



Scaling up biochar based remediation: Continuous column adsorption of toxic elements from oil sands wastewater and sequential valorization of spent biochar in cement

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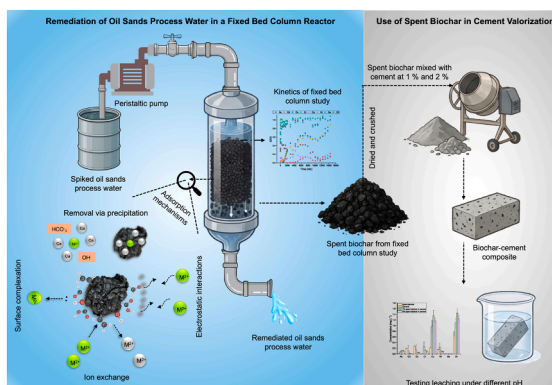
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HIGHLIGHTS

- Fixed bed biochar columns remove co-occurring toxic metals from oil sands water.
- Metal uptake follows $\text{Cd} > \text{Co} > \text{Ni} > \text{Zn}$; copper limited by dissolved organic matter.
- Empty bed contact time is 17–29 min as column scale-up parameter.
- Kinetic models fail for oxyanions; Thomas and Yoon-Nelson fit cationic metals.
- Treatment cost falls 84% by run 100; cement valorization saves CAD 169/kg at scale.

GRAPHICAL ABSTRACT



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ABSTRACT

This study examined simultaneous removal of potentially toxic elements from spiked oil sands process affected water, using canola straw biochar in fixed bed columns. Elements were arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se), and zinc (Zn). Adsorption hierarchy ($\text{Cd} > \text{Co} > \text{Ni} > \text{Zn}$) was consistent with alkalinity governing selectivity. Under optimal conditions (2 mL min^{-1} , 12 cm bed depth, 240 h), maximum equilibrium adsorption capacities 0.279 , 0.210 , 0.126 , 0.104 mg g^{-1} were for Cd, Co, Ni, Zn, respectively. As, Cr, and Se uptake was negligible, consistent with electrostatic repulsion; Cu adsorption was limited by complexation with dissolved organic matter. A 17.2–29.4 min empty bed contact time maximized Cd and Co service time. Thomas and Yoon-Nelson models captured breakthrough behaviour for Cd, Co, and Ni, not oxyanions. A techno-economic analysis showed per litre treatment costs declined 84% (CAD 17.80–2.65). Cement valorization avoided CAD 0.375 kg^{-1} of spent biochar, yielding 168.75 savings over 150 runs across 3 columns at industrial scale. Incorporating spent biochar into cement at 1–2% (w/w) suppressed leaching of most potentially toxic elements; Cr leaching increased in cement treatments, consistent with release from cement, supporting a circular end-of-life pathway for spent biochar.

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1. Introduction

Global industrial expansion and exploitation of unconventional energy reserves have intensified natural resource extraction activities worldwide. This has driven expansion of surface mining and bitumen refining activities, particularly within unconventional oil reservoirs [1]. A major environmental consequence is mobilization of potentially toxic elements (PTEs) into local aquatic and terrestrial ecosystems, driven primarily by anthropogenic pathways such as industrial emissions, mine tailings, waste deposits, coal combustion, and agricultural chemical application [2]. Since elemental PTEs cannot be biodegraded or chemically destroyed, they persist indefinitely and bioaccumulate across multiple trophic levels, triggering overproduction of reactive oxygen species that causes systemic physiological disruption, chronic organ toxicity, and irreversible ecological imbalance [3]. This multi-trophic hazard is widespread, with contaminated waste streams documented across diverse industrial effluents, including mining drainage, pharmaceutical manufacturing waste, and fossil fuel processing byproducts [2]. Among these large-scale industrial sources, oil sands process affected water (OSPW) represents a large and highly complex wastewater stream that compounds elemental toxicity with organic contaminants, magnifying the global remediation challenge [4].

The oil sands of northern Alberta, Canada, constitute the largest global oil sands deposit and a major economic resource for the Canadian energy sector. Petroleum extraction from bituminous sediment requires addition of hot water, generating OSPW, which is toxic to organisms. OSPW is stored in large reservoirs called tailings ponds, which collectively contain more than one billion litres of chemically complex, spatially varied toxic mixtures [5]. Reclamation of these ponds could take 15–70 years, underscoring the urgency of developing effective treatment technologies [6]. Most OSPW research has focused on organic contaminants such as naphthenic acids, with little emphasis on the inorganic fraction (particularly PTEs such as As, Cd, Cr, Co, Ni, Zn) [7]. These PTEs occur at ecologically relevant concentrations and have been associated with bioaccumulation in aquatic organisms and metal concentrations in wildlife.

Various physicochemical and biological treatments for OSPW include advanced oxidation, constructed wetlands, and phytoremediation. While native wetland plants have shown metal removal efficiencies of 74–87% for As, Cr, and Cd [7], phytoremediation remains limited by scalability, selectivity, and cold climate. Biochar is a carbonaceous material produced by biomass pyrolysis under limited oxygen, offering a low-cost, renewable adsorbent for PTE remediation, soil improvement, and carbon sequestration [8]. Its large surface area, porous structure, and surface functional groups facilitate PTE adsorption via ion exchange, complexation, electrostatic attraction, and precipitation [9]. Feedstock materials and pyrolysis conditions significantly influence biochar sorption capacity, underscoring the importance of selecting and testing abundant and economically accessible feedstocks to enable large-scale deployment. In Alberta, canola straw is generated in vast quantities as a low-value agricultural byproduct, offering a suitable option as a feedstock for biochar. Beyond cost, its use valorizes underutilized biomass while providing a regionally relevant remediation tool for organic and inorganic contaminants in water systems affected by energy industry operations [10,11].

Despite the proliferating body of literature on biochar for PTE remediation, critical gaps limit its practical, scalable application. Most studies focus on elimination of a single pollutant, whereas real aquatic environments contain various contaminants that are changeable and complex. Thus, there is a need to investigate simultaneous treatment of multiple contaminants and selective adsorption of specific elements by biochar based materials [12]. Most published studies were conducted in synthetic, single metal aqueous solutions under idealized batch conditions, which fail to capture competitive adsorption dynamics of complex industrial matrices where co-existing ions, organic compounds, and elevated ionic strength can substantially suppress metal uptake [13].

Fixed bed column systems, which better approximate continuous flow engineering scenarios and are more directly transferable to industrial applications, remain underrepresented in the literature relative to batch studies [14]. End-of-life management of metal laden spent biochar represents a significant but frequently overlooked challenge. Where desorption is thermodynamically unfavourable or economically nonviable, responsible valorization of spent biochar is essential to prevent secondary contamination and to justify overall sustainability of the remediation strategy.

One potential valorization pathway is incorporation of spent biochar into cementitious materials. Biochar's porous nature and highly functional surface impart compatibility with cement matrices, providing nucleation sites for hydration reactions and value added properties such as humidity regulation and improved microstructure [15]. Integrating biochar into cementitious composites supports a sustainable approach by valorizing waste derived material, reducing net CO₂ emissions of construction products, and displacing a portion of carbon intensive cement inputs [16]. Application of metal loaded spent biochar in cement thus addresses the post-adsorption management limitation and the need for multi-purpose use of biochar to enhance its economic feasibility, a prerequisite for scaling up biochar based remediation systems [17].

This research addresses key limitations of biochar based remediation by investigating simultaneous adsorption of eight PTEs from real OSPW, an industrially generated water stream where competing ions, dissolved organics, and elevated ionic strength reflect conditions that synthetic systems cannot replicate. This captures competitive interactions and preferential adsorption dynamics critical for practical remediation design. End-of-life valorization is evaluated by incorporating metal laden spent CSB into cement pastes to assess PTE stabilization and leaching suppression. Together, these components form a scale relevant framework advancing biochar based water treatment toward practical deployment.

2. Materials and Methods

Supplementary materials provide details on OSPW collection and spiking procedure (S1); chemical characterization, including nutrient, organic and inorganic matter, and water quality parameters (S2); and analytical methods for dissolved PTEs using ICP-OES (S3). Background PTE concentrations in the collected OSPW were below detection limits for six of the eight target elements; OSPW was therefore spiked with Cd, Co, Ni, Zn, As, Cr, Cu, and Se to concentrations relative to Canadian Council of Ministers of the Environment (CCME) guideline values for each element, enabling quantifiable breakthrough within practical column run times (Tables S1, S2).

2.1. Biochar production and characterization

Biochar was produced from canola straw through controlled pyrolysis. The feedstock was based on previous research that found crop straw biochars, such as canola, performed better than sawdust and manure pellet biochars in adsorption capacity and metal removal efficiency [10, 18]. The biochar was produced at an industrial facility using dried canola straw biomass at 450–500 °C. Canola straw biochar (CSB) physical and chemical properties were characterized (S4). Functional groups were analyzed using Fourier transform infrared spectroscopy (FTIR), surface chemistry and elemental composition using x-ray photoelectron spectroscopy (XPS), surface area and pore structure using nitrogen (N₂) and carbon dioxide (CO₂) adsorption-desorption isotherms with an Anton Paar Autosorb iQ analyzer, and crystalline structure and mineral phases before and after adsorption using a Bruker D8 DISCOVER Plus X-ray diffractometer.

2.2. Fixed bed column adsorption experiments

Detailed design, fixed bed column preparation, and rationale for

column materials, flow rate, and bed depth are provided (S5). Column experiments were conducted in two phases. The first phase tested CSB feasibility as an adsorbent in the column system, using a flow rate of 2 mL min^{-1} and a bed depth of 12 cm. Sampling was at 0, 15, 30, and 45 mins and 1, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 48, 60, 72, 84, 96, 108, 120, 132, 144, 156, 168, 180, 192, 204, 216, 228, and 240 h after experiment initiation. To prevent pump overheating during extended operation, the 12 cm bed depth, 2 mL min^{-1} column was run for 120 h of continuous flow, followed by a single 12 h rest period during which no flow occurred, then resumed for a further 120 h of continuous flow. All reported experimental times represent cumulative pump-on flow time; the total clock time elapsed, including the 12 h rest, was 252 h. In the second phase, 4 and 6 mL min^{-1} flow rates and 2 and 7 cm bed depths were tested. Sampling was at 0, 15, 30, and 45 mins and 1, 3, 6, 9, 12, 15, 18, 21, 24, 27, and 30 h. Sampling and analysis were similar to those of batch adsorption experiments. All experiments were conducted in the laboratory at room temperature ($\sim 22^\circ\text{C}$) with three replicates.

2.3. Kinetics of fixed bed column experiments

Fixed bed column adsorption experiment kinetics were analyzed by fitting breakthrough data to Bohart-Adams, Thomas, and Yoon-Nelson models. The linearized form of these models is provided in Eqs. 1, 2, and 3, respectively.

$$\text{Bohart - Adams : } \ln \left(\frac{C_t}{C_0} \right) = K_{BA} C_0 t - K_{BA} N_0 \left(\frac{z}{v} \right) \quad (1)$$

$$\text{Thomas : } \ln \left(\frac{C_t}{C_0} - 1 \right) = K_{Th} q_0 \left(\frac{m}{Q} \right) - K_{Th} C_0 t \quad (2)$$

$$\text{Yoon - Nelson : } \ln \left(\frac{C_t}{C_0 - C_t} \right) = K_{YN} t - K_{YN} \tau \quad (3)$$

C_0 (mg L^{-1}) and C_t (mg L^{-1}) represent influent and effluent concentrations of the solute at time t (min), respectively. For the Bohart-Adams model, K_{BA} ($\text{L mg}^{-1} \text{min}^{-1}$) is rate constant, N_0 (mg L^{-1}) is saturation concentration, z (cm) is bed depth, and v (cm min^{-1}) is superficial velocity of fluid through the bed. Superficial velocity was calculated as the ratio of flow rate to column cross-sectional area. For the Thomas model, K_{Th} ($\text{mL min}^{-1} \text{mg}^{-1}$) is Thomas rate constant, q_0 (mg g^{-1}) is maximum solid phase concentration (theoretical adsorption capacity), m (g) is adsorbent mass, and Q (mL min^{-1}) is volumetric flow rate. For the Yoon-Nelson model, K_{YN} (min^{-1}) is rate constant, and τ (min) is time for 50% breakthrough of adsorbate. Detailed definition and significance of constants associated with these models are in the referenced literature [19].

Impact of two operational parameters (bed depth, flow rate) on kinetic behaviour of all 8 PTEs was evaluated. Quality of fit to these models was assessed using adjusted R^2 (Adj. R^2), Pearson correlation coefficient (r), root mean square error (RMSE), normalized RMSE (NRMSE), residual sum of squares (RSS), and p -values, collectively providing a comprehensive evaluation of statistical significance and predictive accuracy of each model fit.

2.4. Preparation and curing of biochar amended cement pellets

Following the column experiment, CSB was recovered from the column and oven dried overnight at 85°C to remove residual water content. The dried biochar was stored in airtight glass vials at room temperature prior to use. General use limestone cement (hereafter cement) was the cementitious matrix. Cylindrical silicone moulds were used for casting, and three biochar amendment levels were prepared: 0 (unamended control), 1, and 2% (w/w). For each treatment, biochar and cement were weighed and combined in a plastic container. Dry constituents were mixed thoroughly prior to adding deionized water at a water-to-solid ratio of 0.5 (50 mL per 100 g of dry mixture). The

resulting paste was mixed continuously until a homogeneous consistency was achieved. To minimize air entrapment, 5 mL of each cement paste was transferred into a syringe and tapped 50 times before casting into silicone moulds.

Following casting, moulds were dropped vertically from a height of 5 cm onto a firm surface 20 times to further consolidate the paste and expel residual air bubbles. Twelve cylindrical pellets were cast per treatment, yielding a total of 36 specimens across all three concentrations. The cast specimens were wrapped in polyethylene film and set at room temperature (22°C) for 48 h. Following demoulding, pellets were transferred to a sealed curing chamber at 20°C and greater than 95% relative humidity for 7 days, in accordance with ASTM C192 standard protocols for laboratory preparation and curing of cementitious specimens. Temperature and relative humidity in the chamber were continuously monitored using calibrated sensors to ensure consistent conditions. Upon completion of curing, the pellets were removed from the chamber and immediately used for leaching experiments.

2.5. Cement leaching experiments

Leaching experiments were conducted to evaluate the potential release of adsorbed PTEs from biochar surfaces and biochar amended cement matrices under varying pH. Post-adsorption CSB and biochar amended cement pellets at 1 and 2% (w/w) were assessed. Leaching solutions at pH 4, 7, and 10 were prepared from distilled water adjusted with 0.1 M HCl or 0.1 M NaOH as appropriate. One cement pellet was placed in each container with a reaction volume of 30 mL. Experiments were conducted in triplicate over 96 h at room temperature; containers were manually agitated daily to maintain contact between the leaching solution and sample. After 96 h, the leachate was sampled, passed through $0.45 \mu\text{m}$ membrane filters to remove particulates, transferred to 15 mL polypropylene Falcon tubes, then preserved with concentrated HNO_3 .

To evaluate potentially toxic elements desorption behaviour under acidic conditions representative of a real desorption scenario, all sample types were exposed to 0.5 M HCl for 15 min with a reaction volume of 30 mL. Unamended cement pellets were included following unexpectedly elevated As and Cr concentrations in biochar amended cement, to distinguish contribution of the cementitious matrix from that of the biochar. Leachate from the HCl desorption experiments was collected, filtered, and preserved as described above. Unamended cement pellets (0% biochar) were included as a control for the acid dissolution experiment only; cement only leaching was not evaluated at pH 4, 7, or 10, and PTE contributions from the cement matrix under these conditions are therefore inferred rather than directly measured. All leachate samples were analyzed for As, Cd, Cu, Co, Cr, Ni, Se, and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES) (S3).

3. Results and Discussion

Spiked OSPW was slightly alkaline (pH 8.4), with high buffering capacity (total alkalinity 210 mg L^{-1} as CaCO_3), elevated electrical conductivity ($1300 \mu\text{S cm}^{-1}$), dissolved organic carbon (17.67 mg L^{-1}), naphthenic acids (14.33 mg L^{-1}), and dominant inorganic anions including sulphate (390 mg L^{-1}) and bicarbonate (260 mg L^{-1}) (Tables S1-S3). These geochemical conditions influence PTE adsorption behaviour on biochar and are considered in results interpreting (S2).

3.1. Flow and metal specific adsorption dynamics of CSB in OSPW

CSB adsorption performance varied across PTEs under maximum bed depth and minimum flow rate (Figure S1). Variation in breakthrough curves reflects adsorption affinity differences among PTEs towards CSB (underlying mechanisms in Section 3.3). Some breakthrough curves for cations showed asymmetry and incomplete saturation, indicating adsorption could involve a complex process and does not follow simple

Langmuir and Freundlich behaviour [20]. As, Cr, and Se showed early exhaustion points indicating weaker adsorption; Cd, Co, and Ni showed delayed initial breakthrough indicating more favourable adsorption.

CSB showed PTE specific adsorption capacities and breakthrough % across flow rates and bed depths (Table S4). CSB had higher adsorption capacity for Cd, Co, Ni, and Zn than As, Cr, and Se. For PTEs with poor adsorption, adsorption capacity at full saturation (100% breakthrough) was less than 0.01 mg g^{-1} . Cu had an early initial breakthrough and fluctuated within a narrow range, never reaching midpoint or exhaustion breakthrough, and with lower adsorption capacity. This suggests that while a fraction of Cu in OSPW has affinity for CSB surface sites, the remainder does not, likely reflecting the heterogeneous speciation of Cu in the complex organic rich matrix.

3.1.1. Effect of flow rate on breakthrough and adsorption efficiency

Breakthrough curves for each PTE showed earlier and more rapid breakthrough with increasing flow rate at initial, mid, and exhaustion points (Figure S2). For most PTEs, breakthrough curves became steeper at higher flow rates. Corresponding empty bed contact times decreased, reflecting progressively shorter contact times for adsorption. For As, Cd, Co, and Ni, impact of flow rate change was clear with higher flow rate leading to faster initial breakthrough, mid, and exhaustion points. For Cu and Cr, rate change had a less prominent impact, and Se did not follow any trend.

Steeper and more abrupt breakthrough curves at higher flow rates indicate a shift from equilibrium controlled adsorption to a kinetically limited regime, where reduced contact time prevents PTEs from fully diffusing into CSB pores and active sites before exiting the column [21, 22]. This has direct practical implications; a steeper breakthrough curve means the adsorbent reached operational exhaustion more rapidly, leaving potentially significant residual adsorption capacity unutilized.

CSB exhibited PTE specific adsorption capacity (q_e) trends across flow rates at 7 cm bed depth over the 30 h screening runs (Table S4). For Cd, equilibrium adsorption capacity (q_e) increased progressively with increased flow rates. Corresponding breakthrough % indicated even at the highest flow rate, a large portion of CSB capacity remained in use. CSB could have a higher number of active sites for Cd, hence the rate increase allowed more Cd to interact with and be adsorbed on the CSB surface in a given time. Cu q_e also increased with flow rate, although its breakthrough % remained low. Cd had significantly greater adsorption capacity than Cu across flow rates, suggesting biochar has active sites for Cu, but not all Cu in OSPW interacts with the CSB surface.

Zn adsorption capacity increased steadily as flow rate increased (Table S4). Its adsorption breakthrough curve showed C/C_0 decreased with time, then increased, suggesting Zn adsorption was initially limited but increased with time, consistent with non-monotonic adsorption behaviour. Prolonged exposure of CSB to OSPW might have modified Zn surface properties, increasing adsorption by improving pore accessibility and functional group availability. This could be attributed to an interaction with dissolved organic matter and biochar, and influence of dissolved organic matter on adsorption [23,24]. Adsorbed species could initially create favourable microenvironmental conditions for precipitation by inducing localized pH shifts or forming nucleation sites [25].

For Co and Ni, adsorption capacity increased, then decreased (Table S4). The lower adsorption capacity at highest flow rate was likely due to quicker saturation in breakthrough curves. At 4 mL min^{-1} biochar adsorption capacity was better utilized. At 6 mL min^{-1} breakthrough for Co reached 100% and for Ni 98%, indicating lower adsorption per unit mass of CSB. This suggests Co and Ni have a reasonable affinity towards CSB, with intensity less than that of Cd.

Statistical reliability of adsorptions was assessed with multiple descriptive parameters. Coefficients of variation (CV) for Cd were low across flow rates, reflecting high measurement consistency. Higher Cr and Se CVs indicated high relative variability in adsorption, attributable to very low absolute q_{total} values, where minor measurement noise contributes disproportionately to relative uncertainty. The 95%

confidence intervals and RMSE values further show Cd, Co, and Ni had the most reliable and reproducible adsorption behaviour across flow rates.

3.1.2. Effect of bed depth on breakthrough and adsorption efficiency

Breakthrough curves varied across bed depths at a 2 mL min^{-1} flow rate, reflecting a progressive increase in contact time with bed depth (Figure S3). For most PTEs, increasing bed depth led to longer times for initial, mid, and exhaustion breakthrough. Impact of bed depth was more pronounced for Cd, Co, and Ni than for As, Cr, and Se. A subtle trend of increasing bed depth leading to lower C/C_0 over a given time indicated improved adsorption performance. For Cu and Zn, no strong trend was observed; hence impact of bed depth remains inconclusive.

An increase in bed depth results in less steep and more gradual breakthrough curves. This improvement in adsorption can be attributed to longer residence time and increased contact surface area provided by the deeper bed, allowing for more effective interaction between PTEs and CSB. Increased contact time helps prevent a shift in adsorption from an equilibrium controlled regime to a kinetically limited one; therefore adsorption capacity of CSB is enhanced due to reduced dependency on time limitation. The greater bed depth implies a higher quantity of CSB, which means more available active sites for PTEs, thereby increasing saturation capacity.

Adsorption quantity and capacity increased with bed depth for most PTEs (Table S4). For Cd, total adsorption quantity (q_{total}) increased with bed depth across the 30 h screening runs (2, 7, and 12 cm), and increased further when the 12 cm bed depth condition was extended from 30 to 240 h, confirming a deeper bed provides more active sites and larger empty bed contact times. However, equilibrium adsorption capacity (q_e) did not follow a simple monotonic trend, but decreased then increased. The lower q_e at 7 than 2 cm reflects that at a flow rate of 2 mL min^{-1} , the 7 cm bed did not reach full saturation in the 30 h run time, and not all available active sites were engaged. The higher q_e at 240 h showed that given sufficient contact time, a deeper bed can considerably increase adsorption efficiency.

Impact of bed depth on total adsorption quantity followed a clear trend for Cd, Co, Ni, and Cu (Table S4). With increasing bed depth, more active CSB sites became available for adsorbing PTEs, total adsorption quantity increased, and breakthrough time was extended. These observations are consistent with previous research [26–28]. Breakthrough % provides additional insight; for Cd a very low breakthrough % at 12 cm indicated minimal breakthrough. Co and Ni were higher across bed depths at 30 h, suggesting the 7 cm bed depth under 2 mL min^{-1} flow rate provided the optimal balance between contact time and column utilization for these PTEs.

Zn demonstrated distinctly different behaviour (Table S4). When run time for the 12 cm column was extended from 30 to 240 h, total adsorption quantity and adsorption capacity both increased. This reiterates the hypothesis that a deeper bed may require longer exposure to OSPW, which could progressively activate CSB sites for Zn adsorption through surface modification by dissolved organic matter or precipitation driven nucleation mechanisms. The 240 h extended run included a single 12 h rest period after 120 h of flow, during which no advective flow occurred but the biochar bed remained in contact with residual pore water solute, allowing additional time for intraparticle diffusion toward local equilibrium. Upon flow resumption, previously equilibrated near surface sites may have been re-exposed to fresh influent, potentially contributing to the non-monotonic adsorption behaviour observed for Zn. Because the Thomas and Yoon-Nelson models assume continuous, steady state flow, this rest interval represents a deviation from ideal continuous operation pathway through the run; reported times and associated rate constants (K_{Th} , K_{YN} , τ) are based on cumulative flow time, and this should be considered when comparing kinetic parameters against studies using continuously operated columns.

Statistics support these interpretations (Table S4). CV for Cd was low across bed depths, confirming high reproducibility. For Co and Ni at

12 cm, a moderate CV and wider confidence intervals reflected variability, likely associated with complex adsorption dynamics at greater bed depths and longer runs. As, Cr, and Se continued to show high CVs across all bed depths, attributed to very low adsorption amounts, and consequently high relative measurement uncertainty.

3.2. Kinetic modeling of breakthrough behaviour

The Bohart-Adams, Thomas, and Yoon-Nelson models showed variable goodness-of-fit across PTEs and operational conditions, with acceptable fits primarily for Cd, Co, and Ni (Table S5–S8). The quality of model fit varied significantly across PTEs, operational conditions, and the model applied. Cd, Ni, and Co had consistently stronger fits, particularly at higher flow rates and greater bed depths, with Adj. R^2 values reaching 0.913–0.965 and statistically significant p-values under these conditions. As, Cr, Cu, Se, and Zn had poor fitting across most tested experimental conditions, including several negative Adj. R^2 . Negative Adj. R^2 indicates the fitted model performs worse than a simple horizontal mean line, confirming the complete inadequacy of these models for describing adsorption kinetics of these PTEs under the given conditions.

Several fitted parameters were physically unrealistic, including negative Thomas capacities for As, negative Bohart-Adams saturation capacities for Zn, and negative 50% breakthrough times for Se and Cr; mathematical artifacts that arise when a model is forced to fit data that violates its underlying assumptions and carry no physical meaning. A statistically significant p-value or converged model fit alone does not validate parameter relevance; physical plausibility must always be confirmed before mechanistic conclusions are drawn. These unrealistic values, combined with poor Adj. R^2 values indicate standard kinetic models are unsuitable for As, Cr, Cu, Se, and Zn under the tested conditions, likely because these mechanisms are not captured by the models [29]. Thomas and Yoon-Nelson had slightly better overall fits than Bohart-Adams for model performance across all PTEs and conditions. This advantage aligns with the Thomas and Yoon-Nelson models aiming to describe the entire breakthrough curve, whereas the Bohart-Adams model focuses primarily on its initial linear portion of the breakthrough curve [30,31].

Bed depth effects were examined for Ni and Cd for conditions with higher Adj. R^2 . For Ni, increasing bed depth from 2 to 12 cm at 2 mL min⁻¹ produced a progressive decline in the Thomas rate constant K_{Th} and an increase in maximum adsorption capacity q_0 , reflecting greater mass transfer opportunities and extended residence time from the deeper bed. For Cd, an acceptable model fit was only achieved at 2 mL min⁻¹ and 12 cm, where the Yoon-Nelson model yielded Adj. R^2 indicating a long service life and strong surface affinity. The Thomas q_0 further reflects a high theoretical loading capacity (Table S7). The progressive improvement in Ni model fit with bed depth corroborate this pattern, suggesting deeper beds enhance adsorption capacity and produce more regular, model conforming breakthrough profiles. This is consistent with greater residence time and mass transfer opportunities from deeper beds which allow adsorption to proceed gradually toward equilibrium, reflected in higher q_0 and τ values with declining K at greater depths [32].

For the influence of flow rate at 7 cm bed depth, trends were clear for Ni and Co. For Ni and Co K_{Th} increased with flow rate and q_0 decreased. At 6 mL min⁻¹ best fit for Co shifted to the Yoon-Nelson model with τ substantially shorter than for Cd at 2 mL min⁻¹ and 12 cm, reflecting Co's lower binding affinity relative to Cd under rapid flow conditions. These increasing rate constants and decreasing capacity parameters with increasing flow rate are consistent with expectations for fixed bed columns, as higher flow rates reduce residence time and prevent full diffusion of Co and Ni into internal pores of CSB. Progressive improvement in Adj. R^2 for Ni and Co at higher flow rates at 7 cm bed suggests faster surface kinetics at higher flow rates produce breakthrough profiles that conform more closely to simplified assumptions of these models,

where mass transfer limitations are less pronounced, and adsorption behaviour is more predictable.

Under 2 mL min⁻¹ flow and 12 cm bed depth, Ni had a theoretical Thomas adsorption capacity. Co exhibited q_0 values across tested flow rates at 7 cm bed depth, consistent with the range in the original analysis. An unexpected result was observed for Cr at 2 mL min⁻¹/12 cm, where the Thomas model achieved a relatively high Adj. R^2 with $q_0 = 130$ mg g⁻¹, despite Cr showing poor fits under other conditions. However, the associated RMSE was the highest among all well fitting model results, and Cr's overall breakthrough behaviour across other conditions remained poorly described, so this single apparent good fit should be interpreted cautiously.

The Bohart-Adams, Thomas, and Yoon-Nelson models failed to adequately describe adsorption kinetics for As, Cr, Cu, Se, and Zn, as evidenced by negative Adj. R^2 values, non-significant p-values, and physically impossible parameter estimates across most tested conditions. Acceptable fits were obtained for Cd, Co, and Ni under select operational conditions, with progressive improvement in Adj. R^2 for Ni and Co, highlighting sensitivity of model performance to experimental parameters such as flow rate and bed depth. Nevertheless, these models are built on simplified assumptions that do not fully capture complex reality, particularly in multi-component systems such as OSPW where competitive adsorption and multi-solute interactions can substantially alter breakthrough dynamics [33]. Model outputs should therefore be treated as complementary interpretive tools rather than definitive descriptors of adsorption behaviour, and kinetic parameters must always be evaluated alongside physical plausibility and experimental context before mechanistic conclusions are drawn.

To translate column model outputs into design parameters, service time to 10% breakthrough was plotted against empty bed contact time for PTEs achieving meaningful retention (Figure S4). Service time increased linearly with empty bed contact time for Cd and Co, with Cd showing a steeper slope indicative of intraparticle diffusion limited adsorption consistent with Adams-Bohart MTZ analysis. Cd service time varied with the regression equation predicting a 7 day service life at empty bed contact time of 43.6 min, providing a direct scale-up criterion. Ni broke through only at maximum empty bed contact time of 24 h, while Cu and Zn showed no meaningful retention, attributed to competitive displacement by Cd and Co. Oxyanion PTEs (As, Cr⁶⁺, Se) maintained $C/C_0 \geq 1$ throughout, confirming electrostatic repulsion at pH 8.4 and suggesting sequential treatment with anion selective media for complete OSPW remediation.

3.3. Adsorption mechanisms governing PTEs removal

Biochar clearly had different adsorption abilities for different PTEs. This is due to surface and chemical properties of PTEs, which influence their behaviour in OSPW and interactions with CSB. Evidence for understanding mechanisms of adsorption was obtained by analyzing changes in surface chemistry of CSB before and after adsorption (Fig. 1). Adsorption of PTEs onto CSB followed a multi-mechanism pathway, beginning with a rapid initial stage driven by electrostatic interactions and surface complexation, followed by slower processes including precipitation.

3.3.1. Surface complexation

Surface complexation is one of the primary mechanisms driving adsorption of PTEs on CSB. This becomes clear from the FTIR (Figure S5) and XPS (Fig. 2, Figure S6) spectral analysis of CSB before and after adsorption, which shows a change in band intensity and a slight shift of peak at 3050 cm⁻¹ associated with O-H stretching in alcohols and phenols (Figure S5a). Similarly, a weak peak at 1710 cm⁻¹ representing C=O in carboxylic acids was present in CSB before adsorption, while no such peak was identified post-adsorption [34]. Disappearance of this peak indicates consumption or transformation of carboxylic groups during adsorption, consistent with their direct involvement in metal

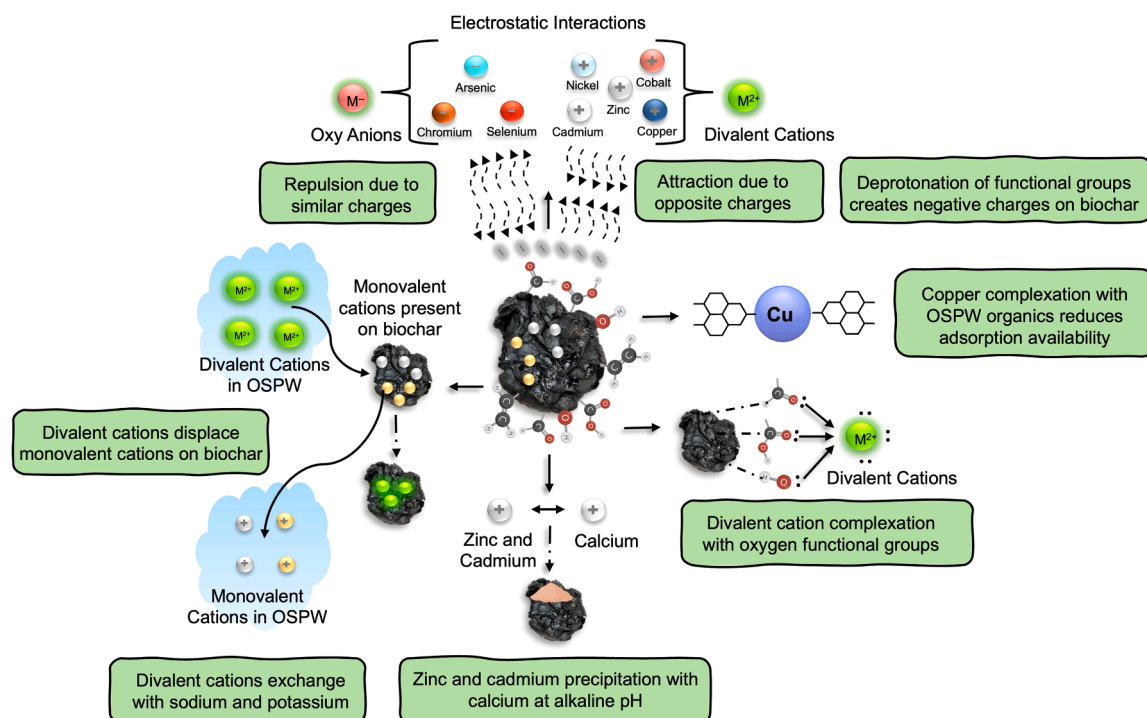


Fig. 1. Schematic illustration of potentially toxic elements adsorption mechanisms on biochar through electrostatic interactions, ion exchange processes, surface complexation, and precipitation reactions.

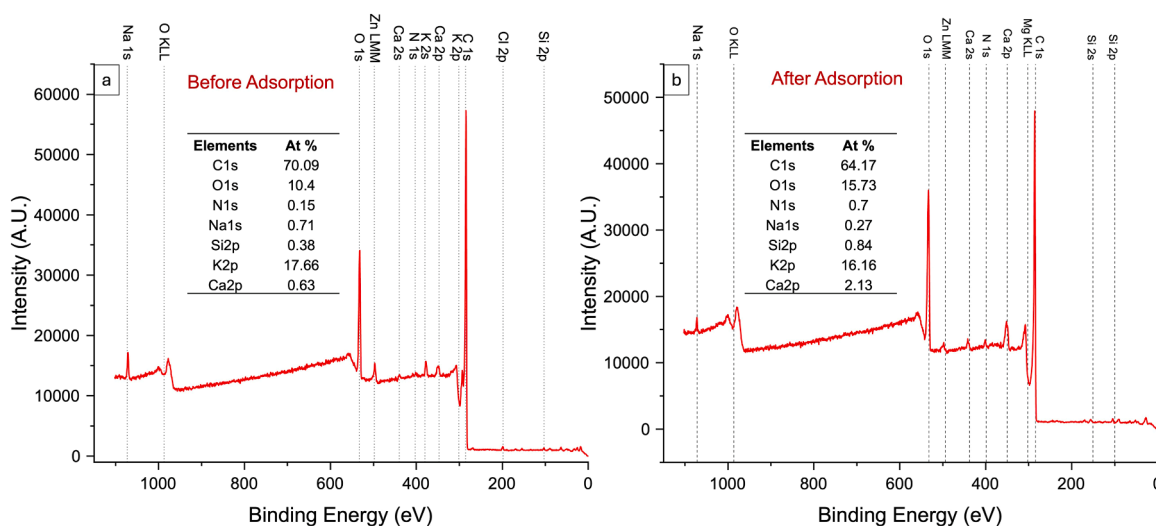


Fig. 2. X-ray photoelectron spectroscopy wide spectral scan analysis of canola straw biochar for potentially toxic elements adsorption studies; (a) elemental composition before adsorption, (b) elemental composition after adsorption.

coordination. A unique peak at 426 cm^{-1} in the post-adsorption FTIR spectrum (Figure S5b) can be assigned to metal-oxygen stretching vibrations [18], indicating direct interaction of oxygen functional groups in CSB with PTEs and formation of surface complexes. The peak at 555 cm^{-1} in the post-adsorption spectrum is attributed to C-Cl stretching (Figure S5b), which may reflect interaction of chloride containing species from OSPW with the biochar surface and should not be conflated with metal-oxygen stretching.

The high resolution spectra of C1s and O1s provide further corroborating evidence for involvement of carboxyl and ester groups in adsorption (Figures S6a-S6d). C=O and O-C=O peaks in the C1s spectra representing carboxylic acids and esters, shifted to a higher binding energy post-adsorption (Figure S6b). This binding energy shift is

characteristic of electron density redistribution from metal coordination with these functional groups, confirming their direct involvement in surface complexation. The O1s spectra of CSB before and after adsorption further confirm involvement of oxygen containing functional groups (Figures S6c, S6d). Deconvolution yielded distinct peaks, representing C=O in quinones and carbonyls, attributed to C-OH (aliphatic hydroxyl) groups, and corresponding to O=C-OR carboxylic anhydride or ester groups. After adsorption, intensity of the O1s spectra increased significantly, with a new peak corresponding to physisorbed or loosely bound water (Figure S6d), consistent with the presence of hydrated metal-ion complexes at the biochar surface, where water molecules remain associated with adsorbed metal ions in their inner or outer coordination spheres. The increase in overall O1s intensity post-

adsorption, further supported by the increase in O1s atomic % in the wide scan XPS (Fig. 2), confirms enrichment of oxygen associated species on CSB surface following PTE adsorption [35].

The aromatic graphitic structure of CSB can participate in metal coordination through π -electron interactions. Peaks at 1590 and 1440 cm^{-1} represent C=C bonds in the aromatic graphitic structure and CH_3/CH_2 groups in aromatic rings of CSB, respectively. Their intensities differed before and after adsorption (Figure S5a), indicating involvement in adsorption [36]. Peaks associated with aromatic out-of-plane C-H bending at 877, 827, and 762 cm^{-1} showed intensity differences pre-adsorption and post-adsorption [37], suggesting structural reorganization of aromatic domains during surface complexation, possibly from monodentate complexation, bidentate chelation, and hydroxyl coordination [38]. Gas sorption analysis provides structural support for these findings, with CSB surface area nearly tripling after adsorption in OSPW. This suggests OSPW constituents progressively cleared occluded pore entrances during column operation, exposing additional active sites for surface complexation. Micropore structure and modal pore width remained unchanged, suggesting that metal ions did not permanently block internal pores and CSB maintained its structural integrity throughout the adsorption process.

3.3.2. Electrostatic interactions and precipitation

OSPW pH can play a crucial role in adsorption. For example, OSPW has an alkaline pH of 8.4, which promotes deprotonation of surface functional groups such as carboxyl and phenolic groups on CSB. This makes the CSB surface more negatively charged, promoting coulombic attraction between cationic PTEs and the CSB surface [39]. Anionic PTEs such as HAsO_4^{2-} , SeO_4^{2-} , and CrO_4^{2-} would experience electrostatic repulsion from the negatively charged surface at this pH, which is consistent with the observed low adsorption affinity of As, Se, and Cr on CSB.

Chemical composition of OSPW can also promote precipitation of PTEs onto the biochar surface. The OSPW's high bicarbonate content (260 mg L^{-1}) at alkaline pH favours metal precipitation as hydroxides or carbonates [40]. CSB can facilitate this by providing heterogeneous nucleation sites that lower activation energy required for precipitate formation. XRD analysis (Figure S7) offers indirect mineralogical evidence consistent with this mechanism, though it does not confirm it directly. Post-adsorption, the calcite signal intensified, suggesting divalent metals, particularly Cd and Zn, may have co-precipitated within a growing carbonate mineral framework at the OSPW alkaline pH. No distinct crystalline metal-carbonate peaks were detected, consistent with formation of poorly crystalline precipitates too small to be resolved by conventional XRD, though this absence of distinct peaks also means the XRD data alone cannot confirm carbonate co-precipitation. Cd and Zn are known to form stable carbonate precipitates (CdCO_3 , ZnCO_3), and given the high bicarbonate concentrations and alkaline pH of OSPW, precipitation is a plausible contributing mechanism to their removal, although this has not been directly confirmed through solution speciation or saturation index modelling. This interpretation is consistent with, though not independently confirmed by, the anomalous time dependent breakthrough behaviour of Zn (Section 3.1), where adsorption appeared to increase after an initial period, an observation that could reflect progressive surface precipitation, but which may also be explained by other time dependent surface processes. Direct confirmation of carbonate co-precipitation would require solution speciation or saturation index modelling (e.g., using OSPW geochemical data to calculate saturation indices for CdCO_3 and ZnCO_3), which was beyond the scope of the present study; the mechanisms proposed here should therefore be regarded as plausible interpretations consistent with the available FTIR, XPS, XRD, and surface area evidence rather than definitively established pathways.

3.3.3. Ion exchange

Ion exchange is known to play a role in adsorption. The XPS analysis

of the CSB before and after adsorption clearly demonstrates involvement of this mechanism (Figs. 2a-2b). Post-adsorption, the CSB spectral elemental composition demonstrated visible changes. After adsorption Na and K decreased, and Ca increased significantly, indicating preferential adsorption of divalent ions from OSPW onto the biochar surface, displacing the originally bound Na^+ and K^+ ions. In OSPW several other divalent cations are present, which would compete with Ca for binding sites in biochar. Smaller ionic radii, a higher electronegativity, and greater polarizability favour adsorption via cation-exchange. XRD analysis supports this mechanism, showing soluble potassium-bearing mineral phases on pristine CSB, including niter, sylvite, and arcanite, which dissolve during adsorption, releasing exchangeable K^+ and exposing previously inaccessible surface sites. Most PTE cations for this study have smaller ionic radii and higher electronegativity than Ca^{2+} ; thus, adsorption of Ca^{2+} indicates potential adsorption of these PTEs on the biochar surface [24]. Adsorption of PTEs on biochar followed a complex reaction mechanism (Fig. 5). Adsorption follows a rapid stage of electrostatic interactions and surface complexation, followed by ion exchange, precipitation, or physical adsorption.

3.4. Speciation and physicochemical controls on PTEs selectivity

Breakthrough and adsorption capacity data (Section 3.1) reveal a clear hierarchy of adsorption affinity of PTEs towards CSB. Each PTE adsorption preference is governed by a distinct combination of ionic speciation, hydration energy, solubility limits, ionic radius, hard-soft acid-base character, and liquid phase complexation affinity, with no single factor providing a complete explanation in isolation (Fig. 3). Cd demonstrated the most consistent and highest adsorption affinity across all tested conditions, with q_e up to 0.279 mg g^{-1} under the 240 h extended run and strong model fits. Cu demonstrated moderate but consistent adsorption affinity. Co and Ni showed good adsorption affinities, though lower than those of Cd. Cu demonstrated lower adsorption capacity ($q_e = 0.006\text{--}0.058 \text{ mg g}^{-1}$, spanning the 30 h runs and the 240 h extended run at 12 cm) relative to Co and Ni under most conditions. Zn showed high ultimate adsorption capacities at extended contact times, but its adsorption behaviour was highly time dependent and likely involved precipitation assisted mechanisms rather than direct surface affinity alone. Therefore, it cannot be straightforwardly related to the other cationic PTEs based on surface binding affinity. As, Se, and Cr had consistently low or negligible adsorption affinity across all conditions.

Solution pH plays a fundamental role in PTE speciation and CSB surface charge. At OSPW pH 8.4, cationic species such as Cd^{2+} , Zn^{2+} , Co^{2+} , and Ni^{2+} are electrostatically attracted to the deprotonated, negatively charged CSB surface, whereas As, Se, and Cr exist predominantly as oxyanions. Arsenate is predominantly present as HAsO_4^{2-} , given its pK_a values, placing pH 8.4 between the second and third dissociation steps. Selenate exists as SeO_4^{2-} above pH 2 and is therefore fully deprotonated at pH 8.4. Cr(VI) at pH 8.4 exists almost exclusively as CrO_4^{2-} , as HCrO_4^- ($\text{pK}_a = 6.49$) is the dominant Cr(VI) species only below pH ~ 6.5 . These anionic species are electrostatically repelled from the negatively charged CSB surface, the primary explanation for their consistently low adsorption affinity [41]. Cu^{2+} undergoes significant speciation changes at pH 8.4, with partial hydrolysis producing $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ species. These neutral or reduced charge species exhibit weaker electrostatic attraction to the negatively charged CSB surface than free Cu^{2+} , thereby reducing concentration of the adsorbable fraction available for surface complexation. According to the Irving-Williams series, Cu^{2+} has the highest complexation stability with dissolved organic ligands among these transition metals, suggesting that the highly organic OSPW matrix could act as a liquid phase chelator. We hypothesize that a fraction of Cu may be bound to soluble naphthenic acids and dissolved organic matter, which would reduce the fraction available to partition onto the solid biochar surface; however, this study did not directly measure Cu speciation or DOM-binding, and this

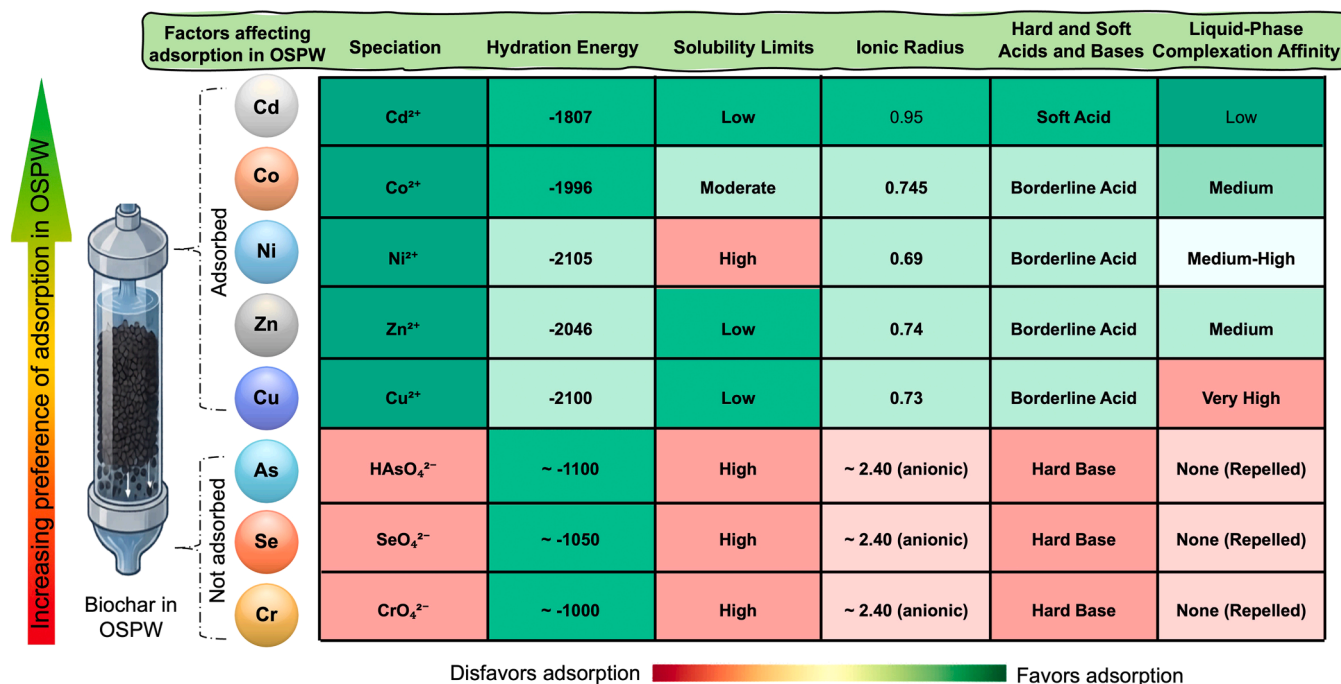


Fig. 3. Physicochemical factors governing preferential adsorption of potentially toxic elements on canola straw biochar in oil sands process affected water.

remains a plausible explanation rather than a confirmed mechanism. If correct, DOM complexation would represent an additional factor beyond Jahn-Teller distortion contributing to Cu's suppressed q_e . Direct confirmation would require Cu speciation analysis (e.g., via voltammetry or size-exclusion chromatography coupled with ICP-MS) or DOM-binding assays, which were beyond the scope of this study.

Affinity order among cationic PTEs is rationalized by hard and soft acid-base theory. Cd²⁺, as a soft acid, has affinity for hard oxygen donor functional groups (carboxyl, hydroxyl, carbonyl) and softer aromatic π -system of CSB, contributing to its superior and consistent adsorption [33]. Co²⁺ and Ni²⁺ are borderline to hard acids with good compatibility with the CSB oxygen donor rich surface; once bound, their regular octahedral coordination geometry confers kinetic stability on the resulting surface complexes. Cu²⁺, a borderline acid, has a greater affinity for N donor and mixed soft donor ligands that are less abundant on the CSB predominantly oxygen donor surface. The Jahn-Teller distortion of Cu²⁺ (d⁹ configuration) increases ligand exchange lability, rendering its surface complexes more susceptible to displacement by competing ions in the multicomponent OSPW matrix, further limiting its effective adsorption capacity relative to Co²⁺ and Ni²⁺.

PTEs with low hydration energies adsorb more readily as less energy is required to displace the hydration shell and enable direct coordination with surface functional groups [34]. Hydration energies of Ni²⁺ (-2105 kJ mol⁻¹) > Cu²⁺ (-2100 kJ mol⁻¹) > Zn²⁺ (-2046 kJ mol⁻¹) > Co²⁺ (-1996 kJ mol⁻¹) > Cd²⁺ (-1807 kJ mol⁻¹), consistent with Cd²⁺ showing highest adsorption affinity and Co²⁺ outperforming Cu²⁺ and Ni²⁺ despite stronger coordination chemistry. Since Cd²⁺ exhibits the lowest hydration energy penalty among these PTEs, it consequently has the smallest hydrated radius. This reduced steric bulk allows Cd²⁺ to diffuse more easily and more deeply into biochar's microporous network than ions such as Ni²⁺, which retain a bulky, tightly bound hydration sphere. For Ni²⁺, a strong crystal field stabilization energy stabilizes surface bound complexes once formed and produces a slow water exchange rate ($\sim 3 \times 10^4$ s⁻¹) that limits adsorption kinetics, consistent with the kinetically constrained breakthrough behaviour observed [36]. The superior performance of Cd²⁺ is further supported by its higher polarizability as a second row transition metal; its larger, more diffuse electron cloud enhances orbital overlap with surface donor atoms,

increasing the covalent character and strength of surface complexes relative to first row divalent cations.

The ionic potential (charge-to-radius ratio) provides an integrative descriptor of these competing effects. A moderate ionic potential optimizes adsorption; sufficient electrostatic attraction to the negatively charged surface without inducing excessive hydration that impedes direct binding. A very high ionic potential promotes tight hydration shell retention and stable hydroxo complex formation in solution at alkaline pH, while a very low ionic potential reduces electrostatic driving force. The adsorption hierarchy observed in this study reflects the net outcome of these interacting mechanisms (speciation, hard and soft acids and bases character, hydration energy, polarizability, ionic potential) operating simultaneously under specific conditions of the alkaline OSPW matrix, with no single factor providing a complete explanation in isolation.

3.5. Cement immobilization of spent biochar: leaching and disposal

Once biochar has been used to remove PTEs from water in a fixed bed column, it becomes a spent material carrying an adsorbed pollutant load, and its safe disposal becomes an important practical consideration. This study explored incorporating spent biochar into cement to immobilize retained PTEs and give the spent material a secondary use as a construction additive.

3.5.1. pH dependent PTE leaching from biochar-cement pellets

At pH 4, mixing spent biochar with cement at 1 and 2% loadings reduced leaching of As, Co, Cu, and Ni relative to spent biochar alone (Fig. 4b, Table S9). This is likely related to physical encapsulation of biochar particles within the cement matrix, which reduces their direct exposure to the leaching solution and limits release of adsorbed PTEs [42]. The alkaline buffering capacity of cement may further contribute by raising local pH around the material, which can encourage metal precipitation and surface retention within the matrix [43]. The 2% blend showed slightly lower leaching than the 1% blend for these elements, suggesting higher biochar content provides modestly better immobilization, although data variability means this difference should not be overstated. Cd leaching was below detection limits for all three

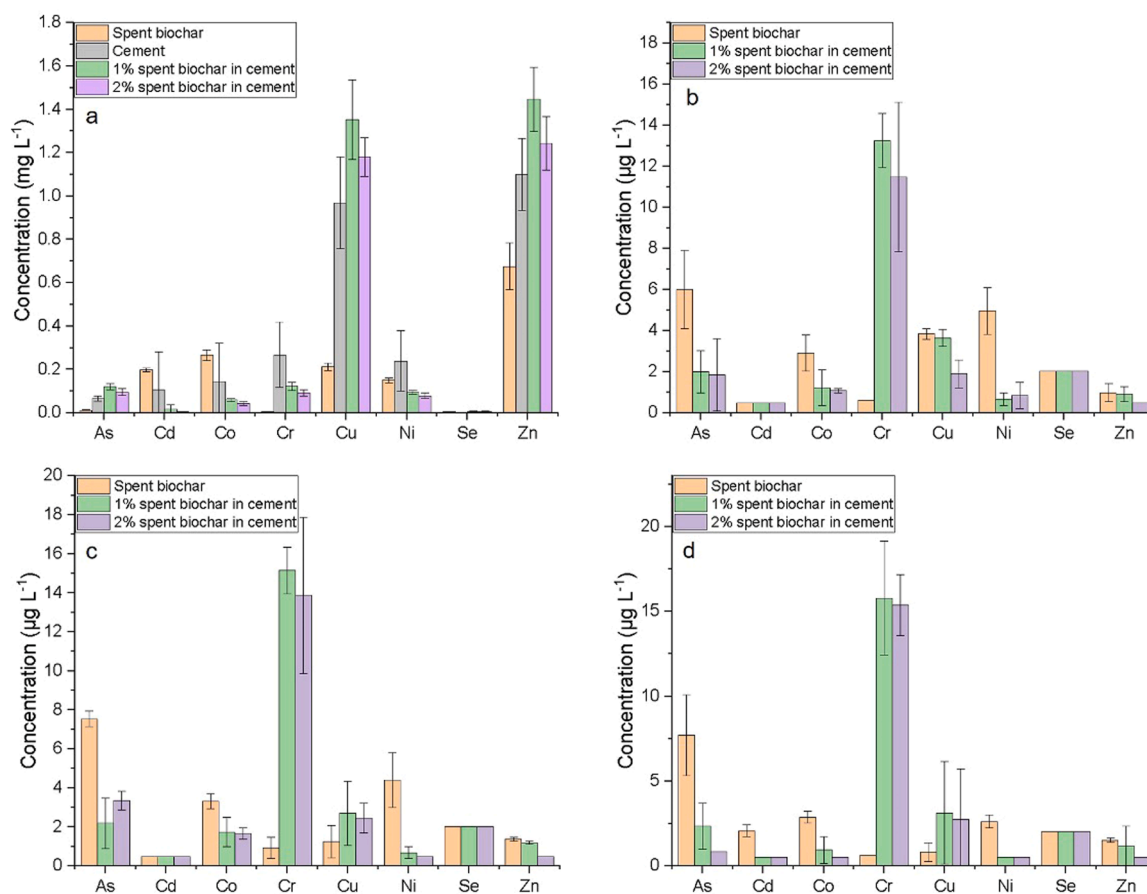


Fig. 4. Leaching concentrations of potentially toxic elements from spent biochar and spent biochar incorporated into cement at 1 and 2% (w/w) under pH 4, 7, and 10, and acid dissolution using 0.5 M HCl; (a) acid dissolution, (b) pH 4, (c) pH 7, and (d) pH 10.

treatments at pH 4, consistent with strong Cd adsorption observed during the column experiment, suggesting Cd was well retained in the composite. Se leaching was similarly low across all treatments and showed no clear difference between spent biochar and cement blends. This is consistent with the low to negligible adsorption of Se onto the biochar observed during the fixed bed column experiment, indicating that little Se was carried into the cement composite. The absence of any significant Se in the cement only control under acid dissolution (Fig. 4a) further suggests the cement matrix does not contribute meaningfully to Se in the leachate.

The most striking observation across all pH conditions was the consistently higher Cr leaching from biochar-cement blends than from spent biochar alone. At pH 4, Cr leached from 1 and 2% blends was higher than from spent biochar alone (Fig. 4b), with similar trends at pH 7 (Fig. 4c) and pH 10 (Fig. 4d). Since column experiments showed no meaningful Cr adsorption onto CSB, the cement matrix is the most plausible source of this Cr, consistent with the elevated Cr observed from the unamended cement control under acid dissolution (Section 3.5.2). Portland cement is known to contain trace amounts of Cr from raw clinker and kiln processing, and chromate species can remain soluble over a wide pH range, which would explain why this elevation persisted across a wide pH range [44]. This interpretation underscores the importance of accounting for inherent elemental composition of cement when evaluating PTE leaching from biochar-cement composites.

At pH 7, 1 and 2% blends produced broadly similar leaching profiles, with no clear differences between the biochar-cement composites for most PTEs (Fig. 4c). Both composites showed lower leaching of Co, As, and Ni relative to spent biochar alone. The 2% blend showed marginally lower Zn leaching than the 1% blend, although given the overlap in error bars, this observation alone is insufficient to draw a firm conclusion

about a dose dependent effect on Zn retention. At pH 10, the biochar-cement composites showed reduced leaching of As, Cd, Co, Ni, and Zn relative to spent biochar alone (Fig. 4d), and the 2% blend performed marginally better than the 1% for As and Zn. The lower leaching under alkaline conditions is consistent with the high pH environment that cement naturally creates, which tends to favour metal hydroxide precipitation [45]. Cr was elevated at pH 10 in cement blends, further indicating the cement is its source.

Across all pH conditions, absolute PTE concentrations in the leachate were low for all elements except Cr in the cement containing treatments. While a formal regulatory assessment is beyond the scope of this study, these concentrations are considerably lower than hazardous leachate thresholds commonly reported in the literature, which is encouraging from a preliminary safety perspective. That said, this study was conducted under controlled laboratory conditions over a limited duration, and longer-term leaching behaviour under field relevant conditions need to be assessed before stronger conclusions can be made. A limitation of this study is that cement only leaching was assessed only under acid dissolution (Section 3.5.2) and not at pH 4, 7, or 10; consequently, the relative contributions of the cement matrix versus the biochar to PTE leaching at these three pH conditions could not be directly isolated and are inferred from the acid dissolution control and column adsorption results.

3.5.2. Acid dissolution of biochar-cement composites

In the acid dissolution experiment the cement control leached notable amounts of Cu and Zn, with smaller detectable amounts of As, Cr, and Ni (Fig. 4a, Table S10), confirming the cement parent material carries its own intrinsic PTE load and serves as an important reference point when interpreting results from the composite materials. Under

acid dissolution, the 2% biochar-cement blend generally showed lower PTE leaching than the 1% blend. Since not all PTEs reached breakthrough during the column experiment, the spent biochar retained residual adsorption capacity at the point of incorporation, and additional biochar in the 2% blend may have continued to contribute to PTE retention through its remaining pore space and active surface sites. However, this interpretation should be treated with caution given data variability, and further work is needed to decouple respective contributions of the cement matrix and residual biochar capacity. Relative to spent biochar alone, biochar-cement blends showed reduced leaching of Cd, Co, and Ni, indicating the cement matrix meaningfully contributes to retaining these PTEs [46]. The higher Cu and Zn in the biochar-cement leachates are attributable to dissolution of the cement matrix, as demonstrated by the cement control, and should not be interpreted as failure of the biochar.

Incorporating spent biochar into cement at 1–2% (w/w) represents a viable approach for managing spent biochar after adsorption based water treatment, at least under the conditions tested. The cement matrix suppressed PTE leachability across a range of pHs, with overall leachate concentrations well below hazardous thresholds commonly reported in the literature, providing a preliminary basis for considering this a safe disposal route. Notably, Cr leaching from the cement blends highlights the importance of accounting for the cement's chemical composition, particularly in environmentally sensitive settings. Beyond safe disposal, this approach valorizes spent biochar as a cement additive, aligning with

material circularity principles, and may conceptually extend to other contaminant systems such as per and poly fluoroalkyl substances laden biochar, where high temperature destruction is the conventional, energy intensive alternative. Dedicated experimental validation would be required before such extensions can be justified. The findings reported here are best understood as a proof-of-concept supporting continued investigation into cement based immobilization as a scalable end-of-life strategy for spent biochar from water treatment.

3.6. Techno-economic analysis of CSB column treatment

A preliminary techno-economic analysis was conducted to evaluate the approximate cost trajectory of a CSB fixed bed column system across repeated operational cycles with 3 replicate columns and 28.8 L per column per run. Costs were classified into capital expenditure (CapEx) and operational expenditure (OpEx). CapEx comprised equipment, laboratory consumables, and setup, totalling $\approx$ CAD 1322, paid once at system commissioning (Fig. 5a). OpEx per column per 240 h run included labour, reagents, and consumables, biochar replenishment, and electricity for the peristaltic pump, totalling $\approx$ CAD 72 per column per run. Biochar was treated as a consumable replenished each run rather than a capital investment, avoiding double counting. At Run 1, the cumulative cost per litre of OSPW treated was $\approx$ CAD 18 L⁻¹, dominated by the 86% CapEx burden; by run 50, this declined by 84% to CAD 2.80 L⁻¹, and reached CAD 2.65 L⁻¹ by run 100, demonstrating rapid

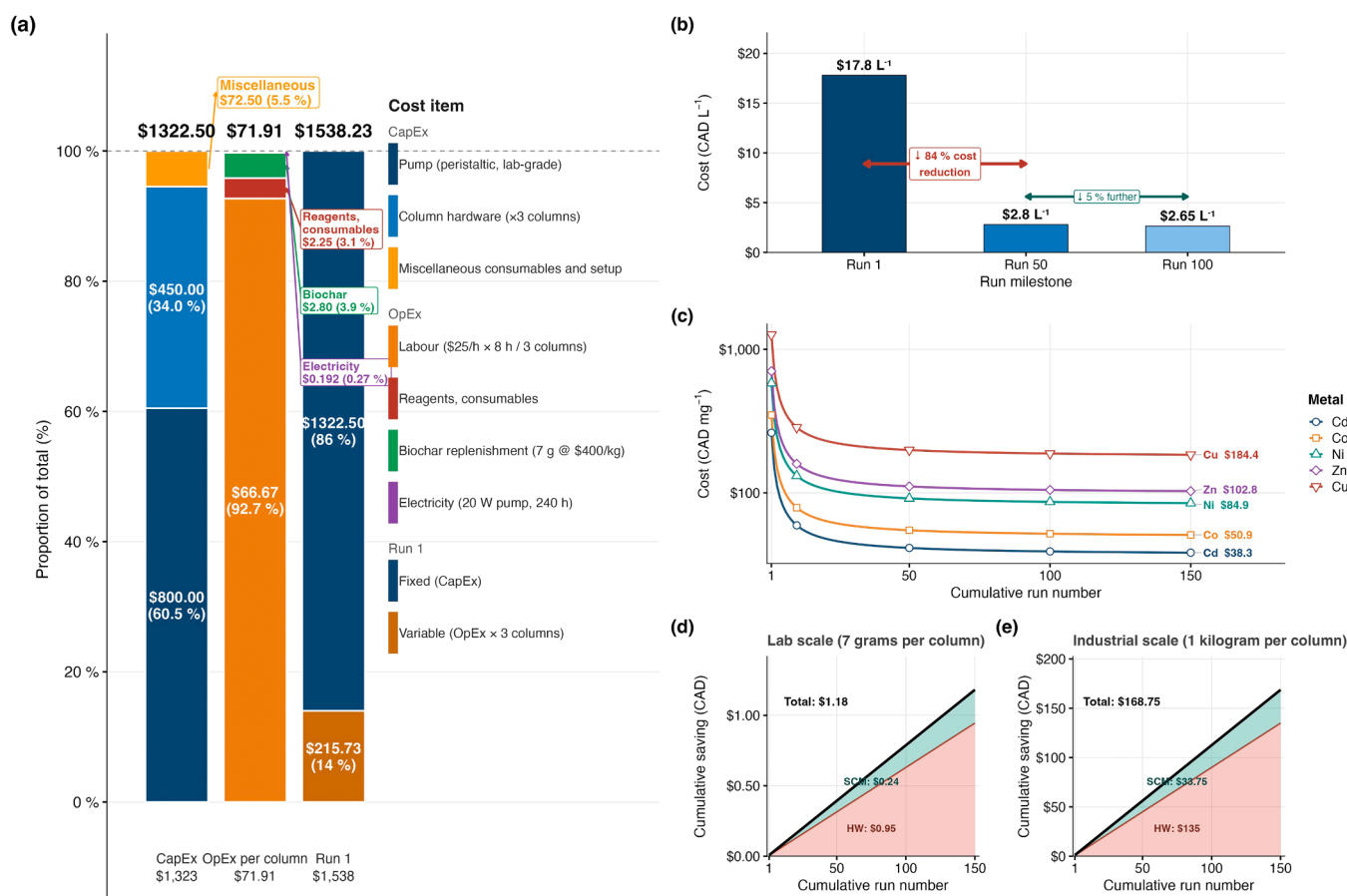


Fig. 5. Techno-economic feasibility of canola straw biochar fixed bed column treatment for OSPW remediation. (a) Capital (CapEx) and operational (OpEx) cost structure as proportion of category total; CapEx = equipment (CAD 1322); OpEx = per-column per 240 h run costs including biochar replenishment at CAD 400 kg⁻¹ (CAD 71.91 total). (b) Cumulative cost per litre of OSPW treated at run 1, 50, and 100, illustrating rapid fixed cost amortisation. (c) Cost per mg PTE removed over 150 runs (log₁₀ scale) at optimal conditions (2 mL min⁻¹, 12 cm bed depth). (d-e) Cumulative economic savings from cement immobilization of spent CSB, based on a combined per-kg savings rate of CAD 0.375 kg⁻¹ (avoided hazardous waste disposal, CAD 0.30 kg⁻¹, plus supplementary cementitious material credit, CAD 0.075 kg⁻¹), summed across 150 runs and 3 replicate columns at laboratory scale (7 g biochar/column/run; total CAD 1.18) and industrial scale (1 kg biochar/column/run; total CAD 168.75). CSB = canola straw biochar; OSPW = oil sands process affected water; PTE = potentially toxic element.

amortisation of fixed costs with repeated use (Fig. 5b) [47,48].

On a metal removal basis, cost per mg of PTE removed followed the adsorption hierarchy established in Section 3.1, with Cd achieving the lowest treatment cost owing to its superior adsorption capacity, followed by Co and Zn, while Cu remained the most expensive to treat consistent with its suppressed uptake under OSPW conditions (Fig. 5c). Commercial granular activated carbon for water treatment at equivalent column loading would yield substantially lower material cost per run but requires energy intensive thermal regeneration that CSB avoids through cement immobilization [49]. The cement valorization pathway avoided CAD 0.375 kg⁻¹ of spent biochar processed (CAD 0.30 kg⁻¹ from avoided hazardous waste disposal and CAD 0.075 kg⁻¹ from supplementary cementitious material market credit). Summed across 150 runs and 3 replicate columns, this yielded cumulative savings of $\approx$ CAD 1.18 at laboratory scale (7 g biochar/column/run) and $\approx$ CAD 168.75 at industrial scale (1 kg biochar/column/run) (Fig. 5d-e). These savings offset a fraction of operational costs at laboratory scale but become economically meaningful at industrial deployment, where the circular end-of-life pathway simultaneously eliminates a disposal liability and substitutes a fraction of carbon intensive Portland cement [50]. Equipment (pump, column hardware) was assumed to remain functional over the 150 run horizon evaluated in this preliminary analysis; equipment replacement costs and lifetime were not explicitly modelled, and this simplification should be addressed in future work incorporating equipment depreciation schedules. Collectively, these results demonstrate that the per litre and per mg treatment costs of CSB columns decrease substantially with operational continuity, and incorporating a cement valorization endpoint strengthens the overall economic case for biochar based OSPW remediation at scale.

4. Conclusions

This study demonstrates that canola straw derived biochar in continuous flow columns is a technically viable and economically characterizable approach for removing multiple potentially toxic elements from real OSPW. The observed affinity hierarchy shows adsorption selectivity in this system depended on the combined influence of ionic speciation, hard-soft acid-base character, hydration energy, and the alkaline matrix, rather than on adsorption capacity alone. This suggests biochar performance in real effluents cannot be inferred from single element batch studies, and selectivity needs to be evaluated under the specific water chemistry it will be applied to. Empty bed contact time provided a practical basis for column sizing and operational scheduling in this system, offering a more directly applicable design parameter than adsorption capacity alone. The inability of the Thomas and Yoon-Nelson models to describe breakthrough for oxyanion forming elements, despite their good fit for Cd, Co, and Ni, points to a difference in removal mechanism between these element groups that single solute kinetic models do not capture. This points to a need for multi-component kinetic models in future work on multi-element systems.

The cost trajectory shows capital expenditure, not ongoing operation, was the dominant driver of treatment cost early in the system's life, with costs falling sharply as fixed costs were spread across more runs. Cement immobilization results add a dimension to this economic picture. Incorporating spent biochar into cement suppressed PTE leaching across a range of pH conditions and generated cost savings through avoided disposal and material substitution, suggesting spent biochar disposal needs not be treated solely as a cost. Future work should examine column performance under field conditions and variable OSPW chemistry over longer durations, the behaviour of intrinsic cement derived PTEs such as Cr in sensitive receiving environments, and whether the adsorption and valorization findings reported here extend to other biochar feedstocks and spent adsorbents.

Environmental Implication

Cadmium, cobalt, nickel, and zinc are persistent, non-biodegradable contaminants documented in industrial wastewaters from mining, metal processing, and energy extraction. This study demonstrates their selective removal from real, multi-element industrial effluent under continuous flow at field-relevant scales, conditions absent from the synthetic single-metal batch systems dominating current biochar literature. Spent, metal-laden biochar is itself a disposal hazard if unmanaged; incorporating it into cement at low amendment rates immobilizes retained metals across a wide pH range, eliminating this secondary risk while partially displacing carbon-intensive cement inputs. Together, these results support a scalable pathway for industrial wastewater remediation and spent-adsorbent valorization.

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CRediT authorship contribution statement

Abhijeet Pathy: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Scott X. Chang:** Writing – review & editing, Supervision. **M. Anne Naeth:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the first author (Abhijeet Pathy) used Claude to improve the sentence structure and readability of some sections of the manuscript. After using this Claude, the author (Abhijeet Pathy) reviewed and edited the content as needed to fit his own writing style and takes full responsibility for the content of the published article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2026.143293](https://doi.org/10.1016/j.jhazmat.2026.143293).

Data availability

Data will be made available on request.

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