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Coal-based granular activated carbon loaded with MnO_2 as an efficient adsorbent for removing formaldehyde from aqueous solution

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ABSTRACT

In this study, coal-based granular activated carbon loaded with MnO_2 (ACLM) was tested as adsorbent for the removal of formaldehyde from aqueous solution. The ACLM was characterized by scanning electron microscopy, energy dispersive X-ray spectrometry, Brunauer–Emmett–Teller, and Fourier transform infrared spectra. The optimized pH of formaldehyde adsorption was 7.0. The removal percentage increased from 21.8 to 72.1% by raising the ACLM dosage from 0.1 to 1.0 g. The formaldehyde adsorption rate increased a little at initial formaldehyde concentrations from 0.6 to 1.8 mg/L. The adsorption equilibrium time was 24 h. The adsorption rate of formaldehyde increased from 58.1 to 61.2% with temperature rising from 298 to 308 K and decreased from 61.2 to 54.0% when temperature from 308 to 318 K. Isotherm modeling revealed that Langmuir equation could better describe the adsorption of formaldehyde onto the ACLM and the maximum adsorption capacity obtained was 4.53 mg/g. Kinetic data efficiently fitted with the pseudo-second order. The decrease of ΔG° from 298 to 308 K suggested more favorable of formaldehyde adsorption onto the ACLM and increase of ΔG° from 308 to 318 K revealed that the sorption was more unfavorable. Results from this study suggest that ACLM is an effective adsorbent for the removal of formaldehyde from aqueous solution in drinking water treatment field.

Keywords: Coal-based granular activated carbon loaded with MnO_2; Formaldehyde; Aqueous solution; Adsorption; Isotherm; Kinetic; Thermodynamic

1. Introduction

Formaldehyde is widely applied in various industries including phenol–formaldehyde resin manufacturing, adhesive production, petrochemical output, disinfectant and preservative production, textile processing, papermaking, and wood and wood-composite fabrication. Industries that utilize or produce formaldehyde usually generate wastewater containing variable concentrations of formaldehyde, ranging from a few to hundreds of milligrams per liter [1,2]. A certain concentration of formaldehyde can also generate in drinking water supplies by the oxidation of natural organic matter or humic using ozone process during water treatment [3,4]. According to the ranking of the environmental impact generated by 45 chemical products, formaldehyde ranks in first place [5]. The sensuous effect of formaldehyde on people is well known to us: irritation of the eyes and upper respiratory tract, nausea, headache, and allergic skin reactions [6]. Exposure to formaldehyde can cause central

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nervous system damage; blood, immune system, and developmental disorders. Based on large-scale human studies conducted by the International Agency for Research on Cancer, formaldehyde was classified as a human carcinogen that causes nasopharyngeal cancer and probably causes leukemia [7,8]. The World Health Organization has established a health-based guideline value of 900 μg/L for formaldehyde in drinking water [9]. It is therefore important to find an effective method that is capable of removing formaldehyde from polluted drinking source water or treated water with ozone technology.

Past studies have reported a series of methods for removing formaldehyde from aqueous solution. The frequently applied methods are microbial degradations including aerobic and anaerobic bioreactors [10,11]. Other methods of formaldehyde removal involved advanced oxidation processes [7]. From these research conclusions on the treatment of formaldehyde, we find that formaldehyde has inhibitory effect on the metabolism of microorganisms and its toxicity in high concentrations impede the application of single biological processes for the removal of highly concentration formaldehyde wastewater. Advanced oxidation processes are generally expensive, process complex, and difficult being controlled in practical application. Furthermore, the main disadvantages of microbial degradation and advanced oxidation processes are low formaldehyde removal efficiency, especially in drinking water treatment area [12].

Therefore, it is important to find effective and economical formaldehyde removal methods from aqueous solution. Adsorption techniques are much preferred for the removal of formaldehyde because of their efficiency, low cost, and operability compared with other removal techniques [12,13]. Activated carbon has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media including formaldehyde due to their abundant micropores, large surface area, fast adsorption/desorption rate, excellent adsorption capacity, and cost-effectiveness [14,15]. The effect of surface functional groups modification on the adsorption behavior of activated carbons has been of great interest over the past years [16,17].

As one of the most important transition metal oxides, manganese dioxide is promising in a wide range of technological applications, including catalysis and ion-exchange, due to their structural flexibility combined with novel chemical and physical properties. MnO_2 nanomaterials have been proven to possess high catalytic activity for effective degradation of formaldehyde and could completely convert formaldehyde into CO_2 and H_2O at low temperatures [18]. However, a catalyst support is usually needed to solve the problem brought by the small specific surface area and to realize an optimized utilization of active sites. Compared with silica-supported and alumina-supported catalysts, catalysts supported by activated carbon hold several advantages: weak interaction between support and active component which leads to an optimized utilization of active sites, high stability in caustic and acidic conditions, high adsorption activity partially due to the enriched surface oxygen complexes [19]. The most common approaches for the synthesis of manganese dioxide are by the oxidation of manganese hydroxide or by the reduction of potassium permanganate using a variety of oxidizing or reducing agents [20]. To our knowledge, there are no previous published reports on the use of coal-based granular activated carbon loaded with MnO_2 (ACLM) as an efficient and novel adsorbent for removing formaldehyde from aqueous solution in drinking water treatment area.

In the present work, we prepared ACLM using a simple method. The overall objective of this research was to investigate the removal characteristics of formaldehyde from aqueous solution using this novel adsorbent. After scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), energy dispersive X-ray spectrometry (EDS) and Fourier transform infrared spectra (FTIR) characterization of the ACLM, the influences of aqueous solution pH, ACLM dosage, formaldehyde concentration, contact time, and temperature were investigated. The isotherm, kinetic, and thermodynamic parameters were also fitted to describe the experimental data. The conclusions of this study will help to promote the use of ACLM as filter media for formaldehyde removal in drinking water treatment works. These issues are addressed in detail in this article.

2. Materials and methods

2.1. ACLM sample preparation and characterization

Samples of coal-based granular activated carbon (12·40 mesh) were obtained from Calgon Carbon Corporation, USA. The activated carbon meets all the requirements of the AWWA Standard for Granular Activated Carbon, edition B604-96, ANSI/NSF Standard 61, and the Food Chemical Codex. The samples were washed using distilled water and dried in a muffle heater at 323 K for 24 h. Firstly, 50 g of coal-based granular activated carbon was immersed in 400 mL of aqueous solution of potassium permanganate with molar concentration 0.079 mol/L in an air bath temperature oscillation maintaining speed shock at room

temperature for 2 h. After the treatment, the samples were filtered to remove excess chemicals from the solution. Then, they were dried at 378 K for 12 h to ensure complete removal of water, while leaving the chemicals in the samples. For the MnO_2 load, samples were placed in the muffle furnace under a nitrogen atmosphere. Then, the temperature was increased in step of 10 K/min to the desired temperature 873 K, which was held constant for 0.5 h. Then, the sample was cooled to ambient temperature. The load process was done under flow of nitrogen (500 mL/min). The prepared ACLM was thoroughly washed with distilled water until a neutral pH was obtained [17–21].

A scanning electron microscope (Model S-3400N II, Hitachi Instrument, Japan) was used to obtain scanning electron microscopy (SEM) micrographs of the ACLM. Samples of ACLM were all gold plated, and an electron acceleration voltage of 20 kV was applied for SEM observation. The BET surface area and total pore volume of the ACLM were determined using a surface analyzer (Model Autosorb-1C, Quantachrome Instrument, USA). Nitrogen was used as cold bath (77.35 K). The predominant elements of ACLM were analyzed using an energy dispersive X-ray spectrometry (EDS) (Model EX-250, Horiba Instrument, Japan). An FTIR spectrometer (Model 360, Thermo Nicolet Instrument, USA) was employed to determine the presence of functional groups in all the adsorbents at room temperature. A pellet (pressed-disk) technique was used for this purpose. The pellets were prepared by mixing the adsorbent with KBr (mass ratio 100:1). The spectral range covered was 4,000–500 cm^{-1}; scanning was performed at a rate of 16 nm s^{-1} [21].

2.2. Analytical measurement of formaldehyde

A stock formaldehyde solution of 1,000 mg/L was prepared from formaldehyde (37% purity, CH_2O, FW: 30.03, Shanghai Pilot Chemical Corporation, China) dissolved with distilled water. This solution was stored at 277 K. The working solutions with different concentrations were prepared by appropriate dilutions of the stock solution. The concentration of formaldehyde in aqueous solution was determined using UV–vis spectrophotometer (Model UV759, Shanghai Spectrum Instrument, China) at 414 nm wavelength using acetylacetone spectrophotometry method [8]. A digital pH meter (Model PHS-3C, Insea Instrument, China) was used for pH measurement.

2.3. Procedure of formaldehyde adsorption experiments

A typical adsorption experiment of formaldehyde was processed using the necessary dosage ACLM in a 250-mL stopper conical flask at desired formaldehyde concentration, temperature, pH value, and contact time. The pH values of the solution were adjusted by adding negligible volumes of 0.1 M HCl or NaOH. The flask was shaken for the desired contact time in a rotary shaker fixed at 100 rpm. The contents of the flask were filtered through a 0.45-μm filter membrane, and the filtrate was analyzed for remaining formaldehyde concentration. The removal percentage of formaldehyde was determined from the initial and final concentrations of formaldehyde in the liquid phases. The pH of the solutions was checked before the beginning of the adsorption experiments. The adsorption experiment was conducted three times for each sample, and each individual chemical assay was conducted in duplicate [21].

The percentage of formaldehyde adsorption by the ACLM was calculated using the equation:

$$\text{Adsorption percentage, } \% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t are the concentrations of formaldehyde (mg/L) in the solution initial and at time t (h). Adsorption capacity was calculated using the mass balance equation for the adsorbent:

$$q = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where q is the adsorption capacity (mg/g), C_e is the equilibrium concentration of formaldehyde (mg/L) in the solution, V is the volume of formaldehyde solution (L), and M is the weight of ACLM (g).

The effect of pH on formaldehyde adsorption was investigated in the initial pH range of 1.0–14.0. Adsorption experiments for the effect of pH were conducted using a 100 mL formaldehyde solution having a concentration of 1 mg/L with an ACLM dosage of 0.5 g for a contact time of 24 h at 298 K. The effect of ACLM dosage on adsorption percent of formaldehyde was studied using a 100 mL formaldehyde solution having a concentration of 1 mg/L. The selected ACLM was used at dosages ranging from 0.1 to 1 g for a contact time of 24 h at 298 K. The effect on the variation of the initial concentration of the solution was studied using a 100 mL formaldehyde solution of varying concentrations (0.6–10 mg/L), a contact time of 24 h, and an ACLM dosage level of 0.5 g at 298 K. Kinetics analysis for the adsorption process was studied on the batch adsorption of a 100 mL formaldehyde solution having concentration of 1 mg/L with an ACLM dosage of 0.5 g. The contact time was varied from 1 to

32 h at 298 K. The effect of temperature was evaluated using a 100 mL formaldehyde solution with a concentration of 1 mg/L with an ACLM dosage of 0.5 g for a contact time of 24 h. The selected temperatures ranged from 298 to 318 K [22].

3. Results and discussion

3.1. Characterization of the ACLM

The scanning electron microscopy (SEM) is the primary tool used for characterization of the surface morphology and fundamental physical properties of adsorbent materials [23]. The SEM images of ACLM under the different magnifications (100, 500, 2,000, and 5,000) were shown in Fig. 1. From Fig. 1, we could find that ACLM has a coarse porous surface with irregular pores similar with coal-based granular activated carbon [24]. The particle size, morphological features, and porosity of ACLM had not been changed through the load process.

The surface area, pore volume, and average pore diameter calculations employed the classical BET method that was also included in the micromeritics software [25]. The BET surface area of the ACLM was 862.04 m^2/g. The pore volume was found to be 0.44 cm^3/g with an average pore diameter (4V/A by BET) of 2.07 nm, indicating a characteristic of microporous and mesoporous material [21,26].

The local elemental composition of the ACLM was studied by EDS as shown in Fig. 2. It confirmed that the main elements of ACLM are composed of carbon being 80.38% and oxygen being 12.88%. A little amount of manganese and potassium with weight percentage 3.01 and 1.20% may be due to the transformation of potassium permanganate to manganese dioxide under high temperature conditions with the load process [27].

The FTIR spectra of ACLM were shown in Fig. 3. As shown in Fig. 3, the infrared spectrum showed a number of adsorption peaks, which suggested the complexity of the ACLM. The strong adsorption band around 3,457 cm^{-1} could be attributed to the vibration of OH stretching, and adsorption band at 2,933 cm^{-1} could be associated with the existence of CH_2 stretching. The peak at 1,648 cm^{-1} was assigned to C=C stretching. It showed the peak indicating N–H stretching appeared at 1,402 cm^{-1}. Besides, the peak at

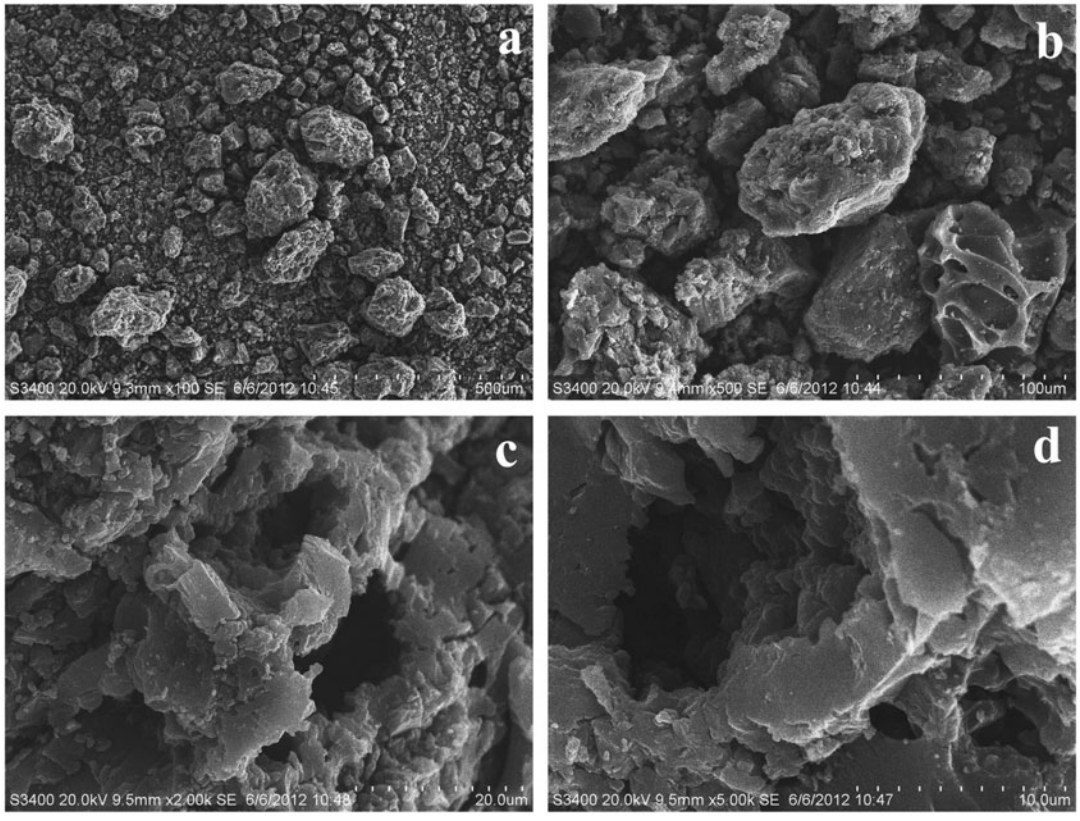

Fig. 1. SEM photographs of ACLM at (a) 100×, (b) 500×, (c) 2,000×, and (d) 5,000× magnification.

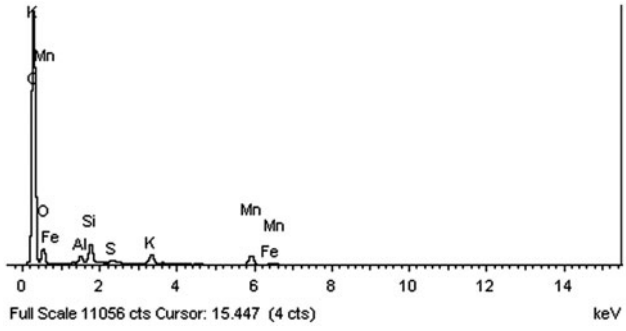

Fig. 2. EDS of ACLM.

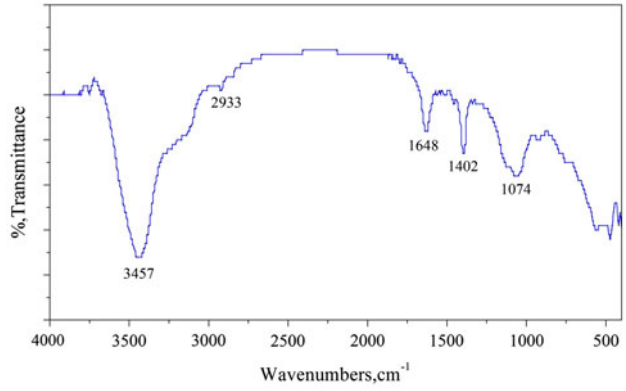

Fig. 3. FTIR spectra recorded for ACLM.

1,074 cm^{-1} may be due to six-member cyclic ether [28,29].

3.2. Effect of solution pH

The solution pH of the system exerts profound influence on the ability of adsorbent surface for interaction and adsorbate molecule tendency for binding to solid surface [30]. The influence of pH on the formaldehyde adsorption onto ACLM was investigated and shown in Fig. 4. Formaldehyde in aqueous solution under low concentration exists in molecular form and is neutral organic substance at different pH values. But it was seen from Fig. 4 the variations of the formaldehyde removal from aqueous solution at different pH values. The maximum formaldehyde adsorption rate took place at pH 7.0. It could be considered that catalytic reaction of manganese dioxide and sorption of adsorbent all play important roles on the removal of formaldehyde onto ACLM [20]. At pH values lower than 7.0, the hydrogen ions (H^+) protonated the nitrogen-containing functional groups, and therefore, formaldehyde removal decreased in strong

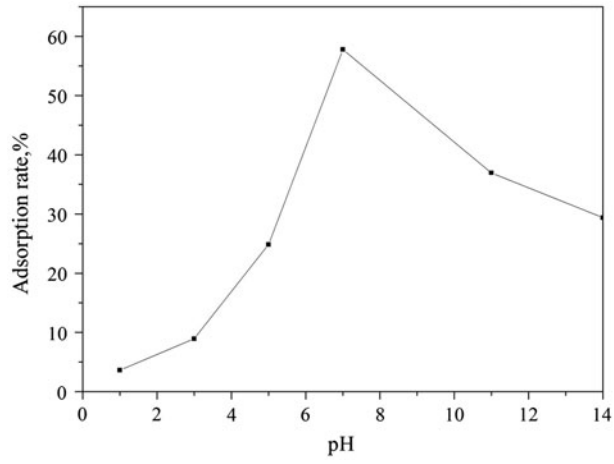

Fig. 4. Effect of pH on formaldehyde adsorption by ACLM.

acidic solutions [12]. At pH values higher than 7.0, the removal percentage significantly decreased due to abundance of hydroxide ions (OH^-) and its competition with formaldehyde molecule for adsorption onto ACLM [31]. Catalytic reaction of manganese dioxide on degradation of formaldehyde was probably not conducive under acidic and alkaline conditions [20]. Existing form of manganese dioxide under low pH values and high pH values might affect the formaldehyde removal rare [19]. By considering the results and in order to apply in actual water treatment works, pH 7.0 as the optimized pH was selected for all subsequent experiments.

3.3. Effect of initial ACLM dosage

The adsorbent dosage is an important parameter because it determines the removal ability of adsorbate [32]. The effect of initial ACLM dosage on formaldehyde adsorption was illustrated in Fig. 5. It could be seen that the removal efficiency increases with increasing ACLM dosage (the removal percentage increased from 21.8 to 72.1% by raising the ACLM dosage from 0.1 to 1.0 g), which could be attributed to the more available active sites and the higher surface area for adsorption. The adsorbent capacity significantly decreased in opposite direction of removal percentage [33].

3.4. Effect of formaldehyde concentration

The effect of formaldehyde concentration on its adsorption by ACLM was investigated, and the percentage of formaldehyde removal at different initial

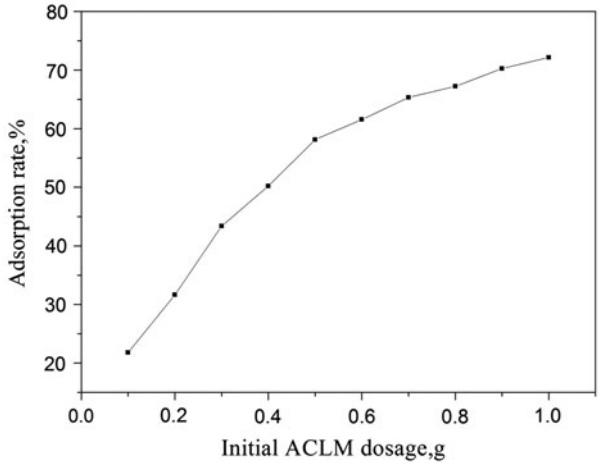

Fig. 5. Effect of initial ACLM dosage on formaldehyde adsorption.

concentrations was depicted in Fig. 6. As shown, the formaldehyde adsorption rate increased a little at initial formaldehyde concentrations from 0.6 to 1.8 mg/L, while the removal percentage significantly decreased with further increase in initial formaldehyde concentrations being 10 mg/L that emerged from saturation and occupation of the available sites on the adsorbents. At low formaldehyde concentrations from 0.6 to 1.8 mg/L, solute to adsorbent vacant sites ratio is high and causes an increase in formaldehyde removal. It seemed that at higher formaldehyde concentration such as 10 mg/L, due to increase in its molecular competition for the low vacant reactive sites, the adsorption process will increasingly slow down [34].

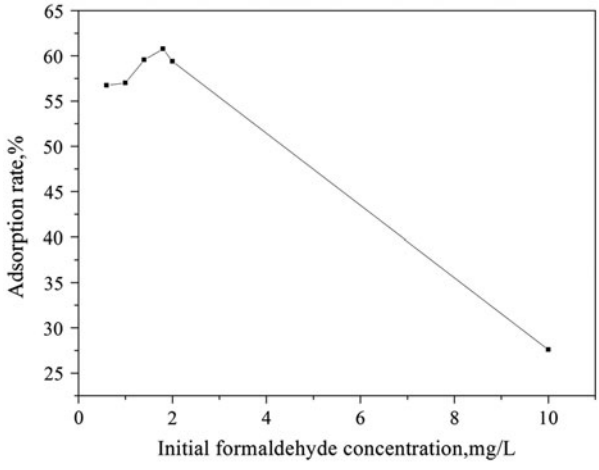

Fig. 6. Effect of initial formaldehyde concentration on formaldehyde adsorption.

3.5. Effect of contact time

The effect of contact time on the amount of formaldehyde adsorbed on ACLM was investigated, and the data were presented in Fig. 7. As shown, the extent of formaldehyde removal by the ACLM was found to increase by rising contact time and reach a maximum value after 24 h. The initial rapid adsorption can be attributed to the availability of the high surface area and due to formaldehyde concentration gradient as driving force for migration and diffusion to the surface of the ACLM [31]. It was found that further addition of time after 24 h has no significant effect in formaldehyde removal due to electrostatic repulsion between the adsorbed formaldehyde onto the surface of the ACLM and the available formaldehyde in solution in addition to the slow pore diffusion of the formaldehyde into the ACLM [34].

3.6. Effect of temperature

The effect of temperature on formaldehyde adsorption rate was investigated, and the data were illustrated in Fig. 8. As shown, the adsorption rate of formaldehyde increased from 58.1 to 61.2% with temperature rising from 298 to 308 K due to a faster rate of diffusion of formaldehyde molecules from the solution to the ACLM at higher temperature [35]. On the other hand, the adsorption rate of formaldehyde decreased from 61.2 to 54.0% when temperature continued to rise from 308 to 318 K due to the interaction between formaldehyde and ACLM surface reduced at higher temperature. Temperature rising led to formaldehyde's molecular diffusivity from ACLM interior to external part enhances, and the desorption

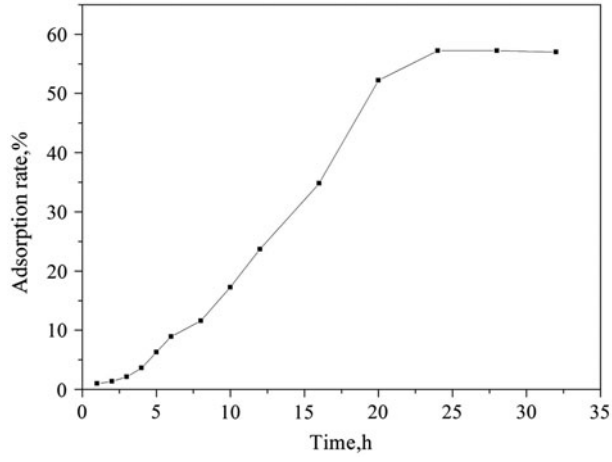

Fig. 7. Effect of contact time on formaldehyde adsorption.

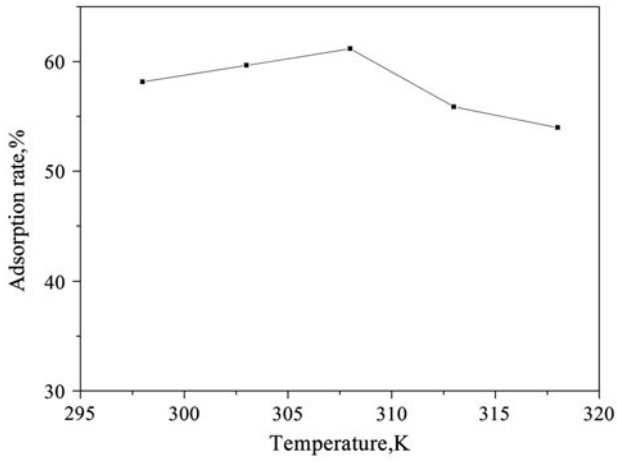

Fig. 8. Effect of temperature on formaldehyde adsorption.

rate of formaldehyde from ACLM to aqueous solution increases [35].

3.7. Adsorption equilibrium isotherm model

Adsorption equilibrium isotherms such as Langmuir and Freundlich represent mathematical relation of amount of adsorbed target per gram of adsorbent to the equilibrium solution concentration at certain temperature. This investigation has great attention from both theoretical and practical point of view to obtain strong knowledge about surface properties of adsorbent and removal mechanism [30].

The theoretical Langmuir isotherm as one of the most traditional models has maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface that calculated according to the well-known procedure [30]. The Langmuir equation is given by the following equation [21]:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{3}$$

where q_m shows the monolayer sorption capacity (mg/g), b is the Langmuir constant (L/mg), C_e is equilibrium formaldehyde concentration in the solution (mg/L), and q_e represents amounts of formaldehyde adsorbed onto ACLM at equilibrium (mg/g). The plot of $1/q_e$ vs. $1/C_e$ was employed to generate the intercept value of $1/q_m$ and slope of $1/(q_m b)$. The calculated conclusions were enumerated in Table 1.

Through calculation, q_m and b were determined to be 4.53 mg/g and 0.061 L/mg, respectively. The correlation coefficient (R^2) was 0.9740. One of the essential characteristics of the Langmuir model can be expressed in terms of the dimensionless constant separation factor for the equilibrium parameter R_L, defined as [21]:

Table 1
Isotherm constant parameters and correlation coefficients calculated for formaldehyde adsorption onto ACLM

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	4.53
	b (L/mg)	0.061
	R^2	0.9740
Freundlich	$1/n$	0.58
	k_F	0.208
	R^2	0.8837

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where C_0 is the maximum initial concentration of formaldehyde (mg/L). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [22]. The R_L value in the study was found to be 0.62, indicating that this adsorption process is favorable.

The Freundlich isotherm model based on the assumption for adsorbent adsorption on heterogeneous surface along interaction can be expressed in linear form as follows [34]:

$$\log\ q_e = \log\ k_F + \frac{1}{n}\ \log\ C_e \tag{5}$$

where k_F and $1/n$ are Freundlich constants, C_e is the equilibrium concentration of the solution (mg/L), and q_e is the equilibrium adsorption capacity per unit weight adsorbent (mg/g).

The equilibrium experimental data were fitted using the Freundlich isotherm, and the fitted conclusions were included in Table 1. The Freundlich parameters k_F, $1/n$, and R^2 evaluated from the nonlinear plot using nonlinear regressive analysis were 0.208, 0.58, and 0.8837, respectively. The Freundlich parameter $1/n$ relates to the surface heterogeneity. When $0 < 1/n < 1$, the adsorption is favorable; when $1/n = 1$, the adsorption is homogeneous and there is no interaction among the adsorbed species; and when $1/n > 1$, the adsorption is unfavorable [22]. In this research, $1/n = 0.580$ indicated that the adsorption behavior of formaldehyde on ACLM was carried out easily and heterogeneous sorption.

From the above calculation and analysis, the correlation coefficient of Langmuir isotherm model being 0.9740 was higher than the correlation coefficient calculated by Freundlich isotherm model being 0.8837. It could be concluded that the Langmuir isotherm model was more suitable for the experimental data than the Freundlich isotherm, and the adsorption in this experiment was monolayer coverage on the ACLM surface [36].

3.8. Adsorption kinetic studies

Adsorption kinetic governs the solute uptake rate and indicates the adsorption efficiency of the adsorbent and determines its applicability for explaining for describing the experimental data such as chemical reaction, diffusion control, and mass transfer via physical or chemical force [35]. The kinetic parameters benefit the reader for prediction of the rate interpretation and modeling the adsorption processes. Thus, pseudo-first-order and pseudo-second-order kinetic models were used for the adsorption of formaldehyde onto ACLM [34].

The adsorption rate of the formaldehyde onto the ACLM was analyzed using Lagergren's first-order rate equation in linear form as follows [35]:

$$\log(q_e - q_t) = \log\ q_e - \left(\frac{k_1}{2.303}\right)t \tag{6}$$

where q_t is the amount of formaldehyde adsorbed onto the ACLM at time t (mg/g) and k_1 is the first-order rate constant (1/h). The plot of $\log(q_e - q_t)$ vs. t should give a straight line with slope of $-k_1/2.303$ and intercept of $\log q_e$ that admit the evaluation of constants of this model of adsorption rate constant. The fitting conclusions were summarized in Table 2. Through calculation, q_e of pseudo-first order and k_1 were determined to be 0.915 mg/g and 0.0023 1/h, respectively. The correlation coefficient (R^2) was 0.9096.

Table 2
Kinetic parameters and correlation coefficients calculated for formaldehyde adsorption onto ACLM

Model	Parameters	Values
Pseudo-first-order kinetic	q_e (mg/g) (calc)	0.915
	k_1 (1/h)	0.0023
	R^2	0.9096
Pseudo-second-order kinetic	q_e (mg/g) (calc)	0.126
	k_2 (g/(mg h))	2.216
	R^2	0.9890

Adsorption process with chemisorptions being the rate-control follows pseudo-second-order model which is presented in linear form as follows [35]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 is the equilibrium rate constant for pseudo-second-order sorption (g/(mg h)). The plot of t/q_t vs. t is a straight line with slope of $1/q_e$ and intercepts of $1/(k_2.q_e^2)$. Accordingly, the q_e value was calculated based on the line slope and the k_2 value was determined from the intercept. The fitting conclusions were presented in Table 2. Through calculation, q_e of pseudo-second order and k_2 were determined to be 0.126 mg/g and 2.216 g/(mg h), respectively. The correlation coefficient (R^2) was 0.9890.

As it was evident above, the R^2 value of pseudo-second-order kinetics model being 0.9890 was higher than that of pseudo-first-order kinetics model being 0.9096. It could be concluded that the adsorption kinetics of formaldehyde on ACLM fit better into the pseudo-second-order kinetics model in contrast to the pseudo-first-order model. The pseudo-second-order rate law expression was based on the assumption that the rate limiting step was chemical sorption [32].

3.9. Adsorption thermodynamic studies

The thermodynamic parameters obtained for all investigated adsorption systems were also calculated using equations, defined as [21]:

$$\ln\ K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

$$K = \frac{q_e \rho}{C_e} \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

where ρ = 1,000 kg/m^3 is the density of the solution, ΔH° is the standard enthalpy change (J/mol), ΔS° is the standard entropy change (J/(mol K)), ΔG° is the Gibbs free energy change of adsorption(kJ/mol), T is the absolute temperature (K), and K is the distribution coefficient. The ΔH° and ΔS° of the process can be determined from the slope and intercept of line obtained by plotting $\ln K$ vs. $1/T$ [21]. The thermodynamic parameters for formaldehyde adsorption of ACLM were shown in Table 3.

Table 3
Thermodynamic parameters for the adsorption of formaldehyde onto ACLM

ΔH° (kJ/mol)	ΔS° (J/(mol K))	ΔG° (kJ/mol)			R^2
9.60	−21.57	298 K	303 K	308 K	0.9998
		3.17	3.07	2.96	
−24.08	−87.97	308 K	313 K	318 K	0.9329
		3.02	3.46	3.90	

Through calculation, the ΔH° and ΔS° were determined as 9.60 kJ/mol and −21.57 J/(mol K), respectively. ΔG° was 3.17, 3.07, and 2.96 kJ/mol for the adsorption of formaldehyde on ACLM at 298, 303, and 308 K, respectively. In addition, the ΔH° and ΔS° were calculated as −24.08 kJ/mol and −87.97 J/(mol K), respectively. ΔG° was 3.02, 3.46, and 3.90 kJ/mol at 308, 313, and 318 K.

The positive value of ΔH° indicated that the adsorption of formaldehyde on the ACLM was an endothermic process at the defined temperature from 298 to 308 K. The negative value of ΔH° indicated that the adsorption of formaldehyde on the ACLM was an exothermic process. In addition, the positive value of ΔS° from 298 to 308 K suggested the increasing randomness at the solid/solution interface and the negative value of ΔS° from 298 to 308 K suggested the decrease of randomness. ΔG° decreased from 298 to 308 K, which suggested more favorable of formaldehyde adsorption onto the ACLM. In addition, with the increasing of temperature from 308 to 318 K, ΔG° increased, which revealed that the sorption process of formaldehyde on ACLM was more unfavorable at higher temperatures [36].

4. Conclusions

In this study, coal-based granular activated carbon loaded with MnO_2 (ACLM) was tested as adsorbent for the removal of formaldehyde. The effects of aqueous solution pH, ACLM dosage, formaldehyde concentration, contact time, and temperature on the removal of formaldehyde were investigated through batch experiments. The optimized pH of formaldehyde adsorption from aqueous solution was 7.0. The removal percentage increased from 21.8 to 72.1% by raising the ACLM dosage from 0.1 to 1.0 g. The formaldehyde adsorption rate increased a little at initial formaldehyde concentrations from 0.6 to 1.8 mg/L, while the removal percentage significantly decreased with formaldehyde concentrations being 10 mg/L. The adsorption rate of formaldehyde increased from 58.1 to 61.2% with temperature rising from 298 to 308 K and decreased from 61.2 to 54.0% when temperature continued to rise from 308 to 318 K. Isotherm modeling revealed that Langmuir equation could better describe the adsorption of formaldehyde onto the ACLM compared to Freundlich model, and the maximum adsorption capacity obtained was 4.53 mg/g. Kinetic data efficiently fitted with the pseudo-second-order better than pseudo-first-order model, and the adsorption rate limiting step was chemical sorption. The positive value of ΔH° indicated that the adsorption was an endothermic process from 298 to 308 K, and the negative value of ΔH° indicated that the adsorption was an exothermic process. The positive value of ΔS° from 298 to 308 K suggested the increasing randomness at the solid/solution interface, and the negative value of ΔS° from 298 to 308 K suggested the decrease of randomness. Decrease of ΔG° from 298 to 308 K suggested more favorable of formaldehyde adsorption onto the ACLM and increase of ΔG° from 308 to 318 K revealed that the sorption process was more unfavorable at higher temperatures. Results from this study suggest that ACLM is an effective adsorbent for the removal of formaldehyde from aqueous solution in drinking water treatment field.

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