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Kinetic of Hexavalent Chromium (Cr(VI)) Removal by Corn Cob-Based Activated Carbon Modified with Nitric Acid

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Abstract

The presence of heavy metal Cr(VI) in water indicates environmental pollution. Heavy metal Cr(VI) that exceeds the standard can be harmful to health because it is toxic and carcinogenic. Activated carbon can be used as a heavy metal adsorbent. Modification of activated carbon using nitric acid can increase metal adsorption capacity. Therefore, the aim of this study is to determine the kinetic of hexavalent chromium (Cr(VI)) removal by corn cob-based activated carbon modified with nitric acid. The modified activated carbon was characterized by Boehm titration and FTIR spectrophotometer. The adsorption capacity was identified in various parameters, involving the initial concentration of Cr(VI), pH value, contact time, and concentration of the adsorbent to obtain the optimal Cr(VI) removal efficiency value. The most optimal Cr(VI) adsorption was obtained at an activated carbon dosage of 3 g/L, pH value of 1, contact time of 140 minutes, and 100 mg/l Cr(VI) concentration. Based on adsorption kinetics data, the pseudo-second-order equation was obtained (R^2 =0.994). The adsorption phenomenon followed the Langmuir isotherm model (R^2 = 0.998) with an optimum adsorption capacity of 28.32 mg/g. Corn cob-activated carbon modified with nitric acid has many acidic groups that act as effective active sites for reducing Cr(VI) from water.

Keywords: Activated carbon, corn cob, Cr(VI) heavy metal, nitric acid modification

INTRODUCTION

The tanning industry is notorious as a major source of water pollution, as the tanning process generates large amounts of wastewater. Various chemicals are used in large quantities during the leather processing process (Nigam et al., 2019). Tannery wastewater contains high levels of heavy metals such as hexavalent chrome (Cr(VI)), which has carcinogenic and teratogenic properties (Katenta et al., 2020). Since its toxicity, reducing Cr(VI) from wastewater is an important requirement. The adsorption process has been identified as an attractive alternative for Cr(VI) removal because of its efficiency, affordability, and ease of use.

The agricultural industry sector in Indonesia is very important in the national industry. However, its by-products, such as corncobs, have not been fully utilized, leaving them only into a pile of waste. The process of converting corn cobs into activated carbon has been researched for many years. Corn cob activated carbon provides a highly effective active surface for the adsorption of heavy metals such as chromium, lead, or others (Kouassi et al., 2023). The content of compounds in corn cobs is 45% cellulose and 40% hemicellulose, which are used as raw materials for making activated carbon (Janani et al., 2019; Majumder et al., 2019).

Chemical modification of the substance can improve its ion exchangeability, increase its binding sites, and make it easier for metals to adsorb (Chulliyil et al., 2024). Acid treatment is generally used to oxidize the surface of activated carbon because it can enhance acid properties, remove mineral components, and increase the hygroscopicity of the activated carbon

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surface (Jha et al., 2021). Nitric acid is useful for modifying activated carbon by forming oxygen functional groups from lactone, carboxylic acid, quinol, and phenolic groups (Sreńscek-Nazzal et al., 2021). The sorption capacity of activated carbon increased in line with the total number of functional groups present on its surface. The rigidity of corncobs and the porous structure are the main reasons for their adsorption ability (Liu et al., 2021). Activated carbon from corn cob modified with nitric acid can be a promising solution for reducing hexavalent chromium from wastewater.

METHODOLOGY

Materials and Instrumentals

In this study, corn cobs from Cangkringan District, Sleman Regency, were used as raw materials. As an initial step, distilled water was used for preparation. Sodium hydroxide, 37% concentrated hydrochloric acid, 65% concentrated nitric acid (HNO_3), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), 97% concentrated sulfuric acid (H_2SO_4), sodium bicarbonate ($NaHCO_3$), phenolphthalein indicator ($C_{20}H_{14}O_4$), methyl orange indicator ($C_{14}H_{14}N_3NaO_3S$), 1,5-diphenylcarbazide, potassium dichromate ($K_2Cr_2O_7$), Whatman 42 filter paper, weighing paper, and N_2 gas were used in this study. All materials were pro-analysis quality.

The equipment used in this research were furnace reactor, magnetic stirrer, vacuum pump (Sigma-Aldrich; Buchi VaC V-500, Z526819), pH meter (Mettler Toledo), stirring hotplate (Thermolyne Nuova), analytical balance (Mettler AE 160), agate mortar, aluminium foil, 100 mesh sieve, shaker (VRN 200), glassware laboratory equipment and oven). UV-Vis spectrophotometer (Genesys 20) and infrared spectrophotometer (FTIR, Shimadzu Prestige-21) were the instruments used for analysis.

Methods

Preparation of CAC

Corn cobs were cleaned using distilled water to release contaminants. They are then dried in the sunlight for 2 days and then placed in oven for 24 hours at 110 °C. After drying, they were then carbonized at 600 °C for 6 hours and activated carbon of corn cob was obtained. The corn cob activated carbon (CAC) was ground and sieved with a 100mesh sieve. Subsequently, the CAC was analyzed using an FTIR spectrophotometer (Hanifa et al., 2023).

Modification of CAC

The surface of the CAC was modified by immersing the sample into a heated 7 M concentration nitric acid solution. The ratio of nitric acid used was 5 mL of nitric acid for 1 gram of CAC. In order for the formation of carboxylic acid functional groups to take place properly, this material was treated for 3 hours. The residue was cleaned using distilled water until its conductivity was equal to wastewater (Huang et al., 2009; Kim et al., 2019). Afterwards, the sample was dried in an oven at 120 °C for 3 hours, and oxidised corn cob-based activated carbon (O-CAC) was obtained. O- CAC was then calcined at 700 °C in a tube furnace for 3 hours to obtain chemically and physically modified corn cob-based activated carbon (M-CAC). Oxidised corn cob-activated carbon (O-CAC) and modified corn cob-activated carbon (M-CAC) were then characterised with an FTIR spectrophotometer.

Determination of Carboxilic Acid Content by Boehm Titration

The calculation of the amount of oxygen functional groups on the surface properties is analysed using the Boehm method (Schönherr et al., 2018). This was done by neutralising 0.1 g of M-CAC with 50 mL of 0.01 mol/L $NaHCO_3$ to estimate the acid centres. The bottle was placed in a shaker for 2 hours. Then, it was filtered. A 10 mL solution was taken for titration using 0.01 mol/L HCl. Phenolphthalein and methyl orange were used as indicators. The calculation of the acidic groups was done using the fact that sodium bicarbonate only neutralises carboxylate groups (Schönherr et al., 2018).

Adsorption Experiments

The adsorption capacity of Cr(VI) was examined by mixing 0.02 g of M-CAC as an adsorbent with 10 mL of Cr(VI) solution. Batch adsorption experiments were carried out for 2 hours at 25 °C with constant stirring speed (130 rpm). The resulting filtrate was then analysed with a UV-visible light spectrophotometer to determine the adsorbed Cr(VI). The sample was prepared in a cuvette to measure using UV-Vis spectroscopy, ensuring it was clear and bubbles free. The cuvette was placed in the spectrophotometer, and the appropriate wavelength was chosen at 540 nm. The optimum appropriate wavelength was determined previously at 450-600 nm with an interval of 5 nm. Lastly, the absorbance of the solution was recorded to determine concentration. The effect of pH value was determined by varying the pH value between 1 and 5 using 0.5 M of H_2SO solution and 0.5 M of NaOH solution. The same procedure was also conducted for batch kinetic experiments with times of 20, 40, 60, 80, 100, 120, and 140 minutes at optimum pH to determine the effect of contact time. Determination of the effect of initial Cr(VI) concentration on M-CAC was done by varying the adsorbate concentration between 20-100 mg/L. The fourth experimental stage used 100 mg/L Cr(VI) solution and known doses of M- CAC (1, 2, 3, 4, 5 g/L) to determine the optimal adsorbent concentration. Calculation of adsorption capacity (q_e) and percentage removal (*R%)* was done using Equation (1) and Equation (2) (Irdhawati et al., 2020).

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

$$R\ (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

The starting concentration (mg/L) of Cr(VI) and equilibrium concentration (mg/L) of Cr(VI) are indicated as C_0 and C_e respectively, and the adsorbent mass in g/L is written as m.

Adsorption Isotherms

The Freundlich and Langmuir isotherms are fundamental models used to describe the adsorption behaviour of solutes onto solid surfaces. The Freundlich isotherm accounts for heterogeneous surfaces and is particularly useful for systems with variable adsorption energies, making it suitable for complex mixtures (Zakir et al., 2022). Its equation is expressed as:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of the adsorbate, K_f is the Freundlich constant, and n n is the heterogeneity factor.

Conversely, the Langmuir isotherm assumes a homogeneous surface with a finite number of identical sites, where adsorption occurs at specific locations and is limited by the number of available sites. Its equation is given by:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

where q_{max} is the maximum adsorption capacity, and K_L is the Langmuir constant. Using both models provides a comprehensive understanding of adsorption mechanisms, as they highlight different aspects of the adsorption process. By comparing results from both isotherms, researchers can determine the nature of adsorption, whether it is more homogeneous or heterogeneous, leading to better insights for optimizing removal efficiencies in various applications.

RESULTS AND DISCUSSION

Properties of M-CAC

The chemical characterization of the activated carbon surface is an essential parameter because it can determine the equilibrium between adsorption and adsorbent adsorbate interaction. The adsorption isotherm will describe the correlation between the number of Cr(VI) concentrations adsorbed and its equilibrium concentration to determine the adsorption capacity (Labied et al., 2018).

The functional groups of the activated carbon were characterized by FTIR Analysis. Figure 1 shows the FTIR spectra of CAC (a), O-CAC (b), and M-CAC (c). As can be shown in Figure 1(a), the -OH stretching vibrations of cellulose, tannin, or lignin are responsible for the broadband at 3433 cm^{-1} . The adsorption peak at 2932 cm^{-1} is associated with the aliphatic C─H stretching vibrations of alkanes (Shrestha, 2023). The adsorption peaks at 1126 and 1620 cm^{-1} are associated with the adsorption at 3433 cm^{-1}, indicating the presence of carboxylic acids. The adsorption peak at 1273 cm^{-1} is the stretching vibration of C─O carbonyl on phenolic C─OH. The adsorption at 1126 cm^{-1} indicates C─O─H stretching vibrations as defined in the scientific literature (Kim et al., 2019; Xu et al., 2015).

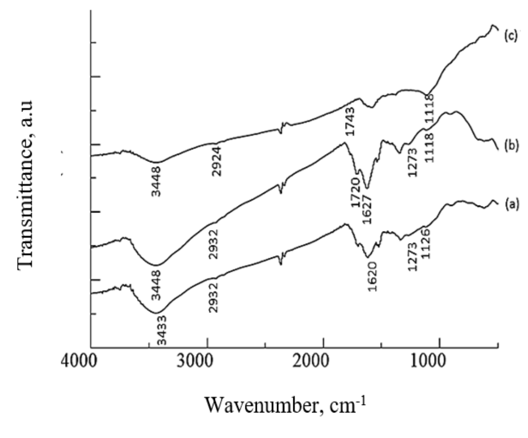

Figure 1. The spectra of the (a) CAC, (b) O-CAC, and (c) M-CAC samples

Figure 1(b) shows the new significant peak at 1720 cm^{-1} assigned to ─C=O stretching type vibrations on the carboxyl group. Carboxylic groups are formed from the oxidation of phenol (hydroxy) groups by nitric acid. Carboxylic groups are one of the acid groups that have a significant role in metal adsorption because they have a high affinity for metal ions to be adsorbed. The peak shift occurs at adsorption 3448 cm^{-1} and 1627 cm^{-1}, which are ─OH stretching vibrations and ─OH bending vibrations, successively. From the adsorption peaks that appear in the O─CAC spectra, the presence of carboxylic and phenol functional groups can be identified. The phenol group is formed due to the presence of nitric acid, which causes the carbon to oxidise and lose its electrons. The carbon on the surface becomes positively charged so that the OH ions in solution are easily bound to carbon and form phenol groups.

The disappearance of the adsorption peak associated with C-O vibrations on the phenolic C-OH at 1273 is depicted in Figure 1(c), which was the spectra of chemically and physically modified corn cob-based activated carbon (M-CAC). This is followed by the disappearance of the -O-H bending vibration at 1627 cm^{-1}. The disappearance of both adsorption peaks indicates that the phenol functional group on the adsorbent surface has disappeared due to calcination. A decrease in transmission intensity occurred at an adsorption peak of 1118 cm^{-1} assigned to the C-O group stretching vibrations. The adsorption shift from 1720 cm^{-1} to 1743 cm^{-1} indicates a decrease in carboxylate functional groups and the formation of lactone functional groups (Shrestha, 2023).

Determination of Carboxilic Acid Content

Since there are more surface carboxylic acid functional groups as a result of the oxidation treatment procedure, the overall surface acidity increases significantly (Jahromi & Ghahreman, 2019). The carboxylic acid functional group contents of O-CAC and M-CAC were 0.176 mmol/g and 0.221 mmol/g, respectively. In conclusion, without modification, corn cob activated carbon already has a small amount of carboxylic groups, but it is still covered by impurities as the FTIR characterisation was performed, and there was a peak at 1720 cm^{-1} at CAC and more significant at O-CAC which is an indication of carboxylate group adsorption. The results of carboxylic acid content obtained are in accordance with the FT-IR characterisation of M-CAC results, which show a decrease in the number of carboxylic groups when compared to O-CAC.

The carbon pore surface of M-CAC undergoes the formation of weak acidic functional groups that are assumed to resemble the oxidation of 9,10-dihydrophenanthrene with nitric acid in Figure 2 (Demiral et al., 2021). On the aliphatic side of the molecule, with side chains having one carbon atom, the formation of a dicarboxylate group occurs. The breaking of the C-C bond at position a of the benzylate carbon atom initiates the reaction.

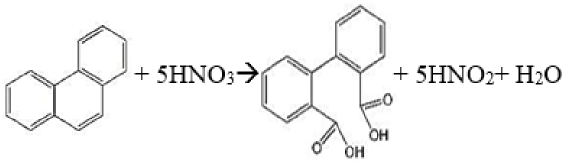

Figure 2. The formation of carboxylic acid groups (Bala et al., 2007)

Batch Adsorption Parameters

Effect of the pH to Cr(VI) Adsorption

The pH of the solution has a significant impact on the adsorption of Cr(VI) on M-CAC, as depicted in Figure 3. Due to the increasing number of acidic functional groups on the surface, this effect is mostly related to the modification of the surface charge of M-CAC.

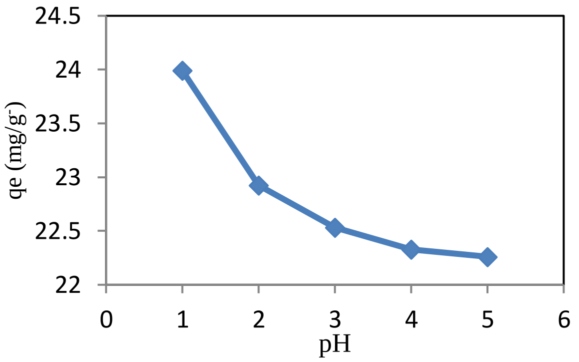

Figure 3. Influence of pH value o on adsorption capacity (C_0 = 100 mg/L)

The phenomenon related to the change in surface charge of the modified corn-cob activated carbon (M-CAC) is crucial to understand in the context of heavy metal adsorption, such as Cr(VI). In high pH solutions, some acidic functional groups on the surface of M-CAC are neutralized, reducing its adsorption capacity. However, at low pH, such as pH 1, acidic conditions allow these functional groups to remain protonated, resulting in a positive charge on the surface. This positive charge is key to attracting negatively charged Cr(VI) ions, thereby enhancing the efficiency of metal removal. Previous studies by Demirbas (2008), Zhang et al. (2010), and Hsu et al. (2009) have shown that M-CAC can effectively adsorb Cr(VI) at low pH, aligning with findings that Cr(VI) ions can be reduced to Cr(III) through interactions with positively charged functional groups. The high redox potential of Cr(VI) and the ability of carboxyl groups on the carbon surface to adsorb Cr(III) aqua complexes also support the reaction mechanism occurring, as described in the reaction equations (Huang et al., 2009). Therefore, the phenomenon of surface charge change in M-CAC, caused by the increase in the number of acidic functional groups, not only enhances adsorption capacity but also strengthens the important redox reactions involved in the reduction of Cr(VI) to Cr(III).

$$3C + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CO_2 + 4Cr^{3+} + 8H_2O \qquad (5)$$

$$3C + 4CrO_4^- + 16H^+ \rightarrow 3CO_2 + 4Cr^{3+} + 10H_2O \qquad (6)$$

Effect of the Contact Time

A dose of M-CAC of 2 g/L at a solution pH of 1 was used to study the effect of contact time on adsorption between 20 to 160 minutes at 25 °C and constant stirring speed (130 rpm). The results are shown in Figure 4.

Figure 4 shows that the adsorption process was rapid in the initial minutes of startup. This is because the adsorbate molecules are still high in the solution, thus lowering the mass transfer barrier between the adsorbent and the adsorbate. The high concentration at the beginning of adsorption also causes a driving force that accelerates the adsorption of chromium metal ions on the adsorbent surface. After that, there was a modest decline in adsorption capacity after 160 minutes of contact time, indicating the optimum adsorption had been reached at 140 minutes. At the optimum contact time, the adsorption of Cr(VI) metal ions was 23.63 mg/g or 94.54% of the initial Cr(VI) concentration. (Huang et al., 2009) obtained a different result regarding the adsorption of Cr(VI) in a solution using modified nitric acid activated carbon, that the optimum contact time occurs at 100 minutes with percentage adsorption above 90%.

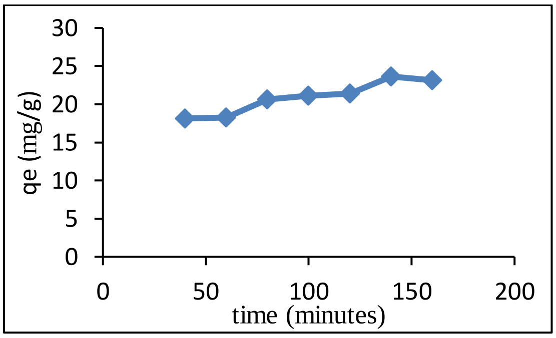

Figure 4. Contact time vs adsorption capacity (C_0 = 100 mg/L)

Effect of Cr(VI) Initial Concentration

The effect of the initial concentration of Cr(VI) on the adsorption capacity of the Modified Carbon Adsorbent Composite (M-CAC) was extensively investigated, as illustrated in Figure 5. By systematically altering the initial concentrations, we observed significant changes in the adsorption capacity of M-CAC. Understanding these relationships is crucial for optimizing the design of M-CAC in real-world applications.

The adsorption capacity increased from 10 to 28.19 mg/g at 25 °C when the chromium metal ion starting concentration was increased from 20 to 100 mg/L, as shown in Figure 5. A comparable finding has been documented regarding the elimination of Cr(VI) using sugarcane bagasse and corn cob (Yao et al., 2017). Figure 5 also illustrates how chromium concentration affects adsorption efficiency. The percentage of chromium removal drops from 100% to 56.39% when the initial concentration of chromium increases.

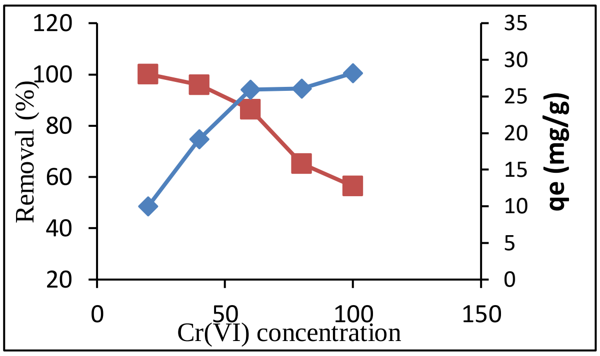

Figure 5. Effect of initial Cr(VI) on adsorption capacity

At low concentrations, the removal might increase because the accessible surface to starting Cr(VI) concentration ratio is larger. Higher concentrations, however, cause this ratio to drop, which could result in a lower percentage of elimination.

Effects of Adsorbent Dosage

The impact of adsorbent dosage on adsorption was studied in the range of 1-5 g/L, while the pH value of the Cr(VI) solution was held constantly at 1, and the contact period at room temperature was set constant at 140 min. The result is depicted in Figure 6.

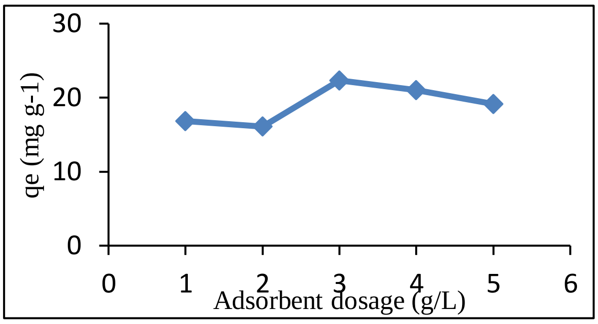

Figure 6. Effect of mass of adsorbent on adsorption capacity.

Figure 6 demonstrates that the percentage of adsorption rose as the M-CAC climbed up to a certain point and then somewhat dropped over a dosage of 3 g/L. This experiment shows that the M- CAC dose of 3g/L is the optimum dose of chromium metal ion adsorption at a concentration of 100 mg/L, which results in an adsorption capacity of 22.33 mg/g. This is because when the adsorbent dosage is raised, the availability of active sites increases. However, since there was No. adsorbent dosage, the optimum adsorbent dosage for increment of adsorption capacity at 4 g/L and 5 g/L this experiment was reached at 3 g/L.

Modeling of Batch Adsorption Kinetic Data

In batch adsorption processes, kinetics studies provide information on optimum conditions, feasible rate control stages and sorption mechanisms. In this study, the pseudo-1st-order kinetic model and the pseudo-2nd-order kinetic model were used to expose the kinetics of the adsorption experiments, as revealed in Equation (7) and Equation (8), respectively.

$$q_e = q_e(1 - e^{-k_1 t}) \tag{7}$$

$$q_e = \frac{q^2 k_2 t}{1 + q_e k_2 t} \tag{8}$$

The validity of these two models can be tested by performing linear fitting of ln (qe-qt) versus t and (t/qt) versus t, respectively. The relationship between contact time and Cr(VI) uptake by 2 g/L of M-CAC for an initial Cr(VI) concentration of 100 mg/L determines the adsorption kinetics. Figure 7 and Figure 8 showcase all the graphs. The results and parameters are provided in Table 1. This allows for the selection of the most suitable model for the experimental data and a better understanding of the adsorption process. Therefore, to evaluate the most suitable model, the writer conducted calculations for correlation coefficients (R^2) (Nilavazhagi & Felixkala, 2021).

Table 1. Pseudo 1st order model and Pseudo 2nd order model parameters

Pseudo 1st order model			
q_e (exp) (mg/g)	k_1 (min^{-1})	q_e (mg/g)	R^2
23.635	0.013	12.322	0.906

Pseudo 2nd order model		
$k_2 \times 10^{-3}$ (mg g^{-1} min^{-1})	q_e (mg/g)	R^2
2.68	24.213	0.994

The correlation between both models generally demonstrates a certain level of linearity in the fitting of data. Nevertheless, when employing a pseudo-first-order model, the correlation coefficient (R2) was determined to be modest, and a significant disparity was observed between the theoretically estimated equilibrium adsorption capacity and the practical findings. This particular model is not consistent with the adsorption kinetics of Cr(VI) onto activated carbon when compared to a pseudo-second-order model. The latter model has a stronger correlation with the experimental data (R2 = 0.994) than the other model (R2 = 0.906). Furthermore, the observed equilibrium adsorption capacity (qe) in the pseudo-second-order model is in remarkable concurrence with the expected value. The data clearly demonstrate a stronger correlation with a pseudo-second-order model than with a pseudo-first-order model. Based on the model, the adsorption process is mostly affected by interactions. The study indicates that M-CAC and Cr(VI) undergo chemisorption, a process involving the sharing or exchange of electrons through valence forces. (Gokce & Aktas, 2014).

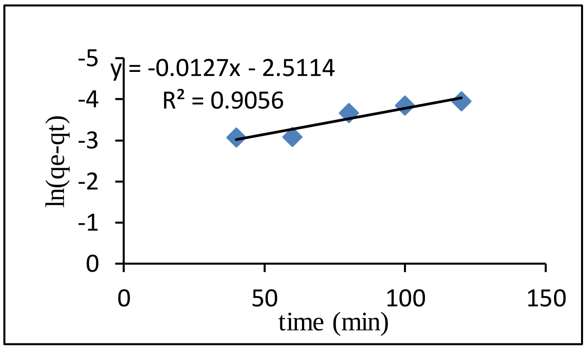

Figure 7. Pseudo 1st order model of M-CAC on Cr(VI).

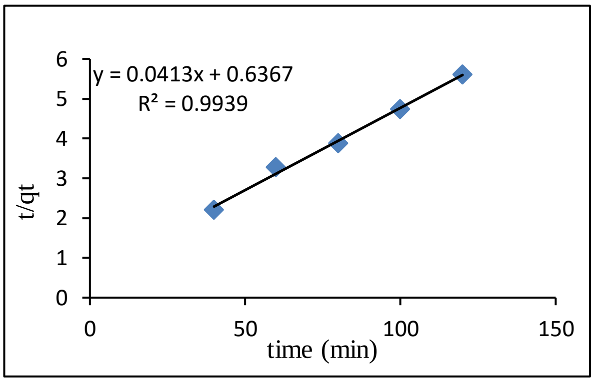

Figure 8. Pseudo 2nd order model of M-CAC on Cr(VI).

Adsorption Isotherms

An adsorption isotherm is important for determining the adsorption potential. The study results for the adsorption of chromium in aqueous solution onto activated carbon are illustrated in Figures 9 and 10. These figures display the Freundlich and Langmuir isotherms, which were generated using 100 mg/L Cr(VI) concentration.

Figures 9 and 10 illustrate the Langmuir and Freundlich isotherms for the adsorption of Cr(VI) onto activated carbon. Table 2 provides the parameters and correlation coefficients for the adsorption isotherms. The experimental data clearly indicates that the Langmuir isotherm model is a better fit than the Freundlich isotherm. These regression correlation coefficients provide strong support for the result. Langmuir isotherm has a high R^2 value of 0.997, indicating a strong correlation, whereas the Freundlich isotherm has a lower R^2 value of 0.872, explaining a weaker correlation.

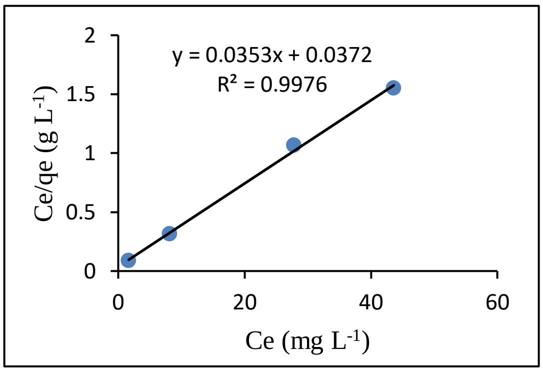

Figure 9. The Langmuir adsorption isotherm of M-CAC on Cr(VI).

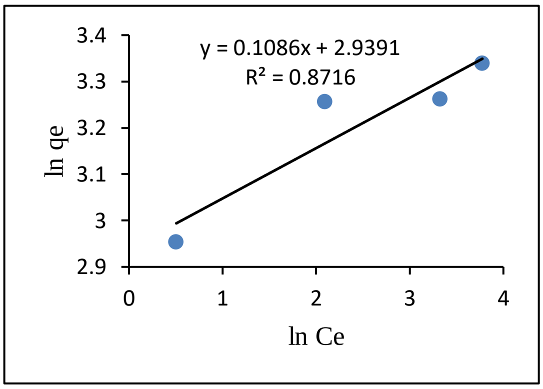

Figure 10. The Freundlich adsorption isotherm of M-CAC on Cr(VI).

In this study, the Langmuir isotherm model exhibited a high R^2 value of 0.997, indicating a strong correlation between the amount of adsorbate and its equilibrium concentration. This suggests that the adsorption of the solute onto the activated carbon follows a monolayer adsorption process, where all adsorption sites are equivalent and saturated. Conversely, the Freundlich isotherm showed a lower R^2 value of 0.872, which reflects a weaker correlation. This indicates that the adsorption may not be uniform across the surface, suggesting a heterogeneous distribution of adsorption sites. Similar findings have been reported in other studies. For instance, Deng et al. (2021) observed a high R^2 value for the Langmuir model in the adsorption of heavy metals onto activated carbon, supporting the notion of monolayer adsorption. In contrast, a study by Mahmoodi et al. (2011) also found a lower R^2 for the Freundlich model when assessing dye adsorption, indicating a heterogeneous adsorption environment. These studies collectively reinforce the interpretation of our results, emphasizing the suitability of the Langmuir isotherm for modelling adsorption in this context.

Table 2. Adsorption isotherm parameter

Langmuir isotherm			
q_m (exp) (mg/g)	K_L (L/mg)	R^2	R_L
28.32	0.947	0,998	0.011

Freundlich isotherm		
N	K_F (L/mg)	R^2
9.208	18.898	0.872

It is believed that electrostatic attraction is the mechanism by which the Cr(VI) anion and the active group on the M-CAC adsorbent surface interact. Active groups such as carboxylate, which are positively charged due to protonation in M-CAC, allow for electrostatic attraction interactions with the dominant negative ion of the Cr(VI) species, $HCrO_4^-$. The approximate model of linkage between the $HCrO_4^-$ ion and protonated carboxylate group of M-CAC can be understood as depicted in Figure 11.

Another assessment of the linkage between the $HCrO_4^-$ ion and the protonated carboxylate group of M-CAC involves hydrogen bonding, which is illustrated in Figure 12. Figure 12 shows that the Cr(VI) ion and the protonated carboxylate group do not interact directly. Hydrogen bridges allow the oxygen atom in the carboxylate group to make hydrogen bonds with the H atom of the water, hydrating the $HCrO_4$-ion and facilitating the interaction. This modelling allows for

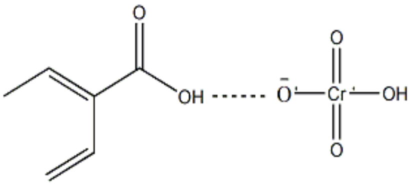

Figure 11. Interaction between the $HCrO4^-$ ion and the protonated carboxylate of M-CAC.

multilayer adsorption where the hydrated $HCrO_4^-$ which has been attached to the adsorbent surface, can bind to other $HCrO_4^-$ molecules (Xu et al., 2015).

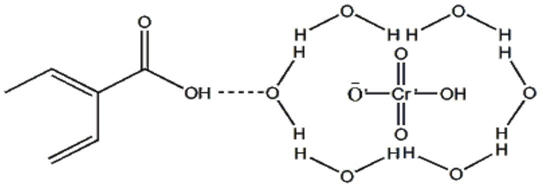

Figure 12. Interaction through hydrogen bonds between the $HCrO4^-$ ion and the protonated carboxylate of M-CAC.

The spectra after adsorption showed a slight shift in several adsorption peaks. The adsorption wave number of 3448 cm^{-1} changed to 3425 cm^{-1}, and the adsorption wave number of 1743 cm^{-1} changed to 1751 cm^{-1}. Following adsorption, spectra of FTIR showed a decrease in peak strength, implying a reduction in the active group on the surface of the adsorbent that had interacted with the Cr(VI) metal.

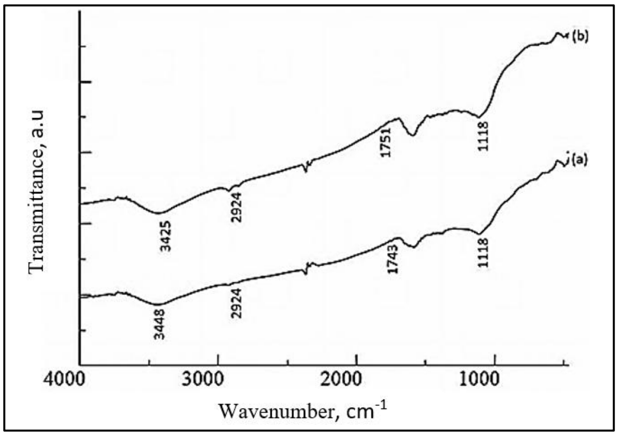

Figure 13. FTIR spectra of M-CAC (a) and M-CAC-Cr (b)

CONCLUSION

It was discovered in this study that activated carbon made from corn cob that had been treated with nitric acid had more surface of oxygen functional groups than activated carbon that had been oxidized. The capacity for Cr(VI) adsorption is enhanced by these oxygen functional groups. At pH 1, 140 minutes of contact time, activated carbon in 3 g/L and Cr(VI) concentration in 100 m/L were shown to be the best conditions for Cr(VI) adsorption. Its kinetics revealed the best correlation with the pseudo-2nd-order equation (R^2 = 0.994). The Langmuir isotherm model (R^2=0.998) was the most fit for describing the adsorption phenomenon, with an ideal fit adsorption capacity of 28.32 mg/g. Hence, it has been observed that the modified activated carbon is efficient in eliminating Cr(VI) from aqueous solutions.

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