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DEVELOPMENT OF COAL MAGNETIC ACTIVATED CARBON FOR Cd(II) REMOVAL: ADSORPTION ISOTHERM AND KINETIC MODELLING

Abstract: The metal coating process produces wastes containing heavy metals such as cadmium that are harmful to health. One method to remove cadmium is adsorption. This research developed an adsorber, specifically magnetic activated carbon derived from coal (CMAC). Activated carbon is modified with a Fe_3O_4 composite to make it magnetic and reusable. The objective of this investigation is to optimise the key parameters of activator concentration and thermal activation conditions for the fabrication of high-quality activated carbon. The investigation will evaluate the characteristics of the resulting carbon and its cadmium removal efficiency. The experimental adsorption data were fitted to both the Freundlich and Langmuir isotherm models and evaluated using kinetic equations. Chemical activators were used in a mixture of phosphoric and hydrochloric acid (1: 1) at concentrations of 0.5 M - 1.25 M. Physical activation was carried out at (873 - 1173) K. The optimal activation temperatures were identified as 1123 K and 1173 K. The CMAC removal percentage for Cd was 98.10 %. The Freundlich isothermal adsorption equation shows $n = 0.4530$ and $K_F = 3.9823 \text{ mg/g}$ with $R^2 = 0.9691$. The adsorption data were well-fitted by the Langmuir model, which yielded a maximum monolayer adsorption capacity q_m of 238.10 mg/g and an affinity constant K_L of 0.0787 L/mg, supported by a high coefficient of determination ($R^2 = 0.9082$). Furthermore, the adsorption kinetics model yielded a pseudo-second-order equation. The regeneration test over five cycles showed decreases in Cd removal efficiency of 97.04 %, 81.89 %, 42.75 %, 13.83 %, and 9.71 %, respectively, indicating limited stability of the adsorbent after repeated use.

Keywords: cadmium, coal magnetic activated carbon, hydrochloric acid, phosphoric acid, regeneration

Introduction

Metal plating is widely used for the manufacture of various goods and products. Metal plating is applied to enhance corrosion resistance and improve surface appearance. However, the proliferation of the metal coating industry contributes to water pollution through waste generated. Metal-coated industrial waste contains several heavy metals, including cadmium, which is highly toxic. During growth, humans do not require cadmium (Cd) because it is highly poisonous. Exposure to Cd, resulting in acute poisoning, can have an impact on gastrointestinal symptoms and kidney health. The clinical symptoms of cadmium poisoning are similar to those of common glomerulonephritis, and only in advanced stages, multiple softening and fractures of the spine can be found. Industrial metal plating waste contains cadmium because a cadmium solution is used in the electroplating process [1-3]. Because cadmium in wastewater poses a significant threat to human health, it is necessary to reduce its levels before discharge into water bodies.

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Due to the environmental and health risks posed by cadmium, a variety of treatment methods have been developed to remove it from wastewater streams, including electrocoagulation [4], electrodialysis, and electrooxidation [5, 6]. Purification was achieved through a series of physical and chemical processes, including filtration [7, 8], ion exchange, and adsorption [9-11]. Among the several alternative treatment methods, adsorption is quite inexpensive and easy to operate. Adsorbents can be made from natural or artificial materials [12-17]. As a highly effective adsorbent, activated carbon is widely used in wastewater treatment [18-21]. It is derived from organic materials with high carbon content. Among these potential precursors, coal is a desirable option for Indonesia due to its local abundance.

The production of activated carbon from a diverse range of precursor materials, such as coal, is a thoroughly documented and mature area of scientific inquiry [22-24]. The utilisation of low-grade bituminous coal has proven highly effective, producing activated carbon with a significant specific surface area of 31.930 m²/g [11-16]. It also exhibited an exceptional iodine uptake of 1.243 mg/g - 1.259 mg/g [9]. While bituminous coal produces activated carbon with substantial surface area, lignite coal has yielded material with a specific surface area of 343 m²/g [25]. Beyond low- and medium-grade coal, high-grade variants such as anthracite have also been investigated as precursors for activated carbon. Notably, the activated carbon, synthesised from anthracite coal, exhibited an exceptional specific surface area of 3,136.80 m²/g, corresponding to methane (CH₄). The material exhibited a high adsorption capacity of 19.31 mmol/g [26]. These studies have successfully produced activated carbon that meets the SNI 06-3730-1995 standard and effectively removes heavy metals. However, activated carbon can be used only once and creates waste that accumulates. This study builds upon previous research by introducing the novel use of Fe₃O₄ composite in the manufacture of activated carbon, enabling the creation of magnetic, reusable activated carbon.

Materials and methods

Materials and tools

This investigation utilised a range of analytical-grade chemicals and standard laboratory apparatus. The key chemicals comprised coal, H₃PO₄ 85 % pro analyses (Merck, Germany), HCl 32 % pro analyses (Merck, Germany), NaOH pro analyses (Merck, Germany), FeCl₃·6H₂O pro analyses (Merck, Germany), FeSO₄·7H₂O, NH₄OH 25 % pro analyses (Merck, Germany), amylum pro analyses (Merck, Germany), iodine pro analyses (Merck, Germany), Na₂SO₃ pro analyses (Merck, Germany), CdCl₂ 99.99 % pro analyses (Merck, Germany), and distilled water (aquadest). The primary equipment employed included hammers, scrapers, an analytical balance, volumetric flasks, burettes, a muffle furnace, beakers, Erlenmeyer flasks, funnels, filter paper, pipettes, clamps, measuring cylinders, and aluminium foil.

Coal raw material testing

One kg of coal is crushed and sifted with a 60-mesh sieve. Furthermore, the coal is tested using proximate analysis to determine its type. The proximate analysis was conducted by determining the water content, WC [%], following ASTM D-3173-87 [27], the volatile matter content, VMC [%], as per BS 1016-104.3 (Coal and Coke Analysis) [28], and the ash content, AC [%], in accordance with ASTM D3174-12 [29]. Fixed Carbon

Content, FCC [%], is determined indirectly through the proximate analysis method based on ASTM D3172-13 [30]. The fixed carbon content was subsequently derived using the equation:

$$FCC = 100 - (WC + VMC + AC) \quad (1)$$

Manufacture of activated carbon magnetic coal

This study outlines a comprehensive procedure for producing activated carbon from coal, which is divided into two main phases: raw material preparation and activation. The preparatory stage involves crushing the coal, followed by sieving through a 60-mesh screen. The fraction passing through the sieve was collected as the precursor for activated carbon. The production phase commenced with sun-drying for 2 days, followed by carbonisation at 823 K for 2 hours, and then chemical activation. In this chemical step, the carbonised coal was impregnated with a mixed phosphoric-hydrochloric acid activator at varying concentrations (0.5 M, 0.75 M, 1.0 M, and 1.25 M, corresponding to Samples A through D). The resulting material was then neutralised with 0.1 M sodium hydroxide and distilled water, and the solid residue was separated on filter paper. Subsequent physical activation was conducted by heating the samples to temperatures ranging from 873 K to 1173 K (in 50 K intervals for Samples A1-D7). Finally, magnetic activation was achieved by immersing the product in a 1:2 molar/1:1 volume mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ for 30 minutes, concluding with a 4-hour heating step in a furnace at 373 K. The characterisation of the activated carbon involved several analytical techniques: proximate analysis (following the standard procedure for coal), iodine number measurement (ASTM D-4607-94) [31], BET surface area analysis, and SEM-EDX for elemental composition.

Testing of CMAC's ability to remove cadmium in synthetic wastewater

The test of CMAC's ability to adsorb Cd(II) ions in synthetic wastewater was conducted using cadmium concentration and contact time as variables. A test with a variable concentration was carried out by inserting 1 g of CMAC into 1 L of cadmium solution with a concentration of 350 mg/L (CdI_1 sample), 325 mg/L (CdI_2 sample), 300 mg/L (CdI_3 sample), 275 mg/L (CdI_4 sample), and 250 mg/L (CdI_5 sample), stirred at 120 rpm for 1 hour, then the sample was separated from CMAC and analysed for cadmium content using the AAS method. Testing with variable contact time was carried out by inserting 1 g of CMAC into 1 L of cadmium solution with a concentration of 350 mg/L, stirred at 120 rpm for 1 minute (Cdk_1 sample), 2 minutes (Cdk_2 sample), 5 minutes (Cdk_3 sample), 30 minutes (Cdk_4 sample), 60 minutes (Cdk_5 sample), 75 minutes (Cdk_6 sample), 90 minutes (sample Cdk_7). The samples were separated from CMAC and analysed for cadmium content using the AAS method (Standard Number 6989.16:2009 of the Indonesian National Standardisation system) [31]. The cadmium removal efficiency demonstrated by the CMAC method was notably high and is expressed as the % of cadmium removal ($\%R_{Cd}$) in equation (2).

$$\%R_{Cd} = (C_i - C_e / C_i) \cdot 100 \% \quad (2)$$

where: C_i and C_e - initial and final Cd concentration in wastewater [mg/L].

The Freundlich isothermal adsorption equation is the following [10]:

$$\log q_e = \log K_F + (1/n) \cdot \log c_e \quad (3)$$

where q_e is the mass of adsorbed Cd(II) ions per unit mass of CMAC [mg/g], K_F is the Freundlich constant, n is an empirical parameter, and c_e is the concentration of dissolved cadmium ions under equilibrium conditions [mg/L]. From equation (2) and the results of the AAS test, the constants K_F and n can be determined.

Next, the Langmuir isothermal adsorption equation is the following [10]:

$$(c_e/q_e) = (c_e/q_m) + 1 / (K_L \cdot q_m) \quad (4)$$

where the constants K_L [L/mg], indicative of the adsorption affinity, and q_m , representing the maximum monolayer adsorption capacity, were subsequently determined by applying the linear form of the Langmuir isotherm model (equation (3)) to the experimental data obtained from AAS measurements.

This study involved a comprehensive kinetic assessment by fitting the experimental adsorption data to a suite of reaction-based models, including zero-order (equation (5)), first-order (equation (6)), second-order (equation (7)), pseudo-first-order (equation (8)), and pseudo-second-order equations (equation (9)). The determination of which order equation to use is based on the R^2 value obtained from the linear regression equation. The equation used is the one with the R^2 value closest to 1.

$$C_t = C_0 - k_0 \cdot t \quad (5)$$

$$\ln C_t = \ln C_0 - k_1 \cdot t \quad (6)$$

$$1/C_t = 1/C_0 + k_2 \cdot t \quad (7)$$

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) \cdot t \quad (8)$$

$$t/q_t = (1/k_2 \cdot q_e^2) + t/q_e \quad (9)$$

Cyclic regeneration test of coal magnetic activated carbon

A regeneration test was conducted to evaluate the reusability of magnetic activated carbon in adsorbing Cd(II) ions. The Cd(II) solution had an initial concentration of 250 mg/L. In the first cycle, 1 g/L CMAC was added to the CMAC solution, which was stirred at 120 rpm using a magnetic stirrer for 60 minutes at room temperature. After adsorption, the CMAC was separated from the solution using filter paper. The residual CMAC concentration in the solution was analysed by atomic absorption spectrophotometry (AAS), and the CMAC removal efficiency was calculated as the difference between the initial and final concentrations.

The used adsorbent was then regenerated by immersing the CMAC in a 0.1 M HCl and 0.05 M EDTA solution for 60 minutes to desorb the CMAC ions. After desorption, the CMAC was washed with distilled water until the pH was neutral, then dried at 378 K for 12 hours. The regenerated adsorbent was then reused under the same adsorption conditions for cycles 2-5. The regeneration test was conducted in five consecutive cycles under identical operating conditions. All experiments were performed in triplicate ($n = 3$). Regeneration performance was evaluated based on Cd(II) removal efficiency and adsorption capacity in each cycle.

The results of the CMAC cyclic regeneration research test were then statistically analysed using the Ryan-Joiner test to assess normality. This matter was followed by a Levene's test to evaluate data homogeneity. If the research data were normally distributed and homogeneous, the ANOVA test was used. If significant differences were found, the Tukey or Duncan test was used at $\alpha = 0.05$ to determine whether the group means differed.

Results and discussions

Coal parameter test results

The coal to be used to make activated carbon is eroded and sifted through a 60-mesh sieve (Fig. 1). Furthermore, coal is tested proximate to determine its parameters. Table 1 summarises the proximate analysis results of the coal sample. As detailed in Table 1, the feedstock coal used in the CMAC production process is bituminous. Concurrently, the parametric analysis of the resulting activated carbon, investigated across varying activator concentrations and activation temperatures, is presented in Figures 2 through 6.

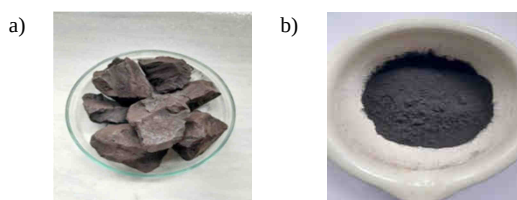


Fig. 1. Physical appearance of coal: a) before being eroded, b) after being eroded and sifted through a 60 mesh size

Coal proximate test results

Table 1

Parameter	Up to [%]	Test method
WC	18	ASTM D3173-87 [27]
VMC	20	BS 1016-104.3 [28]
AC	6	ASTM D-3174-12 [29]
FCC	56	-

As detailed in Table 1, the feedstock coal used in the CMAC production process is bituminous. Concurrently, the parametric analysis of the resulting activated carbon, investigated across varying activator concentrations and activation temperatures, is presented in Figures 2 and 3.

Analysis of activated carbon characteristics

Water content

An analysis of the activated carbon revealed its inherent moisture content, ranging from 1.31 % to 4.48 %, which complies with SNI 06-3730-1995, which stipulates a maximum allowable limit of 15 % (Fig. 2a). The concentration of the phosphoric acid-hydrochloric acid activator had no significant effect on the resultant water content. In contrast, the activation temperature had an apparent effect: a higher temperature range of 898 K - 1023 K yielded activated carbon with a lower average water content than activation at 873 K. The moisture content of the synthesised activated carbon was lower than that of several other precursors and activators reported in the literature [9].

Ash composition

The ash content of the activated carbon, a parameter known for its volatility, ranged from 1.02 % to 8.47 % (Fig. 2b). Despite this variation, the values consistently comply with

SNI 06-3730-1995, which stipulates a maximum allowable ash content of 10 %. As illustrated in Figure 3, there is a direct correlation between activation temperature and ash content. The observed ash parameter is lower than that of ammonium phosphate-activated bituminous coal [9].

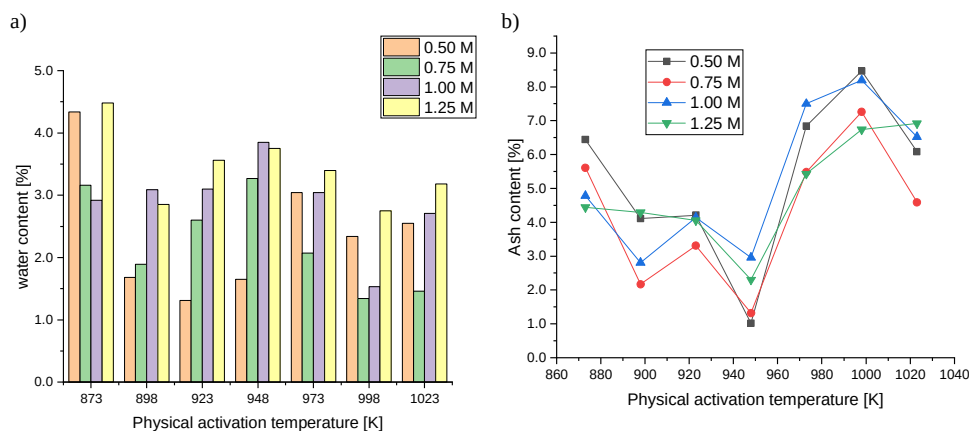


Fig. 2. Characteristic of CMAC on various variables of $\text{H}_3\text{PO}_4\text{-HCl}$ activator concentration and physical activation temperature: a) water content, b) ash content

Volatile content

The volatile content of CMAC, as illustrated in Figure 3a, ranges from 10.87 % to 20.46 %. This result complies with SNI 06-3730-1995, which stipulates a maximum allowable limit of 25 %. This activated carbon is characterised by a relatively low volatile matter content, below levels found in carbons produced from sub-bituminous coal of lower grade and from agricultural waste products, specifically coir and the shells of young coconuts. In contrast, its volatile matter is nearly identical to that of activated carbon derived from *Salacca zalacca* seeds [10].

Fixed carbon

The activated carbon exhibited a fixed carbon content within the range of 68.76 % to 81.99 % (Fig. 3b). Analysis indicated that the concentration of chemical activators did not significantly affect this parameter. In contrast, physical activation temperature exerted a considerable influence. A sharp increase in fixed carbon content was observed at 1048 K and 1148 K, elevating the values to meet the SNI standard minimum requirement of 65 % at these specific temperatures. The fixed carbon composition of activated carbon is the primary determinant of its porous structure, and the overall adsorption capacity derived from low-grade bituminous coal is comparatively low. In contrast, while materials such as *Salacca zalacca* seeds yield higher fixed carbon content, conventional fixed activated carbon shows an intermediate value between these sources [10].

Iodine number

The iodine uptake capacity of the produced CMAC was determined to be 1230.93 mg/g - 1256.31 mg/g. As illustrated in Figure 3c, this result not only meets but also

significantly exceeds the minimum requirement of 750 mg/g stipulated by the Indonesian National Standard (SNI 06-3730-1995). Furthermore, the material's performance exceeds that of activated carbons derived from alternative precursors, such as salacca zalacca seeds and low-grade bituminous coal [9, 10].

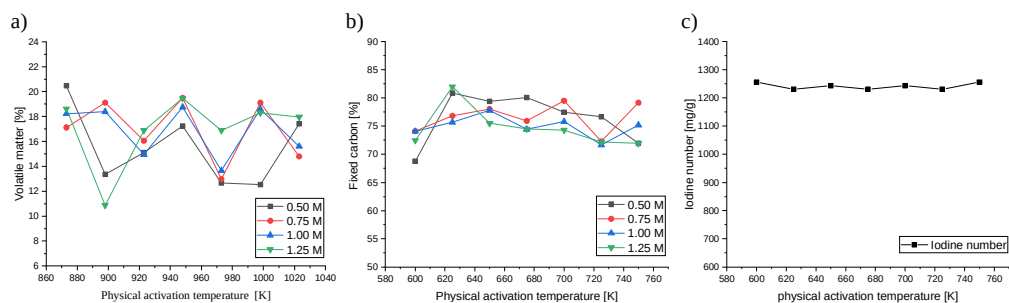


Fig. 3. Characteristic of CMAC on various variables of $\text{H}_3\text{PO}_4\text{-HCl}$ activator concentration and physical activation temperature: a) volatile matter; b) fixed carbon; c) iodine number of CMAC activated with $\text{H}_3\text{PO}_4\text{-HCl}$ concentration of 1 M at various physical activation temperatures

CMAC parameter test results

Proximate analysis of the CMAC sample revealed a composition of 7.22 % moisture, 8.45 % ash, 17.12 % volatile matter, and 67.21 % fixed carbon. Furthermore, its adsorption capacity, as indicated by the iodine number, was measured at 1262.66 mg/g. The surface characteristics, including specific surface area and pore volume of the CMAC adsorbent, were ascertained through Brunauer-Emmett-Teller (BET) analysis performed on a 0.0729 g specimen. The test was conducted using adsorption and desorption methods with nitrogen adsorbent. The test was carried out for 3 hours and 29.7 minutes at 77.3 K. BET test results, utilising the adsorption method, showed that CMAC has a surface area of $177.183 \text{ m}^2/\text{g}$ and a pore volume of $15.3101\text{-}38.5131 \text{ cc/g}$. CMAC exhibits a superior surface area and pore volume ($31.930 \text{ m}^2/\text{g}$ and 0.011 cc/g , respectively) compared to activated carbon derived from the same precursor but treated with ammonium phosphate [9]. Pore volume of CMAC is also higher than that of active carbon from soft brown coal (1.2 cc/g) and bituminous coal (0.487 cc/g) [25, 32].

SEM-EDX

The results of the SEM-EDX test on coal and CMAC are presented in Figure 4. The figure shows that pores are already present in coal, and their size increases when it becomes CMAC. In CMAC, there is a porous surface containing micro-, meso-, and macropores, so that the pore volume varies from 15.3101 cc/g to 38.5131 cc/g . These pores are formed due to chemical and physical activation processes. These pores provide a relatively high specific surface area of CMAC, which is $177.183 \text{ m}^2/\text{g}$. In CMAC, carbon fragments are irregularly shaped due to calcination and activation processes. There are areas with large pores (cracks) and areas with small pores (micropores).

Furthermore, the analytical findings from the material's elemental composition and surface morphology were characterised using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDX) of the CMAC sample (Fig. 4c), which

shows white granules adhering to the surface or entering the pore cavity. The white granules are Fe-oxide particles that are lighter in colour than the carbon matrix. The results of the SEM-EDX show that coal contains 45.30 % Fe, 24.23 % C, 22.60 % O, 4.23 % Na, 1.56 % Mo, and the remaining elements Mg, Al, Si, and Ca. The presence of the Fe element is due to the addition of Fe_3O_4 composites to activated carbon.

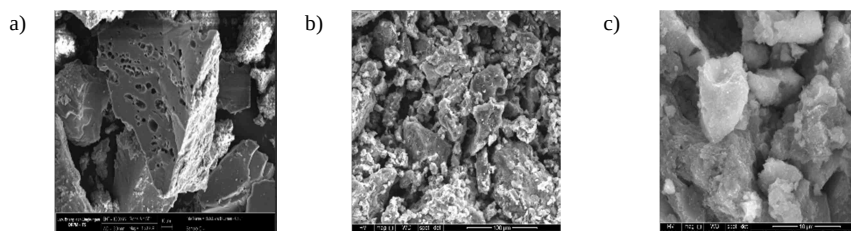


Fig. 4. SEM EDX photo: a) coal (1500 x), b) CMAC (1000 x), c) CMAC (10000 x)

Cadmium removal

The testing of CMAC's ability to remove cadmium was conducted by varying the cadmium concentration in the solution and the CMAC contact time.

Cadmium concentration variables

The percentage of cadmium removal in the samples CdI_1 to CdI_5 after 1 hour of contact with CMAC is shown in Figure 5, ranging from 97.43 % to 97.85 %. The percentage of CMAC removal of Cd(II) is higher than the percentage of Cr(VI) removal by activated carbon from non-magnetically activated coal, which is about 37 % - 53 % [9]. As illustrated in Figure 5, the adsorption capacity of the material reaches its peak when the initial Cd(II) concentration in the aqueous solution is between 250 mg/L and 350 mg/L. The lower the cadmium concentration in the solution, the lower the percentage of cadmium removed. However, the change in the removal percentage is minimal. This incident is likely due to adsorption of Cd(II) at concentrations of 250 mg/L to 350 mg/L, which is close to the saturation point, resulting in an almost constant increase in cadmium removal percentage.

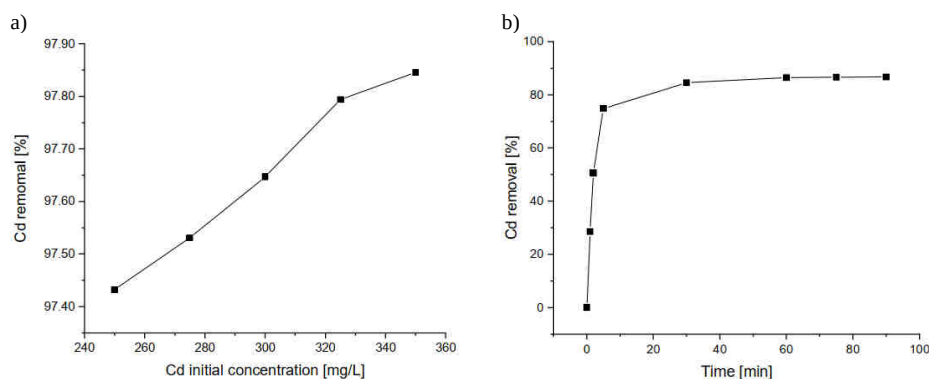


Fig. 5. Diagram of cadmium removal with: a) cadmium concentration variables, b) contact time variables

Contact time variables

The percentage of cadmium removal in samples Cdk_1 to Cdk_7 after contact with CMAC, with time variables ranging from 1 to 90 minutes and an initial Cd(II) concentration of 50 mg/L, is presented in Figure 5. The graph shows that after 60 minutes of contact time, CMAC's adsorption capacity for cadmium is nearly constant. This is because the adsorption of cadmium after 60 minutes is close to equilibrium conditions, and the maximum cadmium adsorption by CMAC has been achieved.

Model adsorption isothermal

The adsorption capacity of CMAC for Cd(II) ions in solution was modelled using the Langmuir and the Freundlich isotherms, as illustrated in Figure 6. The isothermal adsorption equations are presented in equations (10) (Freundlich) and (11) (Langmuir):

$$\log q_e = \log 3.9823 + 1/0.4530 \cdot \log c_e \quad (10)$$

$$c_e/q_e = (c_e/238.10) + (1/18.7381) \quad (11)$$

Table 2

Freundlich and Langmuir equation constants

Adsorption model	Freundlich			Langmuir		
Parameter	R^2 [-]	n [-]	K_F [mg/g]	R^2 [-]	K_L [L/mg]	q_m [mg/g]
Parameter value	0.9691	0.4530	3.9823	0.9082	0.0787	238.10

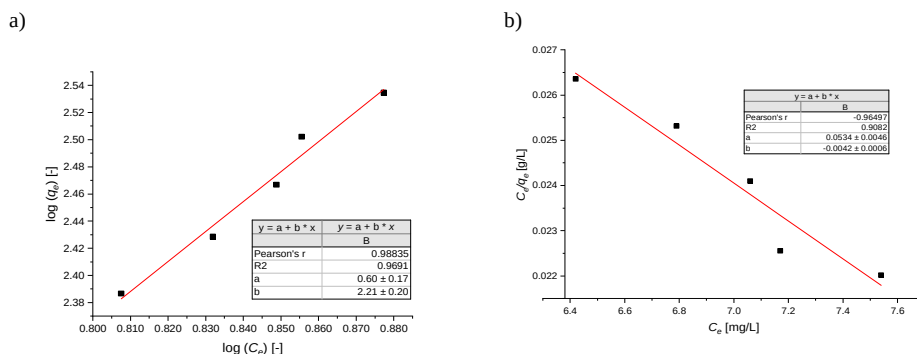


Fig. 6. Graph of the isothermal adsorption test with: a) the Freundlich equation, b) the Langmuir equation

As presented in Table 2, the coefficient of determination R^2 for the Freundlich isotherm model is higher than that of the Langmuir model, with a value much closer to unity. The Freundlich equation is better suited to describe the adsorption of Cd(II) by CMAC, given its heterogeneous surface properties. The pores of CMAC range in size, including macropores, mesopores, and micropores (Figs. 7-9). There are several functional groups, for example, oxygen groups ($-\text{OH}$, $-\text{COOH}$, $-\text{C=O}$) and sulphur groups ($-\text{SH}$, $-\text{S=O}$, $-\text{SO}_2^-$), which have different adsorption energies. Also, it makes the CMAC's surface properties heterogeneous.

Adsorption kinetics model

An adsorption kinetics model illustrates how CMAC's adsorption capacity for Cd(II) ions changes over Time. The adsorption kinetics model is illustrated with the adsorption kinetics equation from order 0 to pseudo-order 2 (Fig. 7). Table 3 shows that the most suitable adsorption kinetics equation for the Cd(II) adsorption kinetics model by CMAC is a pseudo-order 2 equation with an R^2 value of 0.9997.

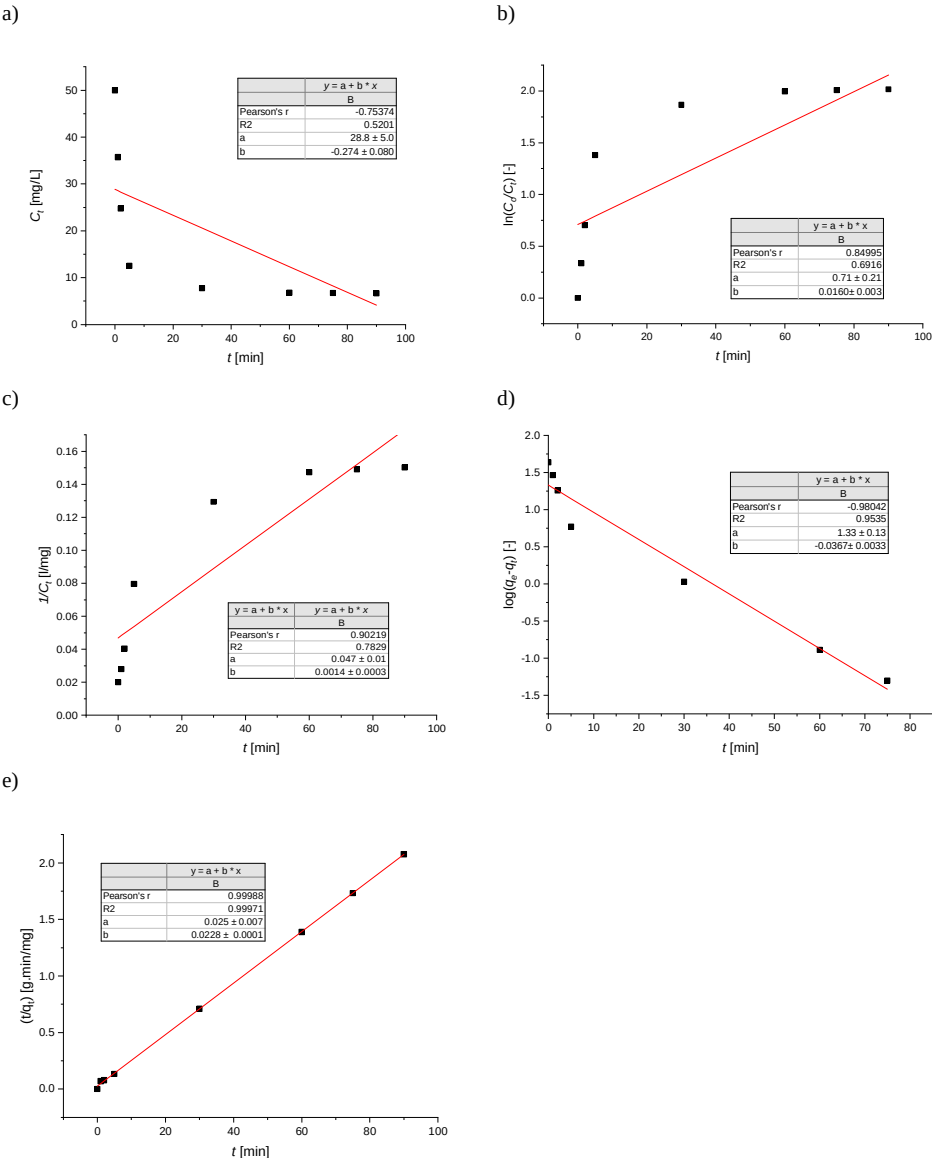


Fig. 7. Adsorption kinetics model graph: a) order 0, b) order 1, c) order 2, d) pseudo-order 1, e) pseudo-order 2

Table 3

The constant of the kinetic equation of adsorption

Adsorption kinetics	Constant	Constant value
Order 0	k_0 [mg/L·min]	0.2745
	R^2	0.5201
Order 1	k_1 [1/min]	0.016
	R^2	0.6916
Order 2	k_2 [g/mg·min]	0.0017
	R^2	0.7829
Pseudo-order 1	pseudo k_1 [1/min]	0.062181
	R^2	0.9535
Pseudo-order 2	pseudo k_2 [g/mg·min]	0.0308
	R^2	0.9997

Cyclic regeneration test of coal magnetic activated carbon

The adsorption capacity test was performed using CMAC over 5 cycles, with 3 repetitions per cycle. The test results are presented in Table 4. Furthermore, the Cd content data from the cyclic regeneration test were subjected to statistical tests as presented in Table 5.

Table 4

Cd removal in cyclic regeneration test

Regeneration	Cd levels in wastewater after contact with CMAC [mg/L]				
	Experiment			Mean	Cd removal [%]
	I	II	III		
R1	7.6	7.2	7.4	7.4	97.04
R2	46.5	43.9	45.4	45.3	81.89
R3	143.6	144.5	141.3	143.1	42.75
R4	215.8	218.1	212.4	215.4	13.83
R5	228.1	223.5	225.6	225.7	9.71

Based on Table 4, the Cd levels in wastewater after contact with CMAC during regenerations 1-5 increased. R1 produced the lowest Cd levels, averaging 7.4 mg/L. In comparison, R5 produced the highest Cd levels, averaging 225.7 mg/L. The following are the results of the normality assumption test using the Ryan-Joiner test statistic.

Table 5

Statistical test of Cd levels in the cyclic regeneration test

Cd levels in wastewater after contact with CMAC [mg/L]								
					95 % confidence interval for mean			
Regeneration	N	Mean	SD	Std. error	Lower bound	Upper bound	Min	Max
R1	3	7.40	0.20	0.12	6.90	7.90	7.20	7.60
R2	3	45.3	1.3	0.8	42.0	48.5	43.9	46.5
R3	3	143.1	1.7	1.0	139.0	147.2	141.3	144.5
R4	3	215.4	2.9	1.7	208.3	222.6	212.4	218.1
R5	3	225.7	2.3	1.3	220.0	231.5	223.5	228.1
Total	15	127	91	24	77	178	7	228

Table 6

Normality test results

Variable	Obs	Pr(skewness)	Pr(kurtosis)	Joint test	
				Adj chi ² (2)	Prob > chi ²
Cd content [mg/L]	15	0.7036	0.0039	7.3	0.026

Based on Table 6, the normality test yields a p-value less than the significance level (5 % or 0.05), indicating that the data on Cd levels [mg/L] are not normally distributed. In this study, a logarithmic transformation was used. The following are the results of the normality test after data transformation. Based on Table 7, it is known that the normality test produces a probability greater than the significance α (5 % or 0.05), so that the data from the Cd levels that have been transformed into logarithms are declared to be normally distributed. Thus, the normality assumption is met. Testing the homogeneity assumption can be seen through Levene's test (Table 8).

Table 7

Normality test results after transformation

Variable	Obs	Pr(skewness)	Pr(kurtosis)	Joint test	
				Adj chi ² (2)	Prob>chi ²
log Cd content [mg/L]	15	0.0848	0.727	3.56	0.1685

Table 8

Homogeneity test results

Levene's Test	Probability
0.986	0.458

Based on Table 8, the data homogeneity test yields a Levene statistic with a p-value $> \alpha$ (5 %, or 0.05), indicating that the model has homogeneous variance. Therefore, the homogeneity assumption is met. Because the assumptions of normality and homogeneity are met, the analysis can proceed with one-way ANOVA. The CMAC regeneration efficiency test on Cd levels [mg/L] was conducted using one-way ANOVA with the following hypotheses: H0: There is no difference in CMAC regeneration efficiency on Cd levels [mg/L]; H1: At least one pair of CMAC regenerations differs significantly on Cd levels [mg/L]. The test criteria state that if the significance value is $\leq$ the level of significance ($\alpha = 5\%$ or 0.05), H0 is rejected. Therefore, it can be stated that at least one pair of CMAC regenerations differs significantly in Cd levels [mg/L]. The results of the CMAC regeneration efficiency test on Cd Levels [mg/L] are presented in Table 9.

Table 9

One-way ANOVA test results

	Sum of squares	df	Mean square	F	Sig.
Between groups	25.095	4	6.274	15831.182	0.000
Within groups	.004	10	0.000		
Total	25.099	14			

Based on Table 9, the test statistic is 15831.182, with a significance value of 0.000. The data show that the p-value is $<$ the significance level (5 % or 0.05), so H0 is rejected.

Therefore, it can be stated that at least one pair of coal magnetic activated carbon regeneration processes is significantly different in Cd levels [mg/L]. To determine whether the regeneration groups differ significantly, a Tukey test was conducted. The results of the Tukey analysis are shown in Table 10.

Table 10

Tukey analysis results

Regeneration	N	Subset for $\alpha = 0.05$			
		1	2	3	4
R1	3	2.0012			
R2	3		3.8123		
R3	3			4.9637	
R4	3				5.3726
R5	3				5.4193
Sig.		1.000	1.000	1.000	0.095

Based on the Tukey analysis, R5 showed the highest Cd levels [mg/L] and was significantly different from R1, R2, and R3. However, it did not show a significant difference from R4. The analysis results show that R5 is the most effective magnetic activated carbon regeneration in increasing Cd levels. However, its effectiveness is still relatively similar to R4.

The adsorbent's regeneration efficiency and cyclic stability

Regeneration cycle tests were conducted to evaluate the stability of adsorption performance and the durability of coal magnetic activated carbon (CMAC) during repeated use for adsorbing Cd^{2+} ions. Regeneration was carried out over five cycles (R1-R5), with the residual Cd concentration after adsorption measured and the removal percentage calculated.

The experimental results showed that in the first cycle (R1), the magnetic activated carbon still exhibited very high adsorption performance, as indicated by a final Cd concentration of 7.4 mg/L and a removal efficiency of 97.04 %. This value indicates that active sites on the carbon surface, including oxygen functional groups ($-\text{OH}$, $-\text{COOH}$), and the magnetic Fe_3O_4 particles, remained optimally available to bind Cd(II) via physical and chemical adsorption mechanisms.

In the second regeneration cycle (R2), the removal efficiency decreased to 81.89%, and the Cd content increased to 45.27 mg/L. This decrease indicates that some active sites are beginning to lose adsorption capacity, possibly due to incomplete release of Cd^{2+} ions during regeneration or changes in the adsorbent surface structure.

The decline in adsorption performance was more pronounced in the third cycle (R3), where the removal efficiency reached only 42.75 %. The relatively high residual Cd content (143.13 mg/L) indicates that most active sites have been permanently saturated, possibly leading to pore blocking and damage to the micropore structure due to repeated regeneration treatments.

In the fourth (R4) and fifth (R5) cycles, the removal efficiency decreased drastically to 13.83 % and 9.71 %, respectively. This condition indicates that magnetic activated carbon has lost most of its adsorption capacity. Repeated regeneration processes may degrade surface functional groups, causing this phenomenon. Irreversible adsorption of strongly bound Cd(II) on active sites and damage to the pore structure also reduce the adsorption

capacity. The decrease in effective surface area, as well as the potential for agglomeration of Fe_3O_4 magnetic particles, also reduces pore accessibility. Overall, the regeneration test results showed that CMAC remained effective after two regeneration cycles, with Cd removal efficiencies above 80 %. After the third cycle, the adsorbent's performance declined significantly, making it less effective for water treatment applications requiring high efficiency.

These findings indicate that although magnetic activated carbon offers the advantage of ease of separation using magnetic fields, optimisation of the regeneration method (e.g., regenerant type, temperature, and regeneration time) is still needed to improve cyclic stability and extend the adsorbent's lifespan [33-35].

Conclusion

The results of the study showed that chemically activated CMAC using a mixture of H_3PO_4 -HCl solution at 0.5 M - 1.25 M and physically activated at 873 K - 1023 K met the SNI 06-3730-1995 activated charcoal standard. The proximate analysis and iodine adsorption capacity of CMAC revealed a moisture content of 7.22 %, 8.45 % ash, 17.12 % volatile matter, 67.21 % fixed carbon, and an impressive iodine number of 1262.66 mg/g. CMAC has a surface area of 177,183 m^2/g and a pore volume of 15.3101 - 38.5131 cm^3/g . CMAC contains Fe at 45.30 %, C at 24.23 %, O at 22.6 %, Na at 4.23 %, Mo at 1.56 %, and the remaining elements, including Mg, Al, Si, and Ca. CMAC has also been shown to remove Cd(II) ions under laboratory conditions, achieving up to 97.85 % removal. Isothermal adsorption analysis of Cd(II) onto CMAC showed a better fit with the Freundlich model than with the Langmuir equation. This phenomenon can be attributed to the non-uniform pore-size distribution on the CMAC surface and the presence of several types of groups on the CMAC, which cause their adsorption power to differ.

This research can be conducted under variable pH conditions in the cadmium solution, allowing determination of the optimal pH for the adsorption process. The study also found that although magnetic activated carbon offers the advantage of easy separation using a magnetic field, CMAC can be used effectively in 2 regeneration cycles, with Cd(II) removal exceeding 80 %. Research is needed to optimise the regeneration method by selecting the appropriate regenerant agent, temperature, and regeneration time to improve cyclic stability and extend CMAC service life.

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