ARID ZONE JOURNAL OF ENGINEERING, TECHNOLOGY & ENVIRONMENT
AZOJETE September 2026. Vol.22(3):689-700
Published by the Faculty of Engineering, University of Maiduguri, Maiduguri, Nigeria.
Print ISSN: 1596-2490, Electronic ISSN: 2545-5818
https://doi.org/10.63958/AZOJETE/2026/22/03/011
www.azojete.com.ng

ORIGINAL RESEARCH ARTICLE

PERFORMANCE EVALUATION OF A CO-PRECIPITATED MAGNETIC ACTIVATED CARBON COLUMN FOR HEAVY METAL REMOVAL FROM SYNTHETIC AND SPIKED MUNCIPAL WASTEWATER

A. Musa [1*], B.S. Sani [2], U.A. Abubakar [2], D.B. Adie [2]

[1] *Department of Chemical Engineering, Nasarawa State University, PMB. 1022, Keffi, Nigeria.*
[2]*Department of Water Resources and Environmental Engineering, Ahmadu Bello University, PMB. 1045, Zaria, Nigeria.*
** Corresponding author's email: musaabdulmalik@nsuk.edu.ng*

ARTICLE INFORMATION

Received: 17th June 2026
Revised: 7th July 2026
Accepted: 10th July 2026

Keywords:
Fixed-bed column
Chromium
Lead
Co-precipitated magnetic activated carbon
Tertiary treatment
Municipal wastewater

ABSTRACT

Residual heavy metals in municipal wastewater effluents remain an environmental issue of concern to wastewater treatment plants. This is because it is difficult to achieve complete removal by conventional treatment processes. The performance of a co-precipitated magnetic activated carbon (CP-MAC) fixed-bed adsorption column was evaluated for chromium (Cr) and lead (Pb) removal in synthetic wastewater (SWW) and spiked municipal wastewater (SPWW) samples. Continuous flow experiments were conducted using a 8.50 g of CP-MAC bed at an optimized bed height of 18 cm. Also, the influent metal concentration used was 11 mg/L and flow rate of 6.30 mL/min. Performance was evaluated using breakthrough curve analysis, adsorption capacity, treated volume, removal efficiency, and bed utilization parameters. The results show that Pb consistently exhibited better adsorption behaviour than Cr under both wastewater conditions. Under SWW conditions, exhaustion adsorption capacities of 1.78 and 1.65 mg/g were obtained for Pb and Cr, respectively, while corresponding values under SPWW conditions decreased to 1.27 and 1.13 mg/g. In comparison to SWW, the more complex SPWW led to a decline in performance, with adsorption capacity reductions ranging from 28.65% to 31.51 %. Additionally, the breakthrough time decreased by 29.15% to 36.70%, and the total volume of wastewater treated before exhaustion dropped by 20.42% to 28.88%. These changes indicate a faster saturation of the adsorption bed and a shorter operational duration for the column. In addition, removal efficiencies of around 54.07% for Pb and 44.97% for Cr were maintained, demonstrating that the CP-MAC column retained its effectiveness even with the presence of competing ions and constituents in the wastewater. It becomes clear that wastewater matrix composition plays a significant role in fixed-bed adsorption performance and the results obtained using SWW alone are likely to overestimate treatment efficiency under practical operating conditions. Therefore, these results support the use of CP-MAC as a tertiary polishing adsorbent for the removal of residual heavy metals from municipal effluents.

1.0 Introduction

Heavy metals are toxic and persistent non-biodegradable contaminants having the tendency to bioaccumulate in environmental matrices and living organisms, making their discharge into surface waters a significant risk to both the environment and human health (Fu and Wang, 2011; Tchounwou *et al.*, 2012). Conventional municipal wastewater treatment plants are configured primarily to treat organic matter, nutrients, and suspended solids, and are not specifically engineered for the efficient removal of dissolved heavy metals (Cantinho *et al.*, 2016; Hargreaves *et al.*, 2018; Sylwan and Thorin, 2021). This inefficiency allows residual heavy metals such as chromium (Cr) and lead (Pb) to be discharged from the effluents into receiving environments such as rivers and lakes.

Adsorption is among the most preferred method for heavy metal removal, attributed to its simple operation, high effectiveness, and suitability for treating effluents containing relatively low metal concentrations (Fu and Wang, 2011). Activated carbon remains the most commonly applied adsorbent. This is attributed to its favourable physicochemical characteristics, including abundant surface area, pore structure, and surface chemical functionalities (Ali and Gupta, 2006). Recently, magnetic activated carbon (MAC), which can be synthesised via different routes such as chemical co-presentation and impregnation is receiving attention (Nguyen *et al*., 2011). It is driven by the advantage of possessing high adsorption capacity of activated carbon with magnetic properties of iron oxides. This combination solves a major bottleneck by making post treatment recovery and regeneration much easier to handle (Ruthiraan *et al*., 2019; Soares *et al*., 2018; Yi *et al*., 2020).

The performance of adsorption systems is frequently investigated using batch experiments (Patel, 2022), real world wastewater treatment plants do not operate this way. In continuous operation, the performance is largely governed by mass transfer processes and hydrodynamic interactions within the system (Dichiara and Weinstein, 2015). This operational complexity makes fixed-bed columns more advantageous, as they are scalable, easier to manage, and suitable for on-site application (Chattergee *et al*., 2018; Patel, 2019). Nonetheless, the effectiveness of these columns depends on a network on interacting factors, including external film diffusion, intraparticle diffusion, axial dispersion, contact duration, and bed utilisation. As a result, analysing breakthrough curves becomes essential for the proper design and evaluation of column systems (Chen and Wang, 2004; Patel, 2019). In fact, fixed-bed experiments provide a realistic insight into how an adsorbent performs under continuous operational conditions, offering more reliable predictions of column lifespan compared to batch studies (Patel, 2020; Rajandran et al., 2025).

Researchers like Kargol *et al*. (2023) and Mahlalela *et al*. (2017) have noted that SWW is often used to optimise treatment systems because it provides a controlled and highly reproducible matrix. Consequently, much of existing literature on fixed-bed adsorption of heavy metals with adsorbents such as activated carbon, mesoporous materials, or magnetic adsorbents, relies heavily on data derived from SWW (Aboussabek *et al*., 2024; Shahbazi *et al*., 2013). However, this approach has limitations. Real municipal effluents are far more complex, containing background dissolved organic matter, suspended solids, and colloidal particles. During continuous treatments, these constituents interact with the adsorbent, competing for active sites, blocking pore access, and disrupting mass transfer pathways (Cantinho *et al*., 2016; Hargreaves *et al*., 2018; O'Flaherty and Gray, 2013). As a result, breakthrough profiles and adsorption capacities observed in SWW rarely reflect actual performance in practical wastewater treatment scenarios. Prior works by Chen *et al*. 2020 and Taty-Costodes *et al*. (2005) have highlighted these discrepancies, attributing it to the interplay between wastewater chemistry, properties of the adsorbent, and operating conditions. To know how newly engineered systems will actually perform, testing them under realistic conditions is mandatory.

Heavy metal removal from fixed-bed adsorption studies have been widely investigated (Malik *et al*., 2018; Patel, 2019). However, only few studies have directly compared column performance using synthetic and real wastewater matrices to behaviour of breakthrough, adsorption capacity, treated volume, removal efficiency, and the utilisation of packed bed (Chatterjee *et al*., 2018; Abdolali *et al*., 2017; Patel, 2019). This provides a practical basis for assessing the reliability of performance estimates derived from SWW and spiked municipal wastewater (SPWW) conditions. As a result, the effect of wastewater matrix composition on the performance of a co-precipitated-magnetic activated carbon (CP-MAC) fixed-bed systems remains insufficiently understood. This work investigated the performance of a CP-MAC fixed-bed column as a tertiary municipal polishing adsorbent for the removal of Cr and Pb under SWW and SPWW conditions.

2. Materials and Method

2.1 Adsorbent Preparation and Properties

The MAC used in this work was produced through a chemical co-precipitation method adapted from Han *et al.* (2015). 50 g of activated carbon was dispersed in 2 L of deionised water under continuous stirring before 36.6 g of $FeSO_4 \cdot 7H_2O$ and 66.6 g of $FeCl_3 \cdot 6H_2O$ were added. The suspension was heated to 70 ℃, then cooled to below 40 ℃, before the pH was raised to 11 using 0.5 M NaOH dropwise to precipitate iron oxides onto the carbon surface. The mixture was allowed to age through the night before decanting and the resulting precipitate was collected using a magnet. The material was rinsed thoroughly with deionised water followed by ethanol, and dried at 80 ℃ for 6 hr. The adsorbent was stored in airtight container as CP-MAC.

The textural and surface characteristics involving the specific surface area and pore volume of the CP-MAC was determined using standard nitrogen adsorption-desorption method by Brunauer-Emmett-Teller (BET).

The surface neutrality was determined according to point of zero charge pH drift method by Mohan *et al.* (2011), while the Fourier-Transform Infrared (FTIR) spectroscopy was used to determine the surface chemical functionalities.

2.2 Wastewater Characterisation

The effluent from a municipal wastewater treatment facility in Abuja, Nigeria, employing a conventional biological process was collected and analysed to obtain baseline characteristics. Using standard APHA (2017) method, the pH, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), nutrients, and selected heavy metals were determined. The obtained results were used as the basis for preparing SWW with characteristics comparable to those of the effluent. The same concentration was adopted in the SWW and SPWW for consistency in evaluating fixed-bed column performance.

2.3 Spiked Wastewater Preparation

The SPWW was prepared by spiking the effluent from the municipal treatment plant with stock solutions of $K_2Cr_2O_7$ and $Pb(NO_3)_2$ to raise the concentrations of Cr and Pb to 11 mg/L according Chatterjee *et al.* (2018). This concentration was adopted from prior preliminary optimisation experiment. The pH of the SPWW was regulated with 0.5 M HCl or NaOH. For quality assurance, the Cr and Pb concentrations were confirmed using atomic Absorption Spectrophotometer (280FS AA, Agilent Technologies, USA) according to standard analytical methods.

2.4 Synthetic Wastewater Preparation

The SWW was prepared by dissolving simultaneously 160 mg of peptone, 110 mg of meat extract, 30 mg of urea, 7 mg NaCl, 4 mg of $CaCl_2 \cdot H_2O$, 2 mg of $MgSO_4 \cdot 7H_2O$, and 28 mg of K_2HPO_4 in a litre of distilled water according to OECD (2001). The solution was agitated vigorously, sterilised at 120 ℃ for 15 min by autoclaving, and then kept to age in darkness for a week.

To obtain a SWW with physicochemical characteristics comparable to those of the characterised municipal effluent, the aged solution was diluted with tap water until a BOD_5 of approximately 25mg/L was achieved. The Cr and Pb concentrations were adjusted to 11 mg/L using stock $K_2Cr_2O_7$ and $Pb(NO_3)_2$ solutions and the pH regulated with 0.5 M HCl or NaOH.

2.5 Fixed-Bed Column Experimental Setup

The CP-MAC fixed-bed column setup for the experiment using the SWW and SPWW is shown in Plate 1. The column geometry was an internal diameter of 1.0 cm and column height of 22.50 cm. The CP-MAC was packed to a bed height of 18 cm, corresponding to an adsorbent bed mass (m) of 8.50 g. The influent wastewater was supplied in a down-flow mode at the flow rate of 6.30 mL/min using a pump (KK300-S25, Kamoer, China).

Prior to each experiment, the packed bed was flushed to remove trapped air to ensure uniform bed packing. Adsorption tests were conducted using both SWW and SPWW, with effluent samples collected at specific time intervals until the column reached its saturation point. Separate adsorption experiments were performed for SWW and SPWW.

2.6 Heavy Metal Analysis

The influent concentration (C_0) and effluent concentrations (C_t) of Cr and Pb were determined using an atomic absorption spectroscopy. Samples were digested according to standard analytical methods.

2.7 Evaluation of Fixed-Bed Column Performance

The adsorption performance of the column was evaluated by constructing breakthrough curves (plot of the effluent to influent concentration ratio, C_t/C_0 against time, t). The breakthrough time (t_b), 50% breakthrough time (t_{50}), exhaustion time (t_e), and saturation time (t_s) were determined at C_t/C_0 values of 0.10, 0.50, 0.90, and 0.95, respectively.

Metal mass balance calculations were used to determine the total influent metal mass, total effluent metal mass, adsorbed metal mass, treated volume, and adsorption capacities at breakthrough, exhaustion, and saturation. Adsorption front propagation and bed utilisation were assessed using the mass transfer zone (MTZ) and length of unused bed (LUB). All parameters were calculated using the equations summarised in Table 1 based on established fixed-bed adsorption relationships reported by Calero *et al.* (2009) Rout *et al.* (2017), Ronda *et al.* (2018) Juela *et al.* (2021) and Mani and Bhandari (2022).

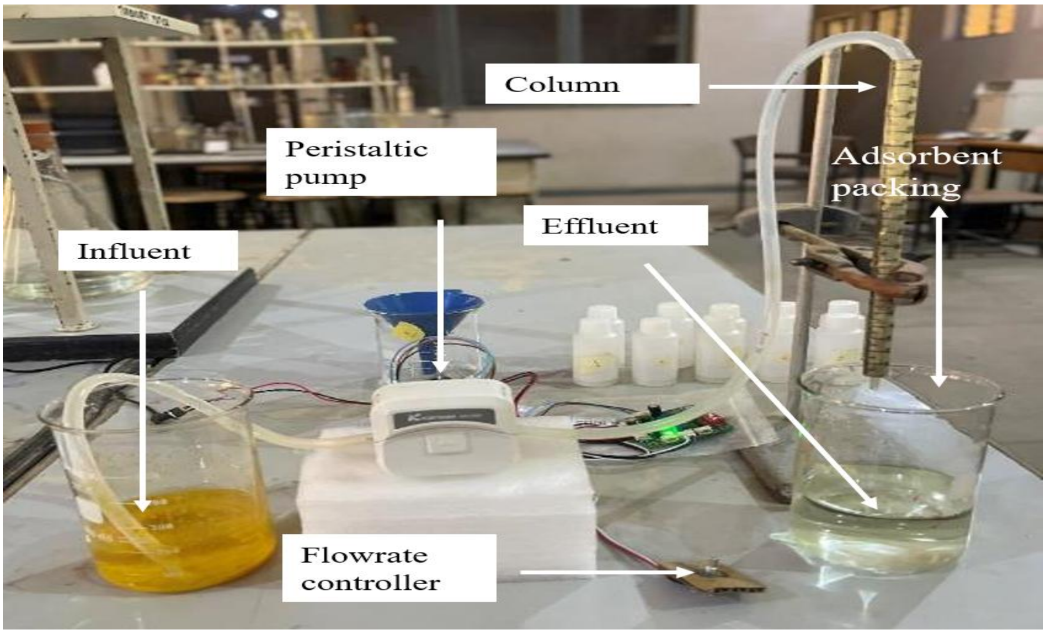

Plate 1: Setup for the CP-MAC fixed-bed column experiments

Table 1: Equations used for evaluating fixed-bed adsorption column performance.

Parameter	Equation	Description
Influent mass (mg)	$M_{in} = QC_0t$	Mass of metal entering the column.
Effluent mass (mg)	$M_{out} = \frac{Q}{1000}\int_0^t C_t dt$	Mass of metal leaving the column.
Adsorbed metal mass (mg)	$M_{ads} = M_{in} - M_{out}$	Mass metal retained by the adsorbent
Adsorption capacity (mg/g)	$q = \frac{M_{ads}}{m}$	Metal uptake normalised to mass of adsorbent.
Treated volume (mL)	$V = Qt$	Volume of wastewater treated.
Mass Transfer zone (cm)	$MTZ = Z\left(1 - \frac{t_b}{t_e}\right)$	Region within the column where active adsorption occurred.
Length of unused bed (cm)	$LUB = Z\left(1 - \frac{q_b}{q_e}\right)$	Portion of the bed that remained unutilised at breakthrough point.

3. Results And Discussion

3.1 Characterisation of Co-Precipitated Magnetic Activated Carbon

The textural and surface characteristics of the synthesised CP-MAC are presented in Table 2, while the FTIR spectrum and corresponding functional group assignments are shown in Figure 1 and Table 3, respectively. The adsorbent exhibited a BET surface area of 254.61 mg/g, a total pore volume of 0.13 cm^3/g, and a point of zero charge of 5.30, indicating the presence of a porous adsorbent with surface characteristics favourable for heavy metal adsorption.

Table 2: Textural and surface characteristics of CP-MAC.

Parameter	Measured value
BET surface area (m^2/g)	254.61
Total pore volume (cm^3/g)	0.13
Point of zero charge	5.30

The FTIR results indicate that oxygen containing functionalities and iron oxide species coexist on the surface the CP-MAC. Their presence provides a variety of active sites available for binding with dissolved metal ions through pathways like electrostatic attraction, surface complexation, ion exchange, and coordination, as reported for MACs (Figueiredo *et al*., 1999; Yi *et al*., 2020; Zhang *et al*., 2013). Additionally, combined with the porous structure of the adsorbent, these surface features help explain the adsorption behaviour observed during the fixed bed column experiments.

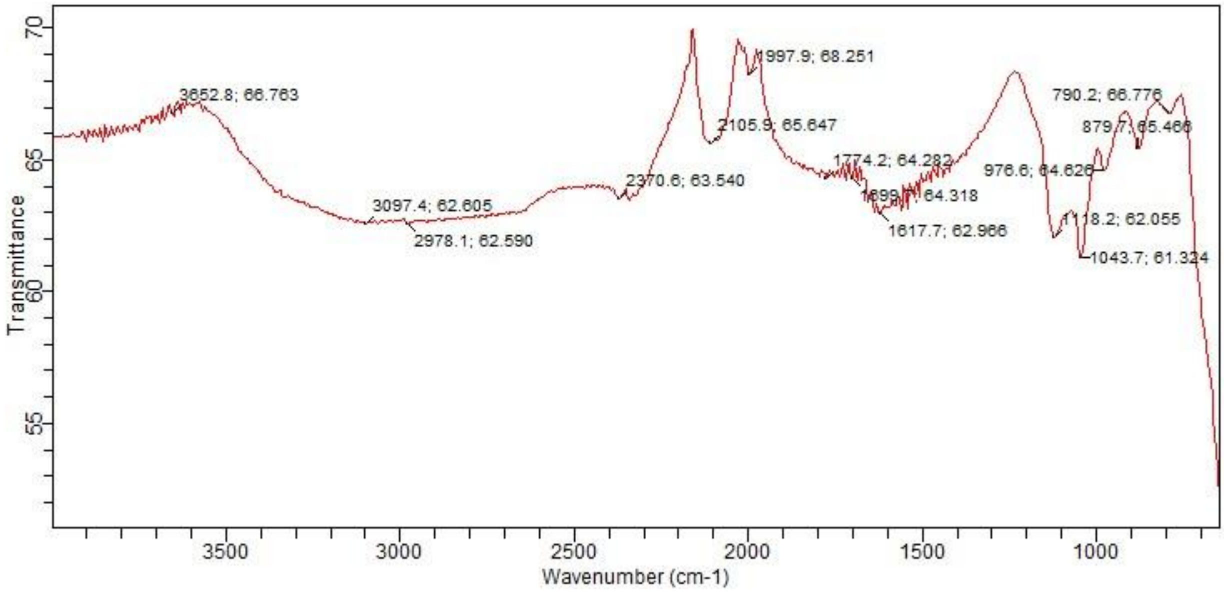

Figure 1: FTIR spectrum of the synthesised CP-MAC.

Table 3: Selected surface chemical functionalities on the synthesised CP-MAC.

Wavenumber (cm^{-1})	Functional group	Assignment
3652.8	O-H	Hydroxyl
2978.1	C-H	Aliphatic
1699.7	C=O	Carbonyl
1617.7	C=C	Aromatics
1118.2	C-O	Alcohol/Ether
790.2	Fe-OH	Iron hydroxyl
879.7	Fe-O	Iron oxide

3.2 Characterisation of Real Wastewater Effluent

The wastewater quality parameters of the treated municipal effluent are presented in Table 4. It was observed that the low BOD_5 and COD values indicate that the biological treatment process was effective. However, the residual concentrations of Cr and Pb remained above the NESREA (2009) stipulated discharge limit of 0.10 mg/L. This is an indication that these metals were not completely removed during treatment using the conventional activated sludge system.

Table 4: Characterisation of collected effluent for baseline physicochemical properties.

Parameter	Measured value	NESREA Guideline
pH	7.10	6.0-8.0
DO (mg/L)	6.2	7.0-10.0
BOD_5 (mg/L)	23	50
COD (mg/L)	71	100
Cr (mg/L)	0.58	0.10
Pb (mg/L)	0.48	0.10
Cd (mg/L)	ND	0.10

ND = Not Detected

The presence of other constituents such as dissolved organic matter and inorganic ions typical of municipal wastewater created a more complex adsorption matrix than the SWW which could influence adsorption by competing for available adsorption sites. For this reason, the treated effluent provided a more realistic medium for evaluating the performance of the CP-MAC fixed-bed column under conditions closer to those encountered in practice.

3.3 Evaluation of Breakthrough Behaviour and Column Performance under SWW

The CP-MAC fixed-bed column breakthrough curves for Cr and Pb adsorption are presented in Figure 2. Typical of continuous fixed-bed adsorption, characteristic sigmoidal curves for both metals were obtained. Malik *et al.* (2018) and Patel (2019) reported that such behaviour reflects the gradual occupation of adsorption sites as the column approached saturation.

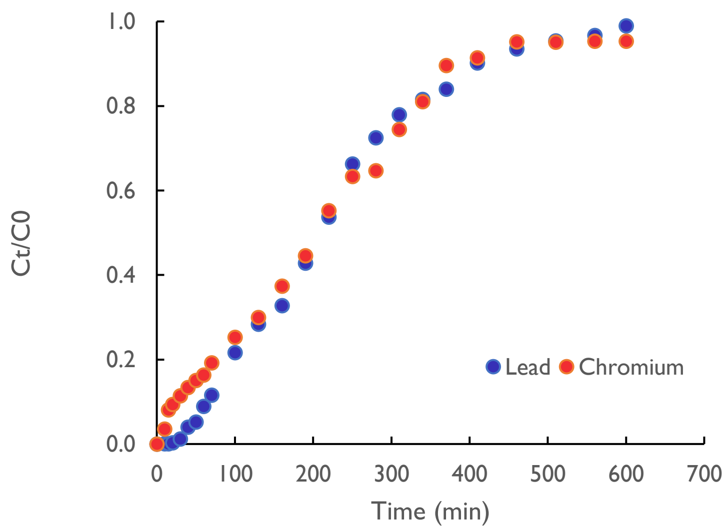

Figure 2: Breakthrough curves for Cr and Pb adsorption on CP-MAC using SWW

Although the breakthrough trends appeared similar, Pb demonstrated significantly better dynamic adsorption performance compared to Cr. The breakthrough point for Pb was observed much later, occurring at 64.04 min, whereas Cr reached breakthrough at 23.05 min. Similarly, the exhaustion time was prolonged, with Pb lasting up to 408.66 minutes before saturation, in contrast to 378.78 min for Cr. This longer timeline indicates a stronger surface affinity for Pb, which helped maintain the operational stability of the adsorption bed for a greater duration. Conversely, the Cr breakthrough curve was notably steeper, indicating a more rapid progression of the adsorption front through the column and resulting in earlier bed saturation. Such kind of breakthrough behaviour in fixed-bed systems is linked to differences in the nature of speciation of the metals, their affinity for adsorption, and how the adsorbate interacts with the adsorbent surfaces (Chen and Wang, 2004; Lim and Aris, 2014; Shahbazi *et al.*, 2013).

From the CP-MAC column parameters presented in Table 5, Pb showed superior performance, with exhaustion adsorption capacities of 1.78 and 1.65 mg/g for Pb and Cr respectively. At saturation, the capacities increased only slightly to 1.83 mg/g (Cr) and 1.73 mg/g (Pb). According to Dwivedi *et al.* (2008) and Shahbazi *et al.* (2013), the superior performance of Pb over other metals usually suggest stronger adsorbate-adsorbent interaction especially with the surface oxygen functionalities.

In terms of throughput of wastewater treated, Pb recorded higher volumes of 403.44 and 2574.53 mL compared to Cr (145.22 mL and 2386.31 mL) at breakthrough and exhaustion, respectively. This greater volumes for Pb can be attributed to the delayed breakthrough recorded. At exhaustion, comparable removal efficiencies were achieved even with differences in the breakthrough behaviour between the metals (53.64% for Pb and 53.57% for Cr). This resulted in both adsorption systems of the metals achieving similar utilisation of the packed bed.

Cr exhibited a wider MTZ of 16.90 cm compared to 15.18 cm for Pb. Calero *et al.* (2009), Rout *et al.* (2017), and Mani and Bhandari (2022) reported that wider zone points to a more sluggish mass transfer and a less efficient movement of the adsorption front. This directly aligns with Cr early breakthrough. Similarly, LUB values of 17.34 cm and for Pb and 17.14 cm for Cr in the 18 cm packed bed. This indicates that breakthrough occurred before complete utilisation of the bed (Chatterjee *et al.*, 2018; Patel, 2019; Ronda *et al.*, 2018).

Table 5: Adsorption performance parameters for Cr and Pb in the CP-MAC fixed-bed column using SWW

Parameter	Chromium	Lead
Breakthrough time, t_b (min)	23.05	64.04
Exhaustion time, t_e (min)	378.78	408.66
Saturation time, t_s (min)	457.86	498.68
50% breakthrough time, t_{50} (min)	205.27	209.80
Adsorption capacity at exhaustion, q_e (mg/g)	1.65	1.78
Adsorption capacity at saturation, q_s (mg/g)	1.73	1.83
Treated volume at exhaustion, V_e (mL)	2386.31	2574.53
Removal efficiency at exhaustion, RE_e (%)	53.57	53.64
Mass transfer zone, MTZ (cm)	16.90	15.18
Length of unused bed, LUB (cm)	17.14	17.34

3.4 Evaluation of Breakthrough Behaviour and Column Performance under SPWW

The CP-MAC fixed-bed adsorption breakthrough curve for Cr and Pb using SPWW (Figure 3) also produced sigmoidal breakthrough curves, signalling the gradual saturation of adsorption sites in the system. The curves obtained under SPWW shifted towards shorter operating times when compared to the SWW condition. Pb continued to exhibit better dynamic adsorption behaviour than Cr. This shift indicates that the more complex wastewater matrix reduced the adsorption performance of the column.

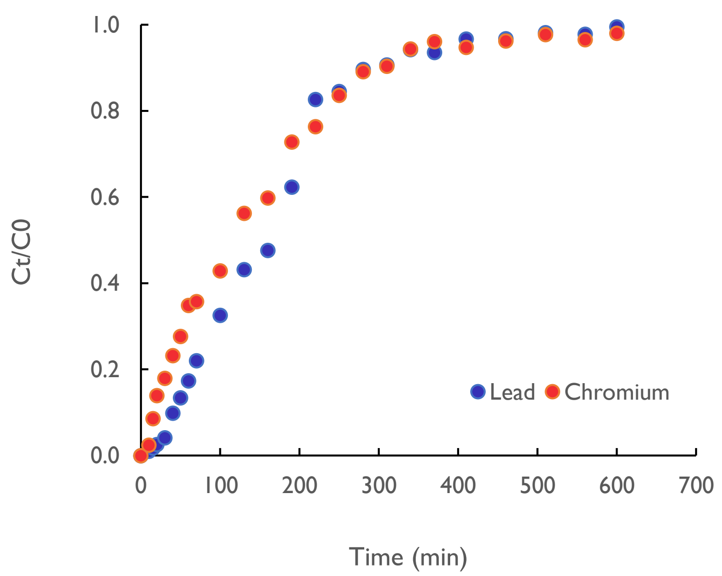

Figure 3: Breakthrough curves for Cr and Pb adsorption on CP-MAC using SPWW

It took longer time for Pb to have a breakthrough (40.54 min) compared to Cr (16.33 min). This indicates that even under a more competitive wastewater condition, similar trend to SWW is maintained. According to Chen and Wang (2004) and Shahbazi *et al.* (2013), such behaviour is commonly associated with the stronger adsorbent affinity and adsorbate-adsorbent interactions.

As summarised in Table 6, at exhaustion, adsorption capacities of 1.27 and 1.13 mg/g were obtained for Pb and Cr, respectively, increasing slightly to saturation capacities of 1.31 and 1.14 mg/g. In comparison to the SWW experiment, these values showed significant decline. This reduction can be attributed to the complex nature of the wastewater, which contains background constituents such as dissolve organic matter and inorganic ions. This blocks access to pores, disrupts mass transfer, and forces target contaminants to compete for a limited number of active adsorption sites (O'Flaherty and Gray, 2013; Taty-Costodes *et al.*, 2005).

Table 6: Adsorption performance parameters for Cr and Pb in the CP-MAC fixed-bed column using SPWW

Parameter	Chromium	Lead
Breakthrough time, t_b (min)	16.33	40.54
Exhaustion time, t_e (min)	301.43	290.64
Saturation time, t_s (min)	351.05	388.18
50% breakthrough time, t_{50} (min)	116.00	164.78
Adsorption capacity at exhaustion, q_e (mg/g)	1.13	1.27
Adsorption capacity at saturation, q_s (mg/g)	1.14	1.31
Treated volume at exhaustion, V_e (mL)	1899.00	1831.01
Removal efficiency at exhaustion, $RE_{,e}$ (%)	44.97	54.07
Mass transfer zone, MTZ (cm)	17.02	15.49
Length of unused bed, LUB (cm)	17.15	17.30

The effects of the matrix were also evident in the treated wastewater volumes. The breakthrough volumes were measured at 255.39 mL for Pb and 102.90 mL for Cr, while the exhaustion volumes reached 1831.01 mL and 1899.00 mL, respectively. Notably, these treatment volumes were significantly lower than those observed under SWW conditions, indicating an accelerated bed saturation. In addition, the removal efficiencies at exhaustions were 54.07% for Pb and 44.97% for Cr, suggesting greater susceptibility of Cr adsorption to interference from co-existing wastewater constituents. It is noteworthy that similar reductions in adsorption performance have been reported elsewhere using SWW suspension (O'Flaherty and Gray, 2013; Taty-Costodes *et al*., 2005).

The MTZ values were 15.49 cm for Pb and 17.02 cm for Cr within the 18 cm bed depth. The broader MTZ observed for Cr indicates greater mass transfer resistance and less efficient progression of the adsorption front (Mani and Bhandari, 2022; Rout *et al*., 2017). The observed LUB of 17.30 cm for Pb and 17.15 cm for Cr suggest that the adsorption process reached breakthrough prior to the exhaustion of the entire packed column. The close similarity in LUB values across different wastewater samples implies that the bed was not fully utilised at the point of breakthrough. This indicates that other factors may be affecting the movement of the adsorption front and the efficiency of the column. Such insights point to potential avenues for optimising the operation of fixed-bed systems to enhance their performance.

3.5 Performance Comparison of the Fixed-Bed Column under Synthetic and Spiked Wastewater Conditions

Table 7 summarises the evaluation of CP-MAC column operation under SWW and SPWW. The increased complexity of the wastewater matrix in real samples led to diminished column performance, evidenced by shorter breakthrough times, and reduced removal efficiencies. In contrast to synthetic samples, real municipal effluents contain various background substances that can compete with target contaminants for adsorption sites and hinder mass transfer processes during treatment (O.Flaherty and Gray, 2013; Taty-Costodes *et al*., 2005).

Table 7: Performance parameters comparison of the CP-MAC fixed-bed column under SWW and CPWW

Parameter	SWW	SPWW	Reduction (%)
Chromium			
Adsorption capacity at exhaustion (mg/g)	1.65	1.13	31.51
Breakthrough time (min)	23.05	16.33	29.15
Exhaustion time (min)	378.78	301.43	20.42
Treated volume at exhaustion (mL)	2386.31	1899	20.42
Removal efficiency at exhaustion (%)	53.57	44.97	16.05
Lead			
Adsorption capacity at exhaustion (mg/g)	1.78	1.27	28.65
Breakthrough time (min)	64.04	40.54	36.70
Exhaustion time (min)	408.66	290.64	28.88
Treated volume at exhaustion (mL)	2574.56	1831.03	28.88
Removal efficiency at exhaustion (%)	53.64	54.07	-0.80

The wastewater matrix effect was evident for both metals. Cr was more strongly affected by the wastewater matrix than Pb. Comparing between the SWW to SPWW conditions, Cr adsorption capacity at exhaustion, breakthrough time, exhaustion treated volume decreased by 31.51%, 29.15%, 20.42%, respectively. This reduction pattern remained closely aligned for Pb. The removal efficiency for Cr declined from 53.57% to 44.97% while Pb maintained almost the same removal efficiency under both wastewater conditions. This behaviour suggests that Pb retained a stronger affinity for the CP-MAC surface and was less affected by competition. Dwivedi *et al.* (2008) has reported the stronger affinity of Pb to activated carbon surfaces compared to other heavy metals. These changes indicate the CP-MAC fixed-bed column under SPWW resulted in faster bed saturation and less effective bed utilisation (Malik *et al*., 2018; Patel, 2019). Practically, this means reduced operating life and increase in adsorbent regeneration or replacement. According to Chatterjee *et al.* (2018) and Patel (2022), this would very much likely have an impact on the wastewater throughput and treatment cost.

4. Conclusion

Wastewater matrix had a profound influence on the behaviour of the CP-MAC fixed-bed column for adsorption of Cr and Pb from SWW and SPWW. The exhaustion adsorption capacities reached 1.78 mg/g for Pb and 1.65 mg/g for Cr when SWW was used. As the column was operated with SPWW, the capacity decreased to 1.27 mg/g (Cr) and 1.13 mg/g (Pb), which represents a reduction of about 28.65% to 31.51%. Similar trends in performance reduction were observed with regards to breakthrough time falling from 29.15% to 36.70% and treated volume (20.42-28.88%). Despite these reductions in performance, the CP-MAC column achieved removal efficiencies of 44.97% for Cr and 54.07% for Pb under SPWW conditions.

This indicates that CP-MAC relatively maintained effectiveness even in conditions that more accurately simulate real municipal wastewater. The findings underscore the significance of validating fixed-bed adsorption processes using realistic wastewater samples and highlight the potential of CP-MAC column as a tertiary treatment option for polishing residual heavy metals from municipal effluents.

References

Abdolali, A., Ngo, HH., Guo, W., Zhou, JL., Zhang, J., Liang, S., Chang, SW., Nguyen, DD., and Liu, Y. 2017. Application of a breakthrough biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column. Bioresource technology, 229: 78–87. https://doi.org/10.1016/j.biortech.2017.01.016

Aboussabek, A., Boukarma, L., El Qdhy, S., Ousaa, A., Zerbet, M., and Chiban, M. 2024. Experimental investigation, kinetics and statistical modeling of methylene blue removal onto Clay@Fe_3O_4: Batch, fixed bed column adsorption and photo-Fenton process. Case Studies in Chemical and Environmental Engineering, 9: 100580, https://doi.org/10.1016/j.cscee.2023.100580

Ali, I. and Gupta, VK. 2006. Advances in water treatment by adsorption technology. Nature Protocols, 1(6): 2661–2667. https://doi.org/10.1038/nprot.2006.370

APHA. 2017. Standard methods for the examination of water and wastewater (23rd ed). Washington, DC: American Public Health Association.

Calero, M., Hernáinz, F., Blázquez, G., Ternorio, G., and Martín-Lara, MA. 2009. Study of Cr (III) biosorption in a fixed-bed column. Journal of Hazardous Materials, 171(1–3): 886–893. https://doi.org/10.1016/j.jhazmat.2009.06.082

Cantinho, P., Matos, M., Trancoso, MA., and Correia dos Santos, MM. 2016. Behaviour and fate of metals in urban wastewater treatment plants: A review. Int. J. Environ. Sci. Technol., 13: 359–386. https://doi.org/10.1007/s13762-015-0887-x

Chatterjee, S., Mondal, S., and De, S. 2018. Design and scaling up of fixed bed adsorption columns for lead removal by treated laterite. Journal of Cleaner Production, 177: 760–774. https://doi.org/10.1016/j.jclepro.2017.12.249

Chen, B., Long, F., Chen, S., Cao, Y., and Pan, X. 2020. Magnetic chitosan biopolymer as a versatile adsorbent for simultaneous and synergistic removal of different sorts of dyestuffs from simulated wastewater. Chemical Engineering Journal, 385: 123926. https://doi.org/10.1016/j.cej.2019.123926

Chen, JP. and Wang, L. 2004. Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors. Chemosphere, 54(3): 397–404. https://doi.org/10.1016/S0045-6535(03)00714-8

Dichiara, AB. and Weinstein, SJ. (2015). On the choice of batch or fixed bed adsorption processes for wastewater treatment. Ind. Eng. Chem. Res., 54(34): 8579-8586. https://doi.org/10.1021/acs.iecr.5b02350

Dwivedi, CP., Sahu, JN., Mohanty, CR., Mohan, BR., and Meikap, BC. 2008. Column performance of granular activated carbon packed bed for Pb (II) removal. Journal of hazardous materials, 156(1-3): 596–603. https://doi.org/10.1016/j.jhazmat.2007.12.097

Figueiredo, JL., Pereira, MFR., Freitas, MMA., and Órfão, JJM. 1999. Modification of the surface chemistry of activated carbons. Carbon, 37(9): 1379-1389. https://doi.org/10.1016/S0008-6223(98)00333-9

Fu, F. and Wang, Q. 2011. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 92(3): 407–418. https://doi.org/10.1016/j.jenvman.2010.11.011

Hargreaves, AJ., Constantino, C., and Dotro, G. 2018. Fate and removal of metals in municipal wastewater treatment: a review. Environmental Technology Reviews, 7(1): 1–18. https://doi.org/10.1080/21622515.2017.1423398

Ibrahim, UF., Adamu, KM., Mohammed, SSD., Chukwu, MN., and Mabekoje, OO. 2024. Bioremediation of Selected Heavy Metals from Industrial Influent Collected at Wupa Wastewater Treatment Plant, Abuja. Nile Journal of Engineering and Applied Science, 2(1): 212–223. http://dx.doi.org/10.5455/NJEAS.193825

Juela, D., Vera, M., Cruzat, C., and Alvarez, X. 2021. Adsorption properties of sugarcane bagasse and corn cob for sulfamethoxazole removal in a fixed-bed column. Sustain Environ Res, 3: 27. https://doi.org/10.1186/s42834-021-00102-x

Kargol, AK., Burrell, SR., Chakraborty, I., and Gough, HL. 2023. Synthetic wastewater prepared from readily available materials: Characteristics and economics. PLOS Water, 2 (9): e0000178. https://doi.org/10.1371/journal.pwat.0000178

Lim, AP. and Aris, AZ. 2014. Continuous fixed-bed column study and adsorption modeling: Removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons. Biochemical Engineering Journal, 87: 50–61. https://doi.org/10.1016/j.bej.2014.03.019

Mahlalela, LC., Ngila, JC. and Dlamini, LN. (2017): Monitoring the fate and behavior of TiO_2 nanoparticles: Simulated in a WWTP with industrial dye-stuff effluent according to OECD 303A. Journal of Environmental Science and Health, Part A, *52*(8): 794–803. https://doi.org/10.1080/10934529.2017.1305176

Malik, DS., Jain, CK., and Yadav, AK. 2018. Heavy metal removal by fixed-bed column–A review. ChemBioEng Reviews, 5(3): 173–179. https://doi.org/10.1002/cben.201700018

Mani, SK. and Bhandari, R. 2022. Efficient fluoride removal by a fixed-bed column of self-assembled Zr(IV)-, Fe(III)-, Cu(II)-complexed polyvinyl alcohol hydrogel beads. ACS Omega, 7(17): 15048–15063. https://doi.org/10.1021/acsomega.2c00834

Mohan, D., Sarswat, A., Singh, VK., Alexandre-Franco, M., & Pittman Jr., CU. 2011. Development of magnetic activated carbon from Almond shells for trinitrophenol removal from water. Chemical Engineering Journal, 172(2–3): 1111–1125. https://doi.org/10.1016/j.cej.2011.06.054

NESREA 2009. S.I. No. 28: National environmental (sanitation and wastes control) regulations. Federal Republic of Nigeria Official Gazette. https://faolex.fao.org/docs/pdf/nig204466.pdf

Nguyen, TD., Phan, NH., Do, MH., and Ngo, KT. 2011. Magnetic Fe_2MO_4 (M: Fe, Mn) activated carbons: Fabrication, characterization and heterogeneous Fenton oxidation of methyl orange. Journal of Hazardous Materials, 185(2–3): 653-661. https://doi.org/10.1016/j.jhazmat.2010.09.068

O'Flaherty, E. and Gray, NF. 2013. A comparative analysis of the characteristics of a range of real and synthetic wastewaters. Environ Sci Pollut Res, 20: 8813–8830. https://doi.org/10.1007/s11356-013-1863-y

OECD. 2001. OECD guideline for the testing of chemicals: Simulation test - Aerobic sewage treatment: 303A: Activated sludge units-303B: Biofilms. Paris, France: OECD Publishing. https://doi.org/10.1787/9789264070424-en

Patel, H. 2019. Fixed-bed column adsorption study: A comprehensive review. Appl Water Sci, 9: 45. https://doi.org/10.1007/s13201-019-0927-7

Patel, H. 2020. Batch and continuous fixed bed adsorption of heavy metals removal using activated charcoal from neem (*Azadirachta indica*) leaf powder. Scientific Reports, 10(1): 16895. https://doi.org/10.1038/s41598-020-72583-6

Patel, H. 2022. Comparison of batch and fixed bed column adsorption: a critical review. Int. J. Environ. Sci. Technol., 19: 10409–10426. https://doi.org/10.1007/s13762-021-03492-y

Rajandran, P., Masngut, N., Manas, NHA., Azelee, NIW., Fuzi, SFZM., and Bunyamin, MAH. 2025. Fixed-bed adsorption for industrial wastewater purification: An in-depth review. Int. J. Environ. Sci. Technol., 22: 3943–3964. https://doi.org/10.1007/s13762-024-06034-4

Ronda, A., Martín-Lara, MA., Osegueda, O., Castillo, V., and Blázquez, G. 2018. Scale-up of a packed bed column for wastewater treatment. Water Sci Technol, 77(5): 1386–1396. https://doi.org/10.2166/wst.2018.020

Rout, PR., Bhunia, P., and Dash, RR. 2017. Evaluation of kinetic and statistical models for predicting breakthrough curves of phosphate removal using dolochar-packed columns. Journal of Water Process Engineering, 17: 168–180. https://doi.org/10.1016/j.jwpe.2017.04.003

Ruthiraan, M., Mubarak, NM., Abdullah, EC., Khalid, M., Nizamuddin, S., Walvekar, R., and Rao, R. 2019. An overview of magnetic material: Preparation and adsorption removal of heavy metals from wastewater. In Abd-Elsalam, K., Mohamed, M. and Prasad, R. (eds), Magnetic nanostructures, pp. 209–243. Springer, Cham. https://doi.org/10.1007/978-3-030-16439-3_8

Shahbazi, A., Younesi, H., and Badiei, A. 2013. Batch and fixed-bed column adsorption of Cu(II), Pb(II) and Cd(II) from aqueous solution onto functionalised SBA-15 mesoporous silica. The Canadian Journal of Chemical Engineering, 91(4): 739–750. https://doi.org/10.1002/cjce.21691

Soares, SF., Fernandes, T., Trindade, TT., and Daniel-da-Silva, AL. 2018. Surface engineered magnetic biosorbents for water treatment. In: Crini, G., Lichtfouse, E. (eds), Green Adsorbents for Pollutant Removal: Environmental Chemistry for a Sustainable World, vol 18. Springer, Cham. https://doi.org/10.1007/978-3-319-92111-2_9

Sylwan, I. and Thorin, E. 2021. Removal of heavy metals during primary treatment of municipal wastewater and possibilities of enhanced removal: A review. Water, 13(8): 1121. https://doi.org/10.3390/w13081121

Taty-Costodes, VC., Fauduet, H., Porte, C., and Ho, YS. 2005. Removal of lead (II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust: Adsorption on a fixed-bed column. Journal of Hazardous Materials, 123(1-3): 135–144. https://doi.org/10.1016/j.jhazmat.2005.03.032

Tchounwou, PB., Yedjou, CG., Patlolla, AK., and Sutton, DJ. 2012. Heavy metal toxicity and the environment. In Luch, A. (eds), Molecular, clinical and environmental toxicology, pp. 133–164). Springer, Basel. https://doi.org/10.1007/978-3-7643-8340-4_6

Yi, Y., Huang, Z., Lu, B., Xian, J., Tsang, EP., Cheng, W., Fang, J., and Fang, Z. 2020. Magnetic biochar for environmental remediation: A review. Bioresource Technology, 298: 122468. https://doi.org/10.1016/j.biortech.2019.122468

Zhang, M., Gao, B., Varnoosfaderani, S., Hebard, A., Yao, Y., and Inyang, M. 2013. Preparation and characterization of a novel magnetic biochar for arsenic removal. Bioresource Technology, 130: 457–462. https://doi.org/10.1016/j.biortech.2012.11.132