Activated Carbon and Manganese Oxide Filler-Based Monolith for Mercury (II) Ions Adsorption from Aqueous Solution

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Abstract

In this study, the authors developed a new adsorbent using activated carbon materials with activated carbon-based monolith adsorbents without and with manganese oxide fillers for removing mercury(II). The response variable of adsorption efficiency, isotherm models, and adsorption kinetics was evaluated in a batch mode by varying concentrations of mercury(II) solution (2, 4, and 6 mg/L) with time (180, 210, and 240 minutes) in solution for each adsorbent without manganese oxide fillers (KM) and with manganese oxide fillers (KMM). The highest removal efficiency obtained with KMM adsorbent was 96%, while the highest removal for KM adsorbent was 47%. Nonlinear models such as Langmuir, Freundlich, and BET were used to calculate adsorption capacity, intensity, and pore volume and to determine the fitting adsorption isotherm. The results showed that the Freundlich isotherm model, with intensity and volume constants obtained respectively 0.291 L/mg and 2.079 L/mg on KMM adsorbents, while on KM adsorbents the intensity and volume constants obtained are 0.042 L/mg and 1.347 L/mg, respectively. The adsorption of mercury(II) ions is according to the pseudo-first-order adsorption kinetics model because it offers the exceptional correlation from the experimental facts, with the adsorption potential and charges steady at the KM adsorbent obtained being 0.083 mg/g dan 0.024 min⁻¹, while the capacity and adsorption rate constants for KMM adsorbents obtained were 0.050 mg/g and 0.007 min⁻¹.

Keywords: Activated carbon, isotherm, manganese oxide, mercury, monolith

1. Introduction

Environmental pollution due to wastewater containing high concentrations of heavy metals is an important environmental problem (Haktanir, 2017). Heavy metal removal from wastewater is critical for human health and the environment. The impact of heavy metals on the environment is hazardous because they are non-biodegradable, and difficult to decompose (recalcitrant), so they can accumulate in soil, biota, and microorganisms (Hussain et al., 2021). One example of the heavy metal produced by industrial waste is the most dangerous metal ion mercury.

Excessive mercury can cause environmental pollution, therefore it needs to be monitored, especially in terms of the amount of its content in the water (Teoh et al., 2013). The maximum limit set by Government Regulation of the Republic of Indonesia or No. 22 of 2021 for mercury(II) ions in water bodies is 0.05 mg/L. In the treatment of hazardous contaminants such as mercury(II) ions in polluted air, various types of adsorbents can be used (Sarah et al., 2021). Various methods have been applied such as adsorption, membrane technology, sedimentation, electrochemical technology, oxidation, reduction, coagulation, and flocculation in wastewater treatment containing heavy metals (Rengga et al., 2019). Adsorption is thought to be the most efficient and appropriate method due to its large absorption capacity, high efficiency, and low-cost materials, given mercury's high volatility and low solubility in water. It is Adsorption has been performed in various studies. The adsorption method is very efficient for the metal desorption process and is more cost-effective than other waste treatment methods. The adsorbent is critical to the adsorption process. The adsorbent that must be chosen has a high pore volume and a large surface area. In various studies, adsorbents can be regenerated and can be used further (Ojedokun & Bello, 2016).

Adsorbents are usually classified based on their origin, namely natural and artificial (synthetic) materials. Natural adsorbents such as clay, bentonite, charcoal, and zeolite. While in the synthetic adsorbent is made from agricultural waste, industrial waste, sewage sludge, etc. Clay (Uddin, 2017), activated
carbon (Singh et al., 2018), biomaterial (Jacob et al., 2018), and natural zeolite (Modeen et al., 2020) have been widely used as adsorbents for organic and inorganic materials from water.

Activated carbon is an adsorbent that is widely used in metal ion removal applications since it has a high surface area (500-1500 m²/g) (Qasem et al., 2021). Activated carbon can be made with various types of raw materials such as plants (rice husks, various types of wood, coconut shells, coffee bean shells), animals (animal bones), and carbon mining materials (coal). When compared with these materials, raw materials from plants such as coconut shells are the best materials compared to other materials to be made into activated carbon because they have high reactivity, low ash content, high water solubility, and many micropores (Saputro et al., 2020). The effectiveness of various activated carbons with high carbon content largely depends on the activation process. Activators can enlarge the surface of the carbon by opening closed pores, thereby increasing the adsorption force.

Manganese oxide is known to reduce heavy metal content in wastewater because it is able to oxidize metals in water (Lin et al., 2009). A single application of MnO₂ is known to reduce the heavy metal content in wastewater because it has an OH functional group that is able to react with metals, has a relatively high surface area, and has a microstructure, phosphate, and other ions (Destiarti et al., 2018). Activated carbon is modified with manganese oxide (β-MnO₂) to absorb Cu²⁺ and Cd²⁺ cations from the aquatic environment (Kulkarni et al., 2017).

Monoliths contain separate holes or solid parallel channels by a thin-walled honeycomb structure. Channels can be hexagonal, circular, rectangular, or triangular (Darmadi et al., 2021). Monoliths are mostly produced by extrusion in particular molds. The extrusion process is formed by pressing through the mold cavity to produce a porous object for adsorption (Akhtar et al., 2014). However, the typically used adsorbents are still in powder shape, so it’s far essential to change the structure of activated carbon by getting readily established adsorbents, i.e. adsorbents with a monolith structure. Monolith adsorbents have the advantages of pressure drop, high specific surface area, reasonable thermal and mechanical properties, good body-interface transfer, easy scale-up, and low manufacturing cost (Nurul et al., 2021). This study developed a new adsorbent using activated carbon with a monolith based adsorbent without manganese oxide (KM) and with manganese oxide (KMM) as filler with the adsorption parameters of mercury(II) metal ions in aqueous solution. Monolith-based was chosen because it has high surface area capability, low production cost, and good body interface transfer (Nurul et al., 2021). The effects of initial mercury(II) adsorption efficiency and contact time on KM and KMM adsorption performance were investigated. To determine optimal values and obtain values for relevant parameters, adsorption isotherm studies were performed using the Langmuir, Freundlich, and BET models. Using pseudo-first-order and pseudo-secondary adsorption kinetic models, the best fits and values of relevant parameters were obtained.

2. Methodology

2.1. Materials

Materials for making KMM are activated carbons from Aceh Besar District, and raw natural clay from Pidie District, as an adhesive in the formation of the monolith. Both locations are in Aceh Province. To make a mercury(II) solution, a mercury standard solution (1000 mg/L, Merck) was used.

2.2. Preparation of monolithic adsorbent

Figure 1 depicts the process of creating an adsorbent with a monolithic structure. The preparation process includes grinding activated carbon and clay into powder with a uniform particle size of 80-100 mesh. Activated carbon and clay in powder form are mixed and then added manganese oxide filler is mixed until a homogenous paste is formed. The extrusion process with a special 316 stainless mold is used in the monolith manufacturing process (1 unit KMM: 1.5 cm diameter; 1 cm high; 7 holes).

**Figure 1.** Monolith structure adsorbent production process.
The molded pasta dough was converted into monolith after 2-days of drying at room temperature, then calcined at 600°C (3 hours) in a Tube Furnace type 21100. The procedure for making KM was carried out with the same treatment.

2.3. Batch Adsorption

The adsorption process was carried out in a batch reactor with 100 ml of predetermined initial concentrations of aqueous mercury (II) ions (1.94, 4.1, and 6.13 mg/L). Mercury Standard Solution is diluted by mixing it with aquadest (1000 mg/L). The initial concentrations determined by the Atomic Absorption Spectrophotometer (AAS) were 1.97, 4.1, and 6.13 mg/L, respectively.

In a Kotterman water bath shaker, add 1 unit of KMM (2.2 g) to each reactor and stir continuously for 240 minutes at room temperature (110 rpm). 5 ml of each mercury (II) ion solution was collected with stirring and subjected to atomic absorption spectroscopy (AAS, Analyst 800 Perkin Elmer Co, Norwalk CT USA). In terms of kinetic data, different samples with initial concentrations of 1.9 and 4.1 mg/L were taken at four different times, namely at 0, 180, 210, and 240 min. Adsorption capacity and efficiency should be measured, and data should be examined to find appropriate isotherm models (Langmuir, Freundlich, or BET) and kinetic equations (pseudo-first-order or pseudo-second-order).

2.4. Isotherms Model

The adsorption equilibrium is important because it shows how the adsorbate molecules are distributed in the liquid and solid phases when the adsorption process reaches equilibrium. The adsorption isotherm experiment adopts three nonlinear isotherm models: Langmuir, Freundlich and BET. The Equations for determining the parameters of the isotherm models are 1, 2 and 3, respectively (Agarwal et al., 2014).

\[ q_e = \frac{k_x \times C_e}{1 + k_y \times C_e} \]  
\[ q_e = K_I \times C_e^{\frac{1}{n}} \]  
\[ \frac{C_o}{q_s/C_s - C_o} = \frac{1}{a_s \times C_s^{\frac{1}{n}}} + \frac{(C_{\mathrm{BET}} - 1) \times C_s}{q_s \times C_{\mathrm{BET}}} \]

In the Langmuir isotherm, \( a_s \) (L/mg) and \( K_I \) (L/g) are the Langmuir constants used to calculate \( Q_o = K_I/a_s \), representing the monolayer capacity (mg/g) of the adsorbent. According to the Freundlich equation, \( 1/n \) and \( K_I \) are empirical constants that depend on the nature of the adsorbent and adsorbate. These two values (1/n and \( K_I \)) are crucial when choosing the adsorbent as the separation medium, where \( K_I \) is the total adsorption capacity (mg/g) and \( 1/n \) is the heterogeneity factor, which indicates the strength of adsorption of the adsorbent. The binding energy between the adsorbate and the adsorbent molecules. \( q_s \) is the adsorption isotherm capacity (mg/g) and \( C_{\mathrm{BET}} \) is the BET isotherm constant (L/mg) in the BET isotherm equation. Because nonlinear equations are inherently more difficult to solve than linear equations, estimating isotherm parameters from them requires additional optimization using additional solver tools in Microsoft® Excel. A suitable isotherm model for each adsorbent was determined by minimizing the nonlinear value of the sum of squared errors (SSE) using a nonlinear analysis method. The resulting isotherm constants (\( a_s \), \( K_I \), \( Q_o \), \( n \), \( K_I \), \( C_{\mathrm{BET}} \), and \( q_s \)) were obtained from the optimization process and are shown in Table 1.

2.5. Adsorption Kinetics

Adsorption kinetics states that there is a process of absorption of a substance by the adsorbent as a function of time. Characteristics of the adsorption ability of the adsorbent on the adsorbate can be seen from the rate of adsorption. The adsorption rate can be determined from the rate constant adsorption (k) and the resulting reaction order of an adsorption kinetics model. Using Equation 4 and 5, the kinetic models commonly used for the kinetics of adsorption processes are the Lagergren pseudo-first-order model and Ho pseudo-second-order model (Musah et al., 2022).

\[ \ln(q_e - q_i) = \ln(q_o) - k_1 t \]  
\[ \frac{t}{q_t} = \frac{1}{k_1 q_o^2} + \frac{t}{q_o} \]

where \( q_t \) (mg/g) is the adsorption capacity (q) at time t (min); \( q_e \) (mg/g) is the value of q at equilibrium; and \( k_1 \) (1/min) is a pseudo-first-order constant; and \( k_2 \) (g/(mg.min)) pseudo second order constant.

The pseudo-first-order and pseudo-second-order kinetic models for each parameter were calculated using the t-slope and intercept plots, as well as t/qt versus t-plots, adapted from ln (qe-qt), the model that fits the research results is a kinetic model with highest \( R^2 \).
3. Results and Discussion

3.1. Adsorption Efficiency

The percentage of metal ions removed by mercury(II) ions adsorbed by KM and KMM adsorbents during contact time is referred to as adsorption efficiency. Figure 2 depicts the effect of adsorbents KM and KMM on adsorption efficiency. The longer the contact time, the greater the adsorption efficiency. During the first 180 minutes, the adsorption efficiency increased dramatically. This was due to a large number of active sites remaining unincorporated with mercury(II) ions on the sorbent's (Martini et al., 2018).

Figure 2. Effect of contact time with variations adsorbent KM dan KMM.

The adsorption efficiency reaches its maximum point at 96% on KMM adsorbents while KM reached 47%. KMM adsorbent produces high efficiency than previous researchers on the adsorption of mercury(II) ions using activated carbon (Park & Lee, 2018). In Figure 2 it can also be seen that the difference in the efficiency of KMM and KM adsorbents is 49%. This shows that the adsorbent with the addition of manganese oxide with a monolith structure is proven to be able to reduce heavy metals mercury(II) ions in water because it can oxidize metal mercury(II). A single application of MnO$_2$ is known to reduce the heavy metal content in wastewater because it has an OH functional group that is able to react with metals, has a relatively high surface area, and has a microstructure, phosphate, and other ions (Destiarti et al., 2018).

Figure 3 shows that the concentration of mercury(II) ions in a solution of 2 mg/L, 4 mg/L, and 6 mg/L resulted in the highest removal efficiencies which were 96%, 91%, and 88%, respectively. A decrease in adsorption efficiency can occur because the adsorbent undergoes desorption. Desorption can be due to the surface of the adsorbent being already in a saturated condition and being in equilibrium so that the mercury(II) metal ions that were initially adsorbed by the adsorbent can be released again.

3.2. Isotherm Model

To determine the optimal isotherm model under Langmuir, Freundlich, and BET (Brunauer-Emmett-Teller), non-linear methods were used to examine adsorption equilibrium data from batch experiments. Because of its stable error distribution, the non-linear analysis method was chosen (Karri et al., 2017). Figure 4 (a) and (b) show the results for the Langmuir, Freundlich, and BET models, and Table 1 contains the constants.

Figure 4 shows that the suitability of the experimental data with the adsorption equilibrium data is based on the isotherm. It can be seen in Table 1 that the minimum SSE value on the mercury(II) ion adsorption data using KM and KMM adsorbents tends to follow the Freundlich isotherm equation, which means that the adsorption takes place by multilayer physisorption. This shows that the adsorbate moves until an adsorption process occur which occurs in many layers of physical adsorption (physisorption) and more absorption occurs on the surface of the adsorbent. Physisorption adsorption occurs because of the attractive force between the surface of the adsorbent and the very weak adsorbate, namely the Van Der Waals force (Sari, et al., 2017).

This allows the adsorbate to move freely until a stratified adsorption process occurs. The use of activated carbon to adsorb heavy metals is more in line with the Freundlich model (Kulkarni et al., 2017). The Freundlich model is an empirical/experimental type used to
explain non-ideal adsorption processes on heterogeneous surfaces such as adsorbent surfaces with different functional groups. As the \(1/nF\) value approaches zero, the adsorbent surface becomes more uneven. In the adsorption process of mercury(II) ions using adsorbents KM and KMM, the value of \(n\) is far from zero and less than 10, thus the adsorption process is on a homogeneous reversible surface (Susanti et al., 2015).

![Graph](image)

**Figure 4.** Equilibrium isotherm on variation of mercury(II) ions adsorbents (a) KM, and (b) KMM.

**Table 1.** Optimization value of adsorption isotherm.

<table>
<thead>
<tr>
<th>Ads</th>
<th>Isoterm Langmuir</th>
<th>Isoterm Freundlich</th>
<th>Isoterm BET</th>
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<tbody>
<tr>
<td></td>
<td>(K_L) (L/g)</td>
<td>(a_L) (L/mg)</td>
<td>(Q_o) (mg/g)</td>
</tr>
<tr>
<td>KM</td>
<td>0,046</td>
<td>0,155</td>
<td>0,296</td>
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<tr>
<td>KM</td>
<td>1,293</td>
<td>4,031</td>
<td>0,321</td>
</tr>
</tbody>
</table>

**Table 2.** Kinetic parameters for mercury(II) ions adsorption.

<table>
<thead>
<tr>
<th>Co</th>
<th>Ads</th>
<th>Methods</th>
<th>(q_e) (_{exp})</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(q_e) (_{cal})</td>
<td>(k_1)</td>
<td>SSE</td>
</tr>
<tr>
<td>2 mg/L</td>
<td>KM</td>
<td>linier</td>
<td>0,041</td>
<td>0,013</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-linier</td>
<td>0,051</td>
<td>0,007</td>
<td>2,15 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>linier</td>
<td>0,084</td>
<td>0,025</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-linier</td>
<td>0,085</td>
<td>0,024</td>
<td>1,55 \times 10^{-6}</td>
</tr>
<tr>
<td>4 mg/L</td>
<td>KMM</td>
<td>linier</td>
<td>0,077</td>
<td>0,017</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-linier</td>
<td>0,083</td>
<td>0,012</td>
<td>3,80 \times 10^{-8}</td>
</tr>
<tr>
<td></td>
<td>KM</td>
<td>linier</td>
<td>0,173</td>
<td>0,021</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-linier</td>
<td>0,170</td>
<td>0,018</td>
<td>1,30 \times 10^{-6}</td>
</tr>
</tbody>
</table>
3.3. Adsorption Kinetics

The study of the rate of adsorption during the adsorption process is known as adsorption kinetics. The kinetic rate and mechanism of mercury (II) adsorption by adsorbents were determined using the pseudo-first-order Lagergren model and the pseudo-second-order model. Regression analysis using linear and non-linear methods was used to find a better fit model for these two equations. Regression analysis using linear and non-linear methods was used to find a better model for the two equations. A linear method that uses equations to analyze experimental data. Non-linear methods, on the other hand, analyze data using data optimization techniques, resulting in very flexible fit function curves and error values (Tran et al., 2017). The kinetic parameters of adsorption are shown in Table 2.

Several parameters are listed in Table 2, including theoretical adsorption capacity (qe,cal), regression coefficient (R²), pseudo-first-order rate constant (k₁), and pseudo-second-order rate constant (k₂) (Delgado et al., 2019). When comparing R², it is clear that the non-linear analysis method is superior.

The regression coefficients (R²) of linear and non-linear models were compared in Table 2 to determine which kinetics model best fits the adsorption process in this study. According to Table 2, the non-linear method’s R² values (R² > 0.99) were greater than the linear method’s. This suggests that the non-linear adsorption kinetic model is more suitable for describing the kinetics of mercury(II) ion adsorption using KM and KMM adsorbents. As can be seen, the difference in SSE values between the two adsorbents was insignificant enough to be used as a determinant. On the other hand, the value of theoretical adsorption capacity (qe cal) obtained from the pseudo-first-order kinetic model was found to be closer to the experimental adsorption capacity (qe exp). Therefore, pseudo-first-order kinetic models were used to describe the adsorption process using KM and KMM adsorbents. The adsorption rate was directly proportional to the availability of free active sites on the adsorbent surface, according to the pseudo-first-order kinetic model. The adsorption driving force (qe-qt), which is directly proportional to the number of active sites, was also influenced by the amount of adsorbate on the adsorbent surface, the higher the adsorption driving force, the more available free active sites (Tran et al., 2017).

4. Conclusion

Regarding the adsorption process, the development of monolithic adsorbents based on activated carbon (KM) and activated carbon with manganese oxide filler (KMM) proved to be an easy and efficient process. The resulting adsorbents show potential use as adsorbents for the removal of mercury (II) with reasonable removal rates and power efficiencies. Activated carbon monoliths containing manganese filler have increased adsorption capacity for mercury(II) metal ions compared to those without manganese filler. The highest efficiency of KM adsorbent in removing mercury(II) was 47% and that of KMM adsorbent was 96%. The Freundlich model was found to be the best fit for adsorption capacity, with volume and intensity constants obtained were 1.347 and 0.041 mg/g for KM adsorbent, while for KMM adsorbent the volume and intensity constants were 2.078 and 0.291 mg/g, respectively. The adsorption of mercury(II) ion is by the pseudo-first-order adsorption kinetics model because it provides the best correlation from the experimental data, with the adsorption capacity and constant rate on the KM adsorbent obtained being 0.050 mg/g and 0.007 min⁻¹, while the capacity and constant adsorption rates for KMM adsorbents obtained were 0.083 mg/g and 0.024 min⁻¹. Optimization of KMM should be considered to achieve a more feasible path in water purification.

References


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