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Abstract. Waste of heavy oil contains a number of substances that can pollute the air, soil and water. Waste of heavy oil may contain metals, chlorine solutions, and other pollutants. One litre of waste heavy oil can damage millions of litres of fresh water from water sources in the soil. If waste of heavy oil spills on the ground it will affect ground water and will be harmful to the environment. This is because heavy oil waste can cause arid soil and loss of nutrients. While waste of heavy oil which cannot be dissolved in water can also endanger water habitat. Waste of lubricating oil is included in B3 waste which is flammable and explosive so that if it is not handled by its management and disposal, it will endanger humans and the environment. So to overcome this problem, it needs to find an effective and efficient method for removing waste of heavy oil from the waters. $\text{Fe}_3\text{O}_4@(\text{CTAB-montmorillonite})$ is one of the materials that can be used to reduce oil waste from waters. This research was conducted to determine the mechanism that occurs in the process of adsorption of waste of heavy oil on the $\text{Fe}_3\text{O}_4@(\text{CTAB-montmorillonite})$ adsorbent, using an isotherm model and an appropriate adsorption kinetics. The research was carried out in a laboratory scale using an artificial solution of heavy oil waste and then mixing $\text{Fe}_3\text{O}_4@(\text{CTAB-montmorillonite})$ adsorbent. So that the results obtained for adsorption of heavy oil waste on adsorbent are more in accordance with Freundlich model, with R^2 value is 0.997 and the corresponding kinetics model is pseudo second order kinetics with R^2 value is 0.997 and k is 3.314×10^{-4} g/mg/minute.

Keywords: Adsorption kinetics, adsorption isotherms, $\text{Fe}_3\text{O}_4@(\text{CTAB-montmorillonite})$

1. Introduction

The area of dense port waters will be anthropogenic activity, besides these waters are also an international path which potentially leads to oil spills which are the rest of the factory and ship fuel. The presence of oil spills into the waters can negatively affect the coastal environment and marine waters primarily through direct contact with aquatic organisms, direct effects on fisheries activities including marine tourism and indirect effects through environmental disturbances. Marine oil pollution can cause wider impacts due to drift and ocean waves. It is often incorporated into clusters of solids, which are those floating on the surface of the water. The oils in the water can come from a variety of sources, including the deposition of Sludge oil cleaning and washing vessels in the sea, ballast water drainage, offshore oil drilling, oil and gas carrier leakage tankers, ship collisions at sea [1-3].

More recently, attention has been paid to heavy oil adsorbent materials that have superhydrophobic and super oleophilic properties as the oil adsorbent. Based on this a large number of natural and synthetic



adsorbents have been widely used for oil adsorption such as sponges [4], film [5], fibres [6-8], activated carbon [9, 10], sawdust [11], straw [12], hybrid foams [13-15]. Generally, the ideal adsorbent material should have a high absorbency, can be recycled, and must be environmentally eco-friendly. However, these natural and synthetic materials show low adsorption capacity, non-selective adsorption, and non-environmentally friendly. In order to overcome this limitation, it has been given special attention in recent years. The oil adsorbent material has a high adsorption capacity, low density, high porosity, large specific surface, hydrophobic and environmentally friendly [16]. Several methods of synthesis have been reported that are sol-gel processes [17, 18], chemical vapour deposition [19], hydrothermal methods and dye-solution processes [20]. Therefore, a simple, quick and economical approach is needed to obtain the ideal adsorbent material.

However, organo-montmorillonite has limitations when applied in water treatment, since colloidal dispersion will form after montmorillonite is dissolved in water. In order to overcome this organo-montmorillonite is modified by the addition of magnetic nanoparticles so as to solve the separation problem through the high efficiency magnetic separation process. However, given the hydrophilic organo-montmorillonite, most of the synthesis processes are limited in aqueous systems, which produce low-quality magnetic montmorillonite with large magnets and are not uniform. Nanoparticles restrain the performance of montmorillonite to some extent. It is, therefore, necessary to develop methods for synthesizing high-quality magnetic montmorillonite [21, 22].

A method of separating oil from water using Fe nanoparticles and magnets has been developed. This technique will allow the oil to be reused, thus offsetting the cleaning costs. The proposed method involves the addition of mixed nanoparticles with iron and then, separating oils using magnets. The researchers suggest that this is a very simple maneuver; however, it should be done in one vessel so that the nanoparticles do not contaminate the oceans. In other works, similar methods have been proposed but have the necessary losses to know the concentration of oil and water in the mixture. The proposed technique is by placing the magnet into the flow, and not beyond it, because in the above method it can always be applied with good results, regardless of the concentration of each component in the mix [23-25].

In this study, organo-montmorillonite modified with magnetic material is used for the remediation of heavy oil spills in the waters. Characteristic of heavy oil spill adsorbability on adsorbent can be seen from its adsorption rate. The adsorption rate can be known from the adsorption rate constant (k) generated from an adsorption kinetics model. Freundlich and Langmuir isotherms model are used to determine the kinetic parameters of an adsorption process.

2. Methodology

2.1. Materials

CTAB-montmorillonite distilled water, distilled water, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (pa) brands Merck, $\text{NH}_3 \cdot \text{H}_2\text{O}$, AgNO_3 (pa) Merck, NaOH (pa) brands Merck. The heavy oil spills in the river water (simulation method).

2.2. Synthesis Magnetite-(CTAB-montmorillonite)

Magnetite-(CTAB-montmorillonite) synthesis was performed by coprecipitation method. First, we created a suspension from Montmorillonite-CTAB. 2 g CTAB-Montmorillonite was dissolved in 100 mL of double distilled water and stirred for 24 hours to form a homogeneous suspension. 50 mL solution prepared consisting of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.8457 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.2992 g) was referred to as a pillar solution. 50 mL of CTAB-montmorillonite suspension was added to 50 mL of pillar solution then stirred under N_2 gas pressure at 80°C for 30 min. 25 mL of 25% (w/w) $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added slowly into the above mixture, stirred for 1 h later. Magnetite-(CTAB-montmorillonite) obtained in the wash with hot distilled water for 5 times was then separated by external magnetic decantation method. Then it was dried at 80°C for 3 hours.

2.3. Adsorption of heavy oil on $Fe_3O_4@(\text{CTAB-montmorillonite})$

First, variation of amount of $Fe_3O_4@(\text{CTAB-montmorillonite})$ from 0.5-3.0 grams was added to the waste oil in the water body. The process was then incubated for 5 hours; 25 mL emulsion solution was removed from the shaker then separated using an external magnet. The adsorbent mass was weighed before and after the adsorption process. This experiment was carried out on different variable conditions, namely variation of contact time, amount of adsorbent and concentration of adsorbate. Furthermore, isothermal adsorption and adsorption kinetics were calculated.

2.4. Adsorption kinetics

Adsorption was carried out by the following methods: Study of kinetics. 20 mL (120 mg/L) agitated with 1.5 g $Fe_3O_4@(\text{CTAB-montmorillonite})$ by being stirred at room temperature for 1 hour, 2 hours, 3 hours, 4 hours, 5 hours and 6 hours. At each time interval, solid particles were removed and adsorption capacity was calculated. The adsorption kinetics were calculated based on the following formula:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (2)$$

$$q_t = \frac{t}{1/k_1 + (1/q_e)t} \quad (3)$$

2.5. Isothermal adsorption

Isothermal adsorption was done to find out how waste oil molecules interact with the surface of the adsorbent. In general, there are two most common equations used in the Langmuir equation and the Freundlich equation. Adsorption was done by the following method: Samples of 20 mL (120 mg/L) were agitated with 1.5 g of $Fe_3O_4@(\text{CTAB-montmorillonite})$ by being rocked at room temperature for 5 hours. With variations in adsorbate concentration 0.5 mg/L, 1.0 mg/L, 1.5 mg/L and 2.0 mg/L. The emulsion solution was removed from the shaker then separated using an external magnet.

2.6. Characterization Method

Analysis using X-ray diffraction (XRD) was carried out to determine the crystalline phase of bentonite which was not modified with modified bentonite. The working procedure is as follows: A total of 0.5 g of the sample is weighed, compacted and placed in a sample container and then inserted into the instrument cell of the diffractometer. The diffractogram pattern is recorded at an angle of 2 times in the interval 10-70° with a speed of 2° / minute in each step 0.02° / minute by an 6000 advanced diffract meter (Shimadzu corporation, Japan) with Cu K α radiation (40 mA, 45 kV). Transmission electron microscope (TEM) images were obtained on a JEOL, JEM 1400 at an accelerating voltage of 200 kV. The magnetization was measured on an Oxford 2,1 vibrating sample magnetometer (in PT BIN BATAN). The reduction in mass and material temperature due to heating was measured on TGA/DTA NETZSCH STA 449 F1 Jupiter.

3. Result and Discussion

3.1. Characterization of Magnetite-(CTAB-montmorillonite)

The incorporation of magnetite material with CTAB-montmorillonite obtained a new material having two functions as an adsorbent derived from montmorillonite structure and can be drawn by magnetite outer magnet. CTAB-montmorillonite (CMt) has been synthesized by Siregar *et al.* [26]. Here, the authors discuss only a little about the characterization of Magnetite-(CTAB-montmorillonite) (MCMt). Fig. 1 explains that the peak intensity of MCMt is higher than that of CMt and Mt, that the magnetite peaks cover the typical peaks of CMt and Mt. This proves that magnetite has been loaded on CMt sheets.

With the diminished peak intensity typical of CMt and Mt then the likelihood of its adsorption capacity was also reduced [27].

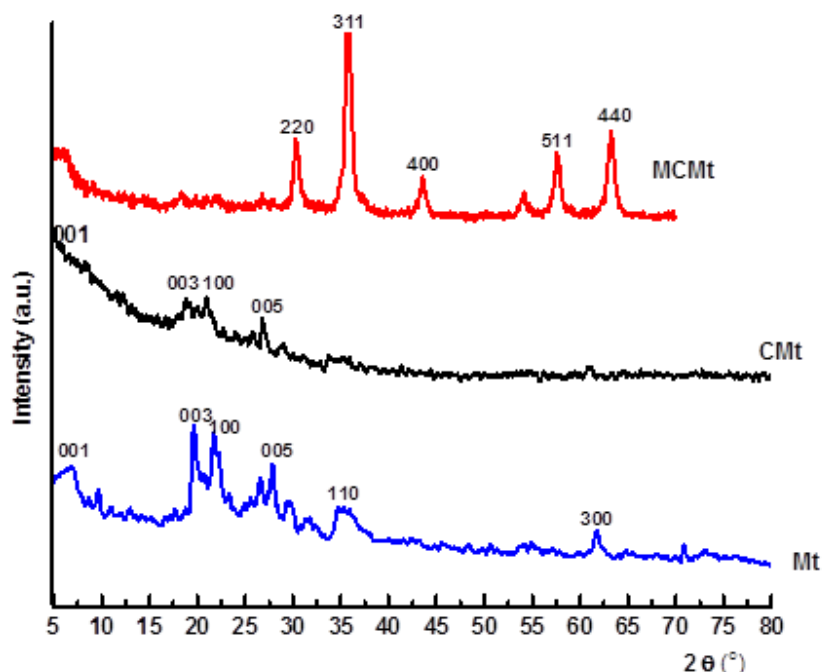


Figure 1. XRD pattern from Montmorillonite (Mt), CTAB-montmorillonite (CMt), and Magnetite-(CTAB-montmorillonite) (MCMt)

TEM image (Fig.2) for Mt and CMt can be seen there are piles of spheres forming dark and bright shadows and the difference of distance between dark and light. This is because the space between the layers of the Mt there is a difference in the width of the space between dark and light. The brightly coloured areas are the elements of C, H, and N. Silicate layers are crossed dark-coloured. Modified Mt to organo-montmorillonite with CTAB surfactant as in TEM photo images, dark areas covered by bright areas. This means that the CTAB that enters the montmorillonite does not coat the montmorillonite surface but enters the montmorillonite cavities, resulting in the increased pore volume of the organo-montmorillonite compared with montmorillonite [28].

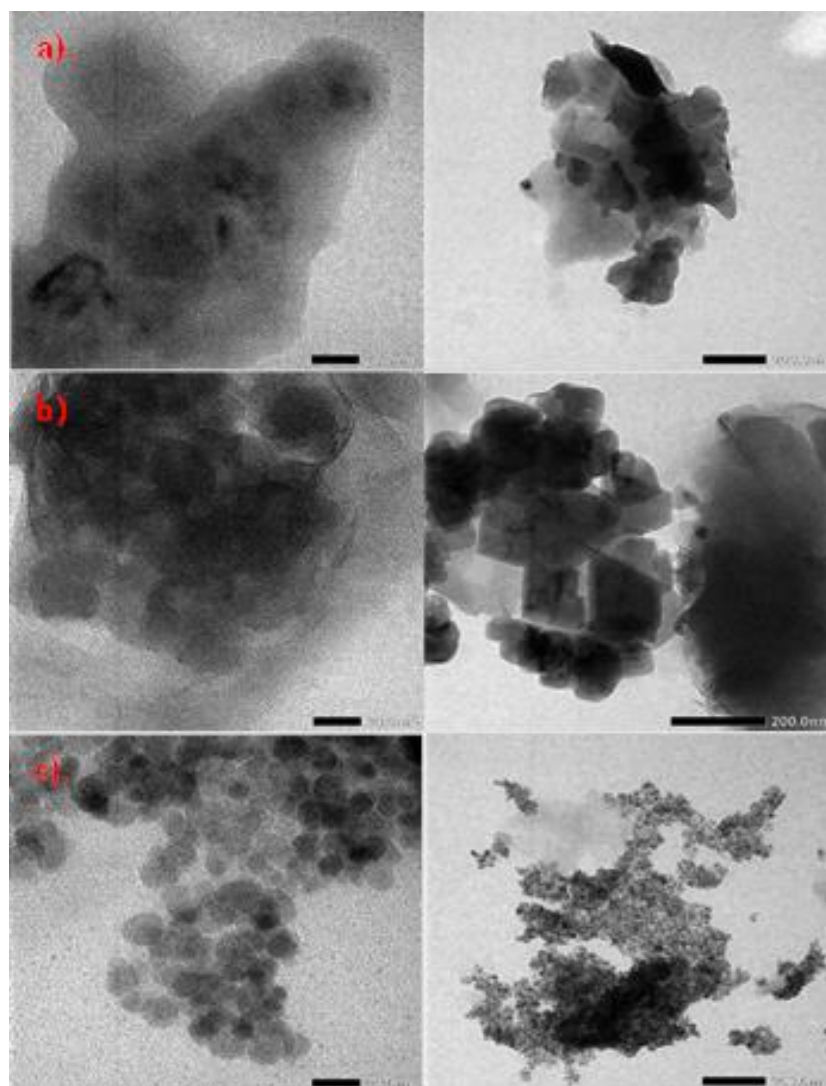


Figure 2. TEM photos of Mt 20 nm and 200 nm (a), CMt 20 nm and 200 nm (b), and MCMt 20 nm and 200 nm

Fig. 3a explains that there are several stages of mass loss observed. The first two stages of Mt mass loss involve dehydration and/or dehydroxylation from a temperature of 20-120°C. Both steps are caused by the dehydration of the adsorbed water, and water molecules around the metal cations such as Na^+ or Ca^{2+} at the exchange site of Mt. Peak loss of mass in the hydration process and water hydroxylation during the adsorption process only appear for unmodified Mt. Fig. 3a shows two steps of thermal decomposition at both 480 and 720°C, caused by dehydroxylation of Mt. Decomposition at a lower temperature of 480°C is due to the loss of the OH unit at the end of the Mt layer, while the temperature at 720°C is caused by dehydroxylation of Mt.

Fig. 3b shows that there are several stages of mass loss of CMt. There are three stages at temperatures of 20-180°C, 180-400°C, and 400-800°C. In the first stage, 20-180°C there is dehydration of water molecules at CMt. In the second stage occurs between temperatures of 180-400°C. At this stage there is degradation of organic molecules from surfactants located on the surface between layers of CMt. While in the third stage at between 400-800°C, surfactant degradation is attached to the wall between the montmorillonite layers. In general, the process of degradation of organic molecules in CMt occurs in two mechanisms, namely on the surface and part of the CMt layer. This proves that the thermal stability

of the surface and the cross-section of the CMt layer is different. Furthermore, calcination at temperatures above 800°C will cause damage to the Mt.

The TGA/DTA analysis for the MCMt sample (Fig.3c) is only through two stages. This is the same as with thermal stability of Mt. In the first stage at a temperature of 20-120°C, at this stage there is a mass loss of 2.86%. The second stage occurs at a temperature of 120-860°C, at this last stage there is a mass loss of 8.27%. Losses in this region are assigned to the decomposition of the guest material placed in the layer, which confirms the interconnection. Mass loss above 400°C is associated with continuous organic degradation of the intercalated and dehydroxylated molecules of the remaining OH group of CMT. The final residue in all cases corresponds to the thermal degradation of phyllosilicate to the amorphous phase [29]. In detail, the thermal stability of this sample can be seen in Table 1. In Table 1, it can be seen that the mass percent is degraded and the remaining mass that is not degraded in each calcination temperature range. TGA / DTA analysis for samples of MCMt only through two stages. This is the same as the thermal stability of montmorillonite. In the first stage at a temperature of 20-120°C, at this stage there is a mass loss of 2.86%. The second stage occurs at a temperature of 120-860°C, in the last stage there is a mass loss of 8.27%.

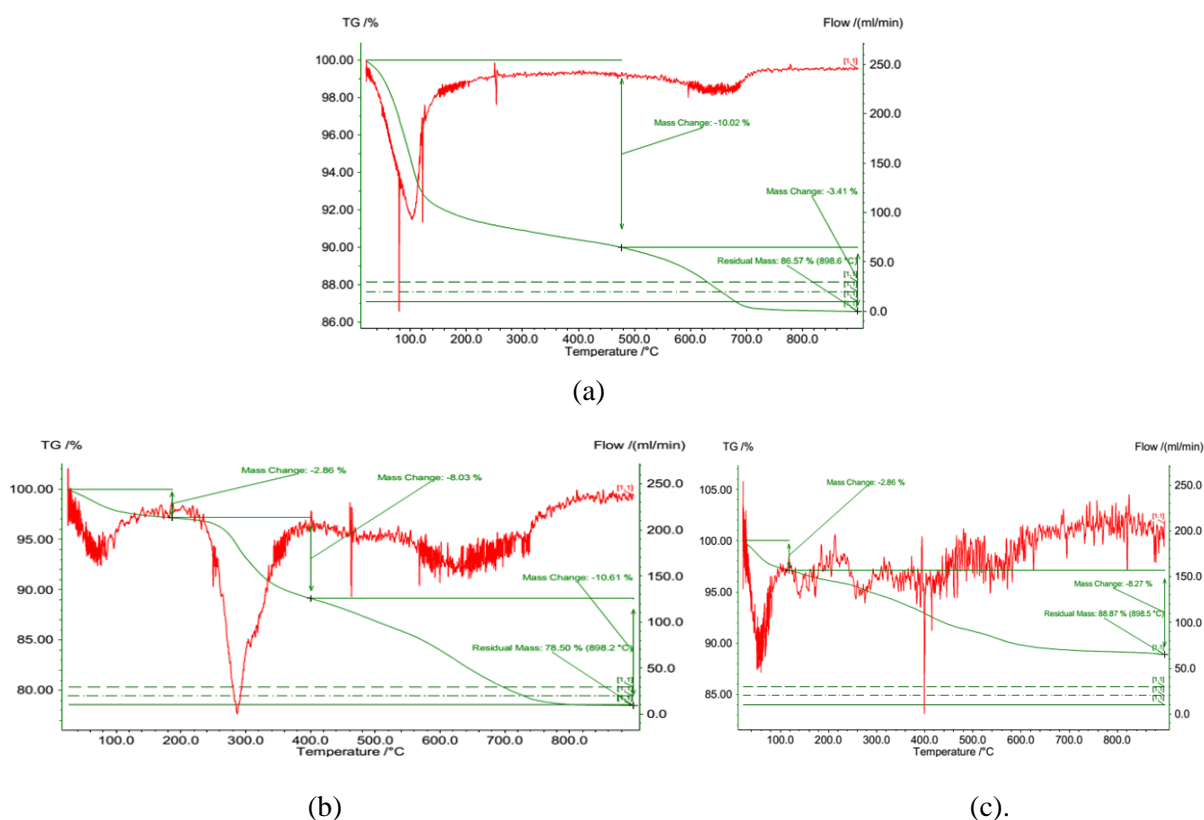
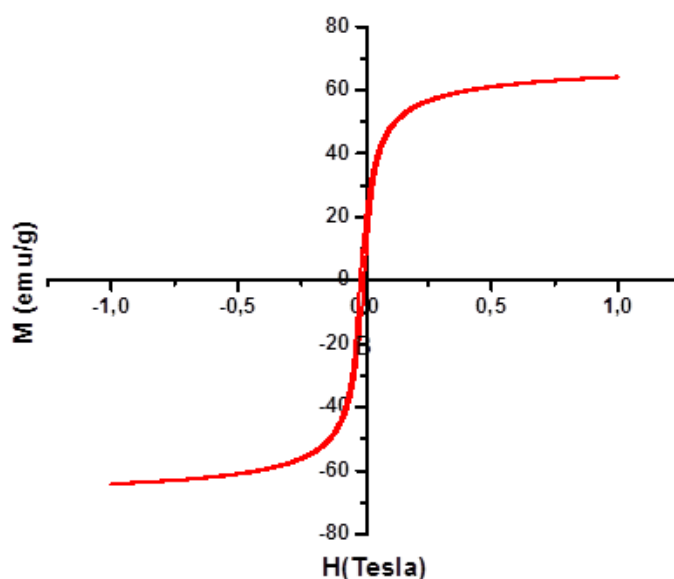


Figure 3. TG curves of (a). Mt, (b).CMt, and (c).MCMt.

Table 1. TG/DTA results for Mt, CMt and MCMt

Sample	The range of Calcination Temperature (°C)	Degraded mass (%)	Residual Mass that is not degraded (%)	ΔH (J/g)
Mt	20-480	10.02		-
	480-800	3.41	86.57	
CMt	20-180	2.86		-879.676
	180-400	8.03	78.50	
	400-800	10.61		
MCMt	20-120	2.86		-134.073
	120-800	8.27	86.87	

Magnetic properties were analysed using a VSM (Vibrating Sample Magnetometer) device in the Compressible-PTBIN-BATAN Magnetic-Field Substance laboratory. The VSM type used is the VSM1.2H Oxford type VSM. Information obtained is in the form of magnitudes of magnetic properties as a result of changes in the external magnetic field that is described by the hysteresis curve. The hysteresis curve can show the relationship between magnetization (M) and the external magnetic field (H). Based on Fig.4, it shows that MCMt composite is a soft magnet, because of the hysteresis curve having almost symmetrical recoil when subjected to the magnetic field and when the magnetic field is eliminated or can be seen from the area of narrow hysteresis curve [30]. The area of the hysteresis curve shows the energy needed for magnetization. The value of M_r , M_s , and H_c are 17.9 emu/g, 64,1 emu/g, and 0.0181 Tesla, respectively.

**Figure 4.** MCMt composite hysteresis curve.

3.2. Remediation of waste oil at Fe_3O_4 @ (CTAB-montmorillonite)

In this study the composite Fe_3O_4 @ (CTAB-montmorillonite) was synthesized as an advanced material for adsorption of oil waste remediation in water bodies. The system used is a modelling system. Used lubricating oil was used to represent waste oil in water bodies. In this oil waste remediation, contact time variation, oil waste concentration and mass of adsorbent were carried out. The optimum conditions

for the composite application of Fe_3O_4 @ (CTAB-montmorillonite) as an adsorbent for remediation of oil waste need to be measured in order to obtain optimum remediation of oil waste. Optimization of conditions in the application was conducted by observing the effect of adsorbent mass variation and contact time on remediation. Organic waste oil molecules can be adsorbed at Fe_3O_4 (CTAB-montmorillonite) because nonpolar groups owned by waste oil organic molecules will interact with CTAB alkyl chains which are hydrophobic. Besides the interaction of CTAB alkyl chains, organic waste oil molecules that have polar groups can interact hydrogen bond with the montmorillonite surface which still has a free silanol group (Si-OH).

3.3. Kinetics of adsorption

Kinetics of adsorption is an important parameter for evaluating the remediation process. In order to see the mechanism of heavy oil spill remediation by MCMt composite, kinetics model of pseudo-first order, and pseudo-second order were used. Lagergren's pseudo order kinetics presented a pseudo-first order equation for describing the liquid phase liquid phase adsorption process based on adsorption capacity. Where q_e (mg/g) and q_t (mg/g) is the amount of heavy oil adsorbed at equilibrium and at time t , and k_1 is the pseudo-first order rate constant. The equation of pseudo-first order kinetics can be seen in Fig.5. Based on Fig.5 concludes that the log plot ($q_e - q_t$) to t , the correlation coefficient value (R^2) of only 0.8846 does not approach the value of $R^2 = 1$. The value of q_e obtained experimentally was much smaller than the calculated q_e value. This indicates that the pseudo-first order kinetics was not appropriate for the heavy oil remediation process.

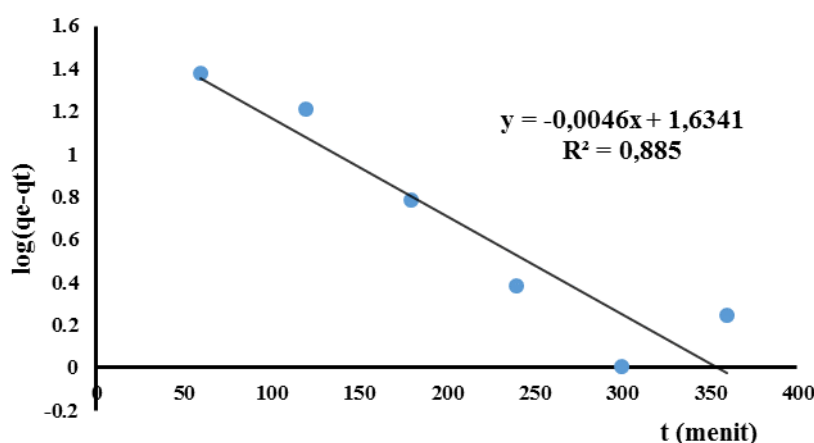


Figure 5. Pseudo-order order kinetic equation model

The pseudo-second order model is dependent on the alleged occurrence of adsorbate chemical adsorption on the adsorbent [31]. Where k_2 (g /min min) is the equilibrium rate constant for the pseudo-second order and q_e can be obtained from the plot t/q_t to t , as shown in Fig. 6. Based on Fig. 6, the plot t/q_t to t produces a line linear with value R^2 is 0.9972 almost close to value $R^2 = 1$.

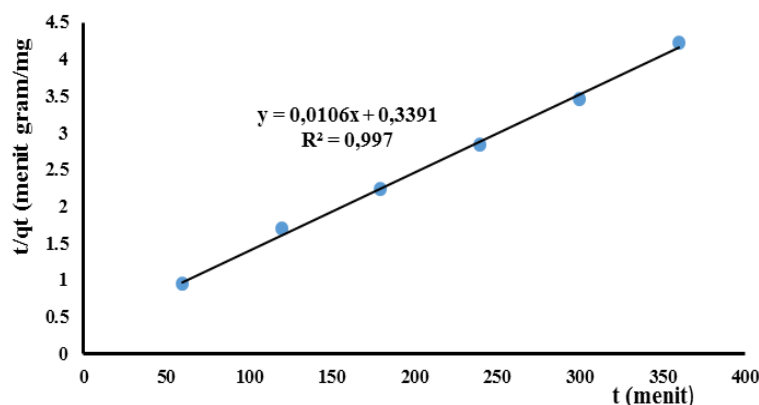


Figure 6. Pseudo second order kinetic equation model

The comparison of the results with the correlation coefficients for the pseudo-first order kinetic and the pseudo-second order kinetic model is shown in Table 2. For the MCMt composite, the pseudo-second order model is the most suitable model for the experimental kinetics data, because of the calculated q_e almost closer to the experimental q_e value and R^2 is greater. This result also shows that the heavy oil remediation adsorption process on MCMt composite followed the application of pseudo-second order equation.

Table 2. The kinetic parameters for heavy oil spill adsorption

Sample	Kinetic model of pseudo-first order			
	$q_{e_{exp.}}$ (mg/g)	$q_{e_{cal.}}$ (mg/g)	k_1 (min^{-1})	R^2
	86.873	43.063	1.06×10^{-2}	0.8846
MCMt	Kinetic model of pseudo-second order			
	$q_{e_{exp.}}$ (mg/g)	$q_{e_{cal.}}$ (mg/g)	k_2 (g/mg min)	R^2
	86.873	94.340	3.314×10^{-4}	0.9972

3.4. Adsorption isotherm

The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a certain temperature. There are several known adsorption isotherms such as Langmuir, Freundlich isotherm models and also Brunauer, Emmet, and Teller (BET) isotherm models. The Langmuir adsorption model is based on absorption in single layers and homogeneous surfaces without interaction between adsorbed species. The Langmuir model assumes that adsorptive forces are similar to the strength of chemical interactions [31]. In addition to the above statement this isotherm also assumes that the adsorption heat, adsorption, does not depend on the area of the gas-covered surface [32].

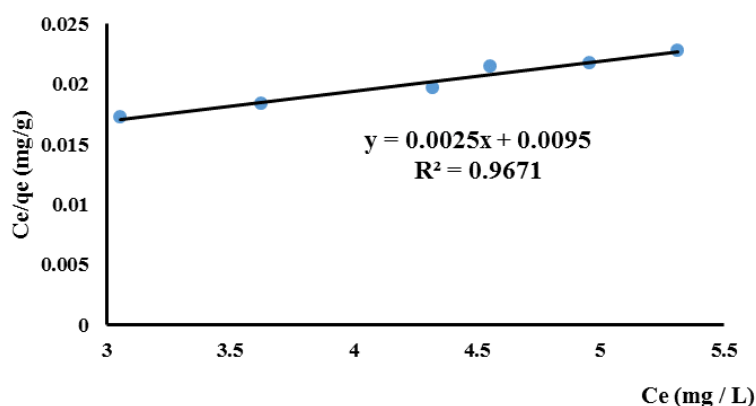


Figure 7. Langmuir model for heavy oil adsorption on MCMt

Based on the results of calculations and Fig. 7 it can be concluded that the relation coefficient R^2 of the Langmuir adsorption isotherm equation is 0.9671. The adsorption capacity at a single layer is 105.26 mg/g and the Langmuir isothermal constant is 0.263 L/mg. Whether the adsorption process run well cannot be known by doing the Langmuir (RL) equation test. The RL value is the value of the dividing factor. The RL value indicates the type of adsorption isotherm that occurs. If the value is $RL > 1$, the adsorption process is not preferred, $RL = 1$, the adsorption process is linear, $0 < RL < 1$, the adsorption process is preferred and if $RL = 0$, the adsorption process cannot be reversed. Based on the explanation above, the R_L value obtained is 0.152. This means that the remediation of oil waste in the water body follows type $0 < R_L < 1$, which is the preferred adsorption process.

The Freundlich model is an empirical formula that applies to surfaces of heterogeneous adsorbents and solutions with low adsorbate concentrations [31]. When viewed from Figure 8, the value of R^2 is 0.997. The adsorption capacity of waste oil remediation in the Freundlich isothermal model is 146.64 mg/g. Other Freundlich constants (n) are empirical parameters that vary with the level of heterogeneity and indicate the level of nonlinearity between the absorption capacity of oil waste and oil that is not absorbed and related to the distribution of ions bound to the sorbent surface. Generally, $n > 1$ indicates that the adsorbate is adsorbed on the adsorbent well and the values of n are higher in accordance with the stronger adsorption intensity. The nF value is 3,626, which shows the strong adsorption intensity between oil and composite waste. A value of $1/n$, is Freundlich constant indicating the type of adsorption that occurs. If the value is $0 < 1/n < 1$, then the adsorption process is preferred, if the value of $1/n = 1$, then the adsorption process takes place irreversibly, and when the value is $1/n > 1$, the adsorption process is not preferred. The value of $1/n$ is 0.2758 in this study; this means that the adsorption process that takes place is preferred or acceptable.

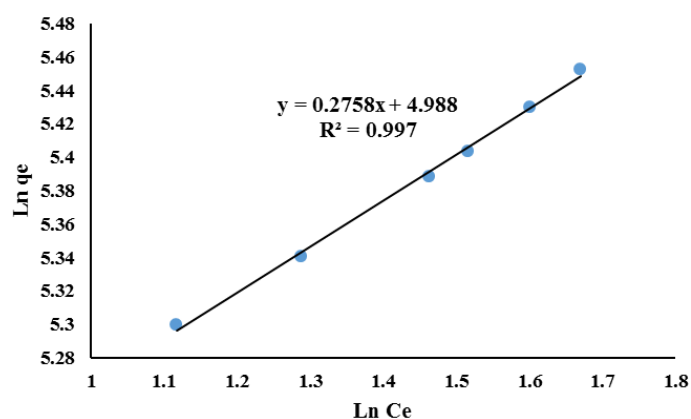


Figure 8. Freundlich model for heavy oil adsorption on MCMt

The relationship ratio of (R) Langmuir and Freundlich is almost close to one, this shows the tendency of the adsorption process not only to occur on a homogeneous surface but also on irregular surfaces. If the adsorbate concentration is reduced, the cation exchange occurs between the layers. Cation exchange but will also adhere to the composite iron oxide between montmorillonite layers and form the tendency of bilayer adsorption [28]. The Freundlich isotherm model is better suited to the remediation of oil waste at Fe_3O_4 @ (CTAB-montmorillonite). Based on the linearity of Table 3, the adsorption of waste oil on Fe_3O_4 @ (CTAB-montmorillonite) composite follows Freundlich adsorption equation. Freundlich's isotherm model explains that the adsorption process on the surface is heterogeneous where not all adsorbent surfaces have adsorption power. The Freundlich isotherm model shows that the adsorbate layer formed on the surface of the adsorbent is many layers. This is related to the characteristics of physical adsorption where adsorption can occur in many layers [28, 30].

Table 3. Isothermal parameters of adsorption and relationship coefficients

Model	Correlation coefficient (R^2)	Parameter	
Langmuir	0.967	$K_L=0.263 \text{ L/mg}$	$q_m = 105.26 \text{ mg/g}$
Freundlich	0.997	$K_F=146.64 \text{ mg/g}$	$n_F = 3.626$

4. Conclusion

Remediation of oil waste in composite Fe_3O_4 @ (CTAB-montmorillonite) follows Freundlich adsorption isotherm with R^2 value is 0.997, $K_F = 146.64 \text{ mg/g}$, $n = 3.626$ and value of $1/n = 0.2758$. The adsorption kinetics equation follows the pseudo second order kinetic equation with the R^2 value being 0.997 and the k value is $3.314 \times 10^{-4} \text{ g/mg min}$.

Acknowledgment

The Authors are grateful to UMRI & UGM for admission and facilities to conduct the research and Kemenristek DIKTI Grant for financial support through Penelitian Disertasi Doktor 2018.

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