Methylene Blue Removal From Aqueous Solution by Manganese Octahedral Molecular Sieve (K-OMS2) Coated on Activated Alumina Ball

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ABSTRACT

Manganese octahedral molecular sieve (K-OMS2) coated on activated alumina ball (Al_2O_3) by using a polyvinyl alcohol (PVA) as a binder for removal of methylene blue (MB). K-OMS2 powder was synthesized by the hydrothermal method followed by coating onto the activated alumina ball (K-OMS2/Al_2O_3-PVA). The K-OMS2 / Al_2O_3-PVA was characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Point of zero charges (pHpzc), and Nitrogen adsorption-desorption. The results showed that K-OMS2 had a cryptomelane crystalline structure with fracturing of the K-OMS2 particle on K-OMS2/Al_2O_3-PVA and pHpzc ≈ 8. The specific surface area was 212.65 m^2/g, 0.45 cm^3/g of the pore volume, while pore size was 4.19 nm. The kinetics study of MB removal showed the reaction rate increased as temperature increased in the range of the temperature investigated (303 – 333 K), which expressed the pseudo-second-order kinetic model. For the thermodynamic study, the reaction involves spontaneous reactions ($-\Delta G°$), in an endothermic nature ($+\Delta H°$), and with increased randomness ($+\Delta S°$).

Keywords: K-OMS2, Methylene blue, PVA

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Introduction

Presently, dyes are used in many industries such as textile, cosmetic, and paper, among others. In the processes of these industries, there is concern about the environment with respect to water being contaminated with synthetic dyes. The dye in water is visible and undesirable. Further, it may affect photosynthetic activity in aquatic life because the color will block the transmission of light into the water. Wastewater containing dyes are subjected to various methods of wastewater treatment such as coagulation, membrane filtration, oxidation, adsorption, etc. [1-2]. Amongst these techniques, adsorption is the most broadly used for color removal in the water due to several advantages including its low cost and the expedience of the operation process. Nevertheless, the effectiveness of the adsorption process is dependent on the performance of adsorbent, the concentration of pollutant and thermodynamics [2-3]. Although the adsorption process is convenient, the final step requires the disposal of adsorbents waste. Meanwhile, the removal process by oxidation can reuse oxidants. Consequently, oxidation is an interesting method.

Nowadays, oxidants are made to be suitable for use with features including highly specific surface area, elegant pore size, large pore volume, and stable structure, providing a variety of applications for use. Manganese octahedral molecular sieve (K-OMS2) is due to the presence of Mn^{2+}, Mn^{3+}, and Mn^{4+} ions in the octahedral framework. These materials have been used for many applications such as catalytic, oxidants, and adsorbent as they are highly porous, non-toxic, and environmentally friendly [4-7].

In this study, K-OMS2 powder was prepared using a hydrothermal process. In the next step, the K-OMS2 coating on alumina ball was done using polyvinyl alcohol (PVA) to improve the alumina ball surface. At the end of this process, the material received will be called K-OMS2/Al_2O_3-PVA. The K-OMS2/Al_2O_3-PVA has been studied for crystallinity, point of zero charges, and surface morphology, as well as surface area, kinetic and thermodynamic studies for methylene blue removal.

Materials and Methods

The chemicals used in this study were of chemical analysis grade. K-OMS2 was prepared from 0.25M of manganese acetate tetrahydrate ($Mn(CH_3COO)_2\cdot 4H_2O$, ACROS Organics) mixed with 0.33M potassium permanganate ($KMnO_4$, CARLO ERBA). The pH of the solution was adjusted to an acidic condition ($pH \leq 3.5$) and stirred well for 1 hr, after which it was transferred to an autoclave for hydrothermal processing for 3 hrs. In the next process, black slurry was washed with Deionized water (DI) ($pH \approx 7$) by centrifuge technique to separate the black sediment. The black sediment was then dried at 373 K for 4 hrs and then at 473 K for 2 hrs [5].

The K-OMS2 powder was characterized for crystallinity using an X-ray diffractometer (XRD) (Model D8 Discover, Bruker AXS Germany) using CuKα with wavelength (λ= 1.51418°A) at 40 mA and 40 kV with 2θ range of 10-80 degrees and increasing step of 0.02 degree. The support materials involved using an alumina ball 4 mm of diameter (Al_2O_3 68.50% SiO_2 28% other 3.5%, BPF 05). The ratio of substance to alumina ball was 2%. Polyvinyl alcohol (PVA) was used as a binder to improve the surface of alumina ball and the concentration of PVA used was 5%

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The PVA solution was prepared from PVA powder in distilled water under heating at 85°C and magnetic stirring for 2 hrs [8]. The next step was the coating process by mechanical orbital shaking technique using 250 rpm for 24 hrs. Subsequently, K-OMS2/Al_2O_3-PVA was dried at 373 K for 24 hrs. The K-OMS2/Al_2O_3-PVA was studied for crystallinity by XRD, identical to the conditions for characterization of K-OMS2 powder. Surface morphology was observed by scanning electron microscopy (SEM) (1450VP, LEO). The point zero of charge (pH_{pzc}) was defined as pH on the charge of the adsorbent surface being zero, used 0.1M solution of NaCl, which was taken in different titration flasks. The pH of the solutions was adjusted to 2-12 using 0.1 M of HCl and 0.1 M of NaOH solution following 2 g of K-OMS2/Al_2O_3-PVA was added in each flask and shaken by a Shakers Incubator at 150 rpm, 298 K of temperature and the final pH measure after 48 hrs by pH meter. The results were plotted as a function of the initial pH of the solution vs. Δ pH. The Brunauer Emmett Teller (BET) and Barrett, Joyner, and Halenda (BJH) methods were used to explain the surface area, pore size, pore-volume, and pore shape.

Kinetics and thermodynamic studies of the removal of Methylene blue (MB) by K-OMS2/Al_2O_3-PVA was tested in the batch experiment with 1 ppm of MB and 40 g of K-OMS2/Al_2O_3-PVA. The temperature used ranged from 303-333 K, with the concentration of MB measured by spectrophotometer using absorbance at λ_{max} = 664 nm.[9]. Kinetic models are used to describe the mechanism of reaction. To examine the potential rate-determining step, pseudo-first order and pseudo-second-order kinetic models were used [10]. The linear form of the pseudo first-order equation is given by :

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

The linear form of the pseudo second-order model is given by :

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{2}$$

Where q_e and q_t are the amounts of MB removed by K-OMS2/Al_2O_3-PVA at equilibrium and at various time t ($mg \cdot g^{-1}$); k_1 is the equilibrium rate constant of pseudo first-order kinetics (min^{-1}); t is the contact time (min); and k_2 is the equilibrium rate constant of the pseudo second-order kinetics ($g \cdot mg^{-1} min^{-1}$)

Thermodynamics study was used to indicate the relationship between energy and entropy, which deals with considering the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These are calculated to evaluate the thermodynamic possibility and oxidation process in nature [2,11]. ΔG° can be calculated in the equation as :

$$\Delta G^o = -RT\ln k_d \tag{3}$$

Where R is the gas constant (8.314 J·mol^{-1} K^{-1}); T is the temperature (K) and k_d is the thermodynamic equilibrium constant of the oxidation process (L/g), reflecting MB distribution between the solid and liquid phases at equilibrium. Equilibrium constant is estimated as :

$$k_d = q_e/C_e \tag{4}$$

According to the van't Hoff equation:

$$\ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{5}$$

The values for ΔH° (kJ·mol^{-1}) and ΔS° (J·mol^{-1} K^{-1}) were evaluated from the slope and intercept of the van't Hoff plots.

Activation energy (E_a) is the amount of minimum energy that is needed for the chemical reaction (kJ/mol).[12]. The activation energy for a given reaction depends on the types of bonds broken and formed in the reaction.[13]. E_a for the methylene blue removal is calculated from Arrhenius equation [14].

Results and Discussion

1. Characterizations

In the coating process, PVA is used as a polymer binder to improve the surface of alumina ball. Comparison of PVA concentration is appropriated between 5%PVA and 10%PVA by the weighing method of K-OMS2/Al_2O_3-PVA after it is dried. The results showed that K-OMS2 can be coated on alumina ball with 10%PVA binder better than 5%PVA, determine from the weight of alumina ball after the coating process, which can be 86.40%, while 5%PVA can be coated at 80.26%. Therefore, 10%PVA was used for K-OMS2 coating in this study.

The suggested structures of K-OMS2 and K-OMS2/Al_2O_3-PVA were confirmed from XRD, as shown in Figure 1. The crystallinity of K-OMS2/Al_2O_3-PVA is decreased when compared to K-OMS2 powder because the coating process by mechanical orbital shaking technique affects the crystallinity of K-OMS2.

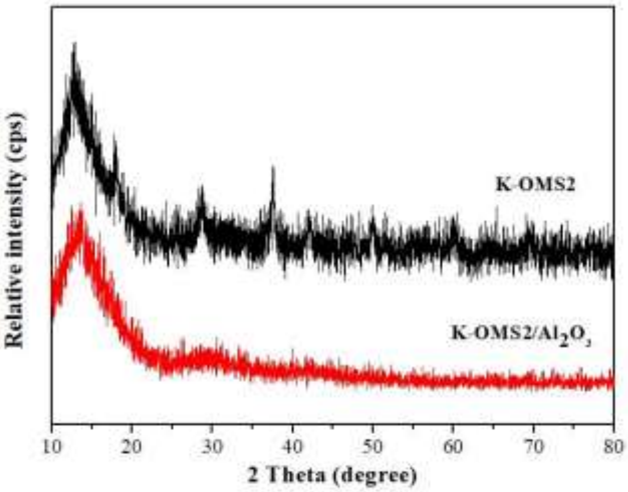

Figure 1 XRD pattern of K-OMS2 and K-OMS2/Al_2O_3-PVA

The surface morphology of K-OMS2/Al_2O_3-PVA was described by SEM, as seen in Figure 2, which found that the K-OMS2 particles have broken and combined agglomeration due to shaking from the coating process. For defining the surface charge of K-OMS2/Al_2O_3-PVA, as shown in Figure 3, the point zero of charge is 8. The pH is greater than 8, so the surface has negative charges. While pH was lower than 8, it will have a positive charge at the surface of K-OMS2/Al_2O_3-PVA. The pH_{pzc} of K-OMS2/Al_2O_3-PVA was different from K-OMS2 powder (pHzpc = 5) because Al_2O_3 have other elementals contents and functional groups of PVA induce to different functional groups thus a greater mass portion, which effect to active sites that will protonate excess H^+ [15].

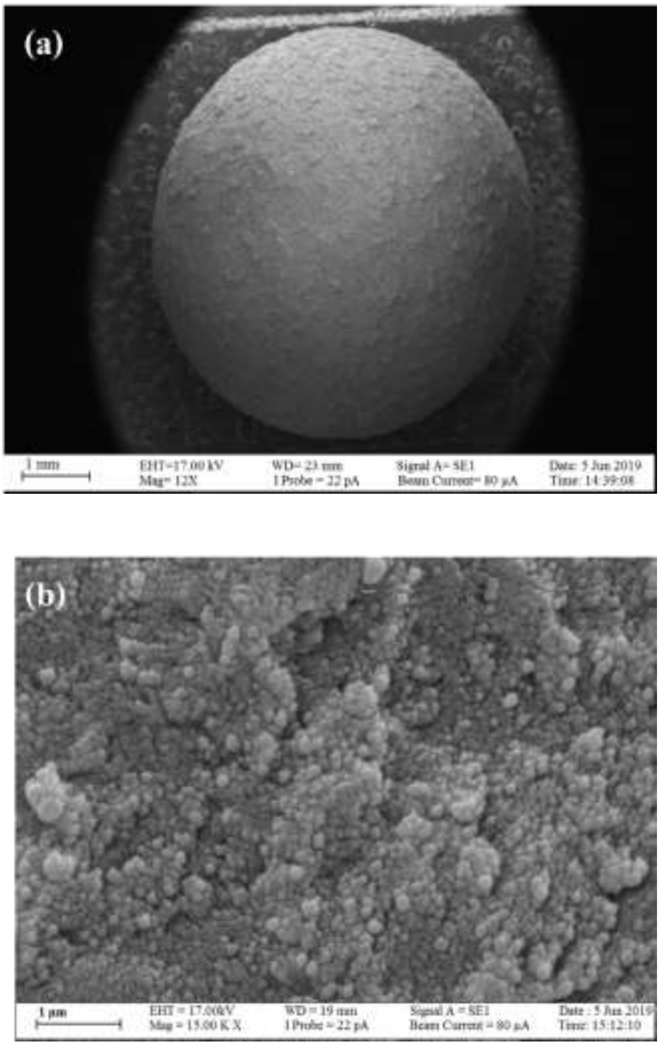

Figure 2 SEM image of K-OMS2/Al_2O_3-PVA (a) 12x and (b) 15,000x

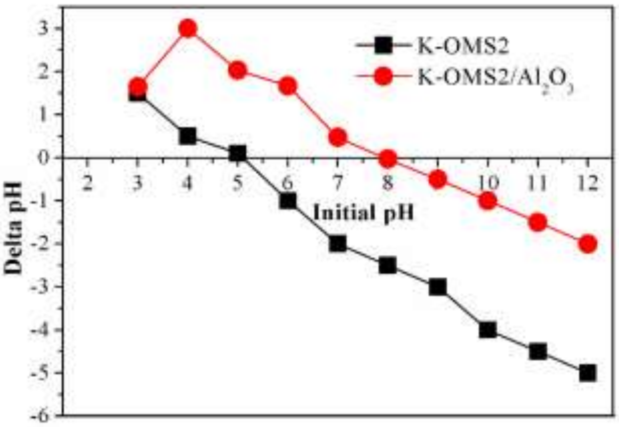

Figure 3 Point of zero charge of K-OMS2 powder and K-OMS2/Al_2O_3-PVA

In addition to the above properties, this study also analyzed the specific surface area, pore-volume, and pore size. The BET surface area and pore volume of adsorbent are 212.65 m^2/g and0.45 cm^3/g, respectively by BJH method. The diameters of the size of K-OMS2/Al_2O_3-PVA pore size distribution are the range of 2–50 nm and consisted of one sharp peak centered at 4.19 nm, with its mesopore following the IUPAC definition (2-50 nm) [16-17]. Figure 4 represents the N_2 adsorption/desorption isotherm for K-OMS2/Al_2O_3-PVA. According to the IUPAC classification of adsorption, the isotherm is a type IV isotherm, which is a hysteresis loop. This is associated with capillary condensation taking place in the mesopores [18-19]. The hysteresis loops are used to indicate pore shape, with the results showing the hysteresis loop is type H3, which is slit-shaped pores [18-20].

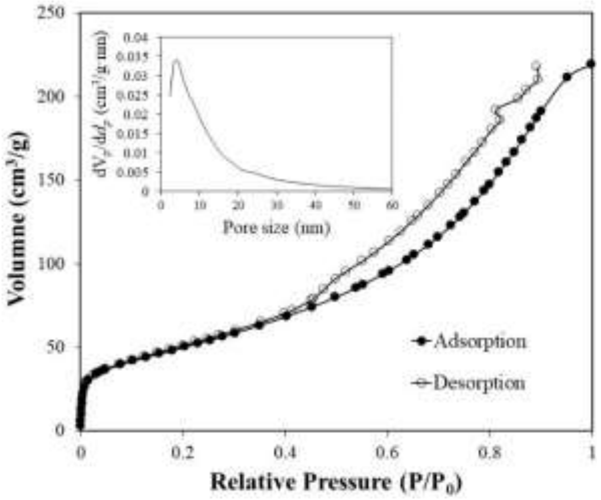

Figure 4 N_2 adsorption/desorption isotherm of K-OMS2/Al_2O_3-PVA, the insert shows the pore size distribution.

2. Kinetic and thermodynamic studies

2.1 Kinetic of MB removal by K-OMS2/Al_2O_3-PVA

Kinetic modeling allows the estimation of sorption rates and leads to a suitable condition rate of feasible reaction. The MB removal by K-OMS2/Al_2O_3-PVA was studied at different temperatures, as seen in Figure 5. It can be observed that the efficiency of MB removal increases as contact time and temperature increase. To determine the mechanism, the result is described with the kinetic model. Table 1 summarizes the calculated parameters for kinetic modeling. The R^2 value is used for deciding the model. According to results, the kinetics model for MB removal was fitted with the pseudo-second-order model. It implied that the process is controlled by the adsorption reaction at the liquid/solid interface in the adsorbent [10,21] . In addition, k_2 increased when temperature increased, meaning that the kinetic constant of this reaction depends on the temperature.

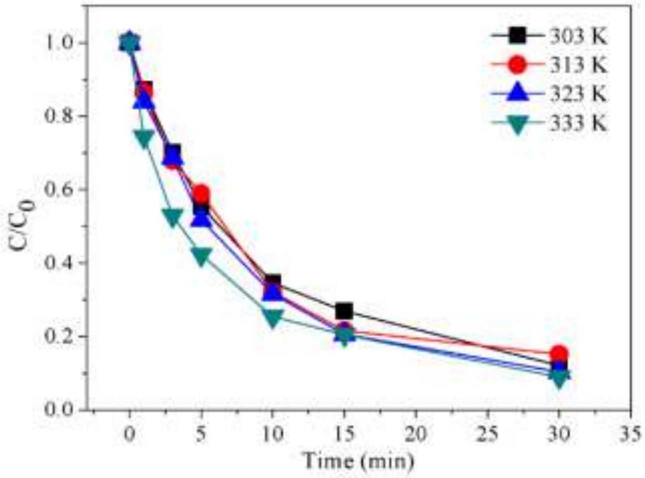

Figure 5 The relationship between contact time and concentration of MB at different temperature.

Table 1 Kinetic parameter for calculated

T (K)	Pseudo-first order			Pseudo-second order		
	k_1 (min^{-1})	q_1 ($mg{\cdot}g^{-1}$)	R^2	k_2 ($g{\cdot}mg^{-1}{\cdot}min^{-1}$)	q_2 ($mg{\cdot}g^{-1}$)	R^2
303	0.225	1.031	0.990	0.131	1.369	0.995
313	0.197	1.124	0.980	0.178	1.306	0.996
323	0.197	1.095	0.996	0.211	1.298	0.997
333	0.270	1.065	0.996	0.342	1.323	0.999

2.2 Thermodynamic of MB removal by K-OMS2/Al_2O_3-PVA

Thermodynamics can be used to describe the related parameters of standard free energy (ΔG^o), as in Equation 3. Enthalpy change (ΔH^o), and entropy change (ΔS^o) were calculated to consider the nature of MB removal by K-

OMS2/Al_2O_3-PVA, by linear van't Hoff equation following Equation 5. The results of the thermodynamic calculations in Figure 6 show the relation of $\ln k_d$ between 1000/T, while Table 2 shows the thermodynamic parameters. The negative values of ΔG^o indicate that the oxidation process can be spontaneous. Furthermore, an increase in the temperature causes a decrease in ΔG^o, which reveals the increased reaction rate at higher temperature. The activation energy (E_a) is 25.522 kJ/mol related to ΔG^o [22]. The positive value of ΔH^o indicates that the reaction of the MB removal by K-OMS2/Al_2O_3-PVA can be endothermic. Positive ΔS^o values indicate an increase of the randomness at the interface during the reaction of MB removal.

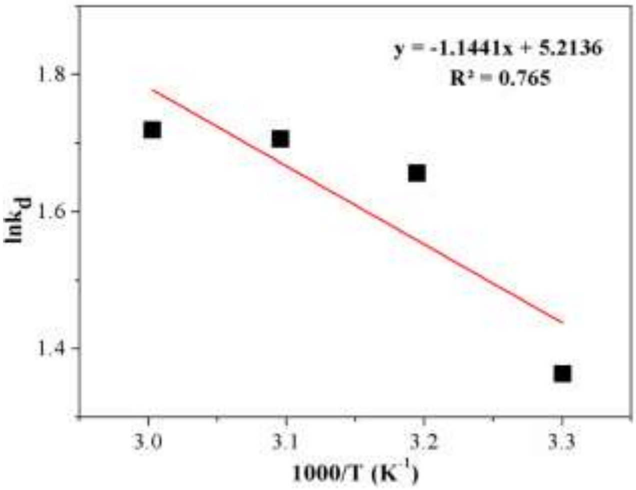

Figure 6 Plot of $\ln k_d$ vs 1000/T for MB removal by K-OMS2/Al_2O_3-PVA

Table 2 Thermodynamic parameter for MB removal by K-OMS2/Al_2O_3-PVA

Temp (K)	**k_d ($L \cdot g^{-1}$)**	**ΔG ($kJ \cdot mol^{-1}$)**	**E_a ($kJ \cdot mol$)**	**ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)**	**ΔH ($kJ \cdot mol^{-1}$)**
303	2.418	-3.434	25.522	43.346	11.980
313	5.240	-4.310			
323	5.506	-4.581			
333	5.580	-4.759			

Conclusions

K-OMS2/Al_2O_3-PVA has some features different from K-OMS2 powder. The results of pH_{pzc} clearly show that the characteristics of K-OMS2 in pH_{pzc} studies change from pH 5 to pH 8 after being coated on alumina ball with PVA. The kinetics of MB removal fitted well with the pseudo second-order kinetic model. The process of MB removal by K-OMS2/Al_2O_3-PVA occurred spontaneously ($-\Delta G°$), in an endothermic nature ($+\Delta H°$), and increased randomness ($+\Delta S°$). According to the results, K-OMS2/Al_2O_3-PVA has potential for use in the removal of MB from wastewater.

Further studies on the adsorption isotherm and measurement of total organic carbon (TOC) are needed to explain the mechanism of MB removal by K-OMS2/Al_2O_3-PVA.

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