Heavy metals removal from landfill leachate by coagulation/flocculation process combined with continuous adsorption using eggshell waste materials

A. Q. Jaradat a,*, Dua’a B. Telfah a and Rabah Ismail b

a Department of Civil Engineering, Yarmouk University, Irbid, Jordan
b Department of Civil Engineering, Jadara University, Irbid, Jordan

*Corresponding author. E-mail: ayman.j@yu.edu.jo

ABSTRACT

The use of agricultural waste materials to remove heavy metals from wastewater is attractive due to its simplicity and economic efficiency. In this study, the applicability of calcined eggshell waste materials (CES) for heavy metals removal from real wastewater were examined via transport column experiment preceded by coagulation/flocculation process. A column packed with granular activated carbon (GAC) is operated in parallel to CES column to evaluate the adsorptive attributes of CES. The findings are assessed from another set of column experiments consisting of sand followed by CES column to evaluate the effect of particulate matter (PM) on CES performance toward heavy metals removal. In coagulation experiment, alum addition at an optimum dose (3.0 g/L) reduced the total suspended solids (TSS) by 80%, whereas the Fe, Pb, Zn, Cu, Ni, and Cr were reduced by 80%, 77%, 76%, 73%, 56%, and 49%, respectively. Under the current applied hydrodynamic conditions, using sand column before CES column improved the removal efficiencies of Fe, Pb, Cu, Zn, Ni, and Cr from 50% to 92%, 55% to 93%, 60% to 87%, 53% to 76%, 45% to 65%, and 41% to 60%, respectively. The whole results illustrate that CES can be competitive to GAC for heavy metals removal from landfill leachate, mainly if applied after PM removal by sand filtration.

Key words: coagulation, eggshell, heavy metals, landfill leachate, removal efficiency

HIGHLIGHTS

- Total suspended solids and heavy metals are effectively decreased by adding 3.0 g/L alum.
- Heavy metals are effectively eliminated from landfill leachate using calcined eggshells.
- Particles facilitated heavy metal movement via the filter media.
- Sand pretreatment improved the performance of calcined eggshell to remove heavy metals.
- The research findings may lead to more cost-effective landfill leachate treatment technology.

INTRODUCTION

Landfill leachate represents a serious environmental problem due to high organic, inorganic, and heavy metals content and toxicity characteristics. The presence of heavy metals in landfill leachate is of considerable concern because of their non-biodegradability, mobility, and toxicity (Vaverková et al. 2020). As a result, removing heavy metals from landfill leachate is a hot topic that has garnered much press in recent years (Kanmani & Gandhimathi 2013). Various physico-chemical methods were used widely and effectively to remove toxic heavy metals from wastewater streams, either pre-treatment or as the last purification (Mojiri et al. 2021). Adsorption is superior to other techniques due to its high removal efficiency, cost efficiency, simplicity of design, and ease of operation (Mojiri et al. 2021). Although activated carbon (AC) has been extensively used as an effective adsorbent for heavy metals removal from wastewater streams, its application is limited due to the high cost of AC materials and the need for regeneration (Tariq et al. 2018). In order to reduce the treatment cost, the effectiveness of the adsorption process for metal removal has been intensively investigated by using either raw or modified low-cost adsorbents derived from agricultural, industrial, or other natural waste materials (Banerjee et al. 2018; Núñez et al. 2019; Tariq et al. 2018; Patel 2020; Mojiri et al. 2021).

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Among agricultural waste materials, natural hen eggshell waste (ES) materials have been recognized as a potential worldwide available by-product and environmentally useful adsorbent (Ahmad et al. 2021). The ES have a porous, fibril structure with a high surface area and specific functional groups, including hydroxyl (-OH), thiol (-SH), carboxyl (-COOH), and amino (-NH₂) (Mittal et al. 2016). Due to these structural features, ES is considered an attractive natural bio-adsorbent for removing heavy metals from wastewater streams (Mittal et al. 2016). Furthermore, it has been reported that calcination of ES at temperature >700 °C increases its adsorptive surface area (Zaman et al. 2018). A review of the literature reveals that the use of eggshell waste materials, whether raw or processed, has provided excellent results for the removal of heavy metals from wastewater streams (Park et al. 2007; Mittal et al. 2016; Zhang et al. 2017; Tarig et al. 2018). Most of these applications were tested in batch studies and mainly on synthetic wastewater. It has been noticed that there is a clear knowledge gap in the performance of treatment methods for heavy metals removal from real wastewater streams because most studies used synthetic wastewater in which only one or few metals are present. Accordingly, conducting research using real wastewater for treating different contaminants is encouraging. Real wastewater such as landfill leachate usually contains suspended solids and colloidal particles (0.01–1.0 μm) that can sorb considerable amounts of strongly sorbing contaminants, causing increased mobility in the performance of treatment processes (Metreveli & Frimmel 2007; Won et al. 2019). Heavy metals have been discovered to have a strong affinity for colloids (Baun & Christensen 2004). This suggests that removing PM from landfill leachate samples prior to filtration will reduce the concentrations of particles and associated metals and, consequently, prolong the filter service time. To date, the only study aiming to remove heavy metals from real wastewater stream in column mode experiment was performed by Zhang et al. (2017). They investigated the applicability of ES as alkaline sorbent to remove typical heavy metals from acid mine drainage under various flow rates and bed depths. However, the effect of PM on heavy metals sorption onto ES was not considered in their work. In this study, we investigated the removal of heavy metals from landfill leachate using CES in the form of continuous flow column experiments considering the effect of PM on the adsorption performance of the filter media. Coagulation/flocculation experiment was performed before column experiments to lower the PM concentrations, allowing the following column experiments to run smoothly without interference from PM. The aims of this work are (i) to assess the potential use of CES material for removal of heavy metals from landfill leachate, and (ii) to investigate the effect of PM on heavy metals sorption onto CES. This work could contribute to innovative and cost-effective technology for treating landfill leachate containing heavy metals.

MATERIALS AND METHODS

Filter media
The ES materials were collected and prepared in the same way that they had been in previous research (Jaradat et al. 2022) except that the dried fraction of ES was calcined (CES) in this work at 800 °C for 3 h using a muffle furnace (Carbolite, Sheffield-England). This calcination temperature (800 °C) was chosen to obtain a complete calcination of ES materials as was suggested by others (Park et al. 2007). In their work, the ES sample was burned up to 800 °C. Calcination of eggshell began approximately at 650 °C and then near complete calcination was observed at 770 °C, resulting in phase-change in the sample. Furthermore, the micropores in ES are enhanced by calcination at temperature >700 °C, giving higher specific surface area and consequently higher sorption capacity (Zaman et al. 2018). Ahmad et al. (2021) found that the Brunauer–Emmett–Teller (BET) surface area of CES at 800 °C increased from 0.56 m²/g to 2.98 m²/g. Granular activated carbon (GAC) with an effective size of 0.71 mm diameter (Calgon Carbon Corporation, Huntington, WV) was obtained from the domestic market and was used as a standard filter media to evaluate the adsorptive attributes of CES. This size of GAC was selected to minimize the pressure drop in column system and to provide adequate surface area. Quartz sand (Ottawa, IL), obtained from the domestic market, was used in one set of column experiments as a pretreatment step to remove PM. ES and CES were studied using scanning electron microscopy (SEM) (FEI QUANTA 600) to assess their shape and surface morphology, while the mineral composition was determined using X-Ray Fluorescence Analyzer (XRF-FEI QUANTA 600). Fourier transform infrared spectroscopy (FTIR) (Bruker Tensor 27 IR spectroscopy) was used to examine the functional groups on the surface of eggshell before and after calcination at 800 °C. The spectra were recorded for the range of 4,000–400 cm⁻¹ with a spectral resolution of 4 cm⁻¹ at 298 K.

Leachate characterization
Leachate samples (150 L) were collected from a leachate collection system at the Al-Akaider landfill site in the northern part of Jordan. Details of sample collection and preparation are described elsewhere (Jaradat et al. 2022). Selected relevant
physico-chemical parameters for the leachate samples were analyzed three times (the mean data values are reported). The studied parameters are electrical conductivity (EC), pH, turbidity, total suspended solids (TSS), particle size distribution (PSD), and heavy metals (Fe, Ni, Cr, Cu, Cd, Pb, Zn). All of the tests were completed following the Standard Method for the Examination of Water & Wastewater (2012). Direct measurements for pH, EC, and turbidity were taken using a pH-meter (370 JENWAY), a conductivity meter (470 JENWAY), and a turbidity meter (Lovibond-PC checkit), respectively. 1.0 L of raw leachate was filtered using a 0.2 μm polycarbonate membrane filter to determine TSS concentrations (Osmonics, Inc., CA). Fritsch Analysette Equipment was used to determine PSD (Analyzer Micro Tec Plus). Elemental analysis was conducted using Atomic Absorption Spectrophotometer (AAS 800F Analytical Jan). The flame atomizer in AAS was supplied with air/acetylene at 60 L/h for Fe, 65 L/h for Pb, 55 L/h for Ni, and 50 L/h for Cu, Cd, and Zn. The xenon lamp was used as the radiation source for all elements. Detection wavelengths were 248.3 nm for Fe, 217 nm for Pb, 232 nm for Ni, 324.7 nm for Cu, 228.8 nm for Cd, and 213.8 nm for Zn.

**Jar test experiment**

The purpose of this jar test experiment was to use the coagulation-flocculation process to lower PM concentrations, allowing the following column experiments to run smoothly without interference from PM, which could reduce adsorption performance. The procedure followed in this jar test is analogous to that used in previous work (Jaradat et al. 2022) by using a conventional six-station jar test apparatus supplied by six beakers (Stuart SW6). Six different doses (1.0–6.0 at 1.0 g/L interval) of coagulant material (alum) were added into all beakers previously filled with 500 mL of leachate sample. The contents of the glass beaker were treated to 3 minutes of rapid mixing (120 rpm), 30 minutes of slow mixing (20 rpm), and then 1.0 hours of settling time.

The optimum alum dose was determined as the dose corresponding to the maximum turbidity and TSS removal. The rest of all leachate samples were treated in the same manner at a predetermined optimum alum dose. The supernatant solution was then drained, gathered, and used in the column tests that followed. Part of the supernatant solution was filtered using filter paper (Whatman 40) and analyzed for the same parameters as the raw leachate to determine the influence of coagulation on leachate quality. The tests and sample analysis were carried out in triplicate at 25 ± 1 °C without pH adjustments.

**Column experiments**

Two column experiments were operated in parallel for 15 days under conditions typical for slow sand filtration (Table 1) using CES and GAC as filter media. Figure 1 shows the column configuration employed in this study. A peristaltic pump was employed at a constant flow rate of 2.0 mL/min to transfer the leachate, pretreated by coagulation, into the columns. The empty bed contact time (EBCT) was 11.0 min, which is within the recommended design values for GAC contactors (5–30 min) (Moona et al. 2021). Effluent leachate samples from the columns were collected daily at fixed time intervals and analyzed for the same parameters tested for raw leachate. The flow rates were checked twice a week to ensure that a constant flow rate is attained during the column operational time. Details of column components and preparation are available elsewhere (Jaradat et al. 2022).

To evaluate the effect of PM on the performance of CES toward heavy metals removal, another set of column experiments consisting of two columns in series (Figure 1) was conducted in parallel to CES and GAC columns. In this experiment, the leachate influent into the CES column is pretreated first by sand column to reduce the TSS load entering the CES column.

**Table 1** | Experimental operation conditions for all column experiments

| Parameter                  | Unit   | CES | GAC | Sand-CES |
|----------------------------|--------|-----|-----|----------|
| Flow Rate (Q)              | mL/min | 2.0 | 2.0 | 2.0      |
| Diameter (D)               | cm     | 2.0 | 2.0 | 2.0      |
| Length (L)                 | cm     | 7.0 | 7.0 | 7.0      |
| Porosity (n)               | ...    | 0.45| 0.47| 0.46     |
| Adsorbent Mass (M₀)        | g      | 25.5| 25.1| 25.5     |
| Hydraulic loading rate (HLR) (L/m².min) | L/m².min | 6.37| 6.37| 6.37     |
| EBCT                       | min    | 11.0| 11.0| 11.0     |
This step was conducted based on the recognition that removing PM from leachate samples may enhance filter media’s adsorption performance and prolong the filter service time (Baun & Christensen 2004; Won et al. 2019).

Breakthrough curves, which reflect the loading behavior of the target pollutant onto the adsorbent in a continuous flow column (Patel 2020), are used to investigate the performance of all packed bed columns toward particle and heavy metals removal based on experimental data from all column trials. In this work, the breakthrough curves are expressed in the normalized concentration ($C/C_{in}$) determined at the column effluent as a function of pore volumes (PV). Data from the obtained breakthrough curves were used to estimate the adsorption capacity of the filter media at the end of the experiment ($q_e$) and at breakthrough time ($q_b$) as in Equation (1):

$$q_e \left( \frac{mg}{g} \right) = \frac{M_S}{M_0} = \frac{Q \int_{t=0}^{t=t} (C_0 - C_t) dt}{M_0}$$

(1)

where $M_0$ is the mass of adsorbent (g); $M_S$ is the adsorbed mass (mg); $Q$, is the flow rate (L/min); $C_0$ and $C_t$ are the inlet and effluent concentrations (mg/L). The adsorption capacity at breakthrough time ($q_b$) is estimated when $t$ is equal to the breakthrough time ($t_b$), which is defined here as being reached when effluent concentration ($C_t$) satisfies the wastewater discharge limits for studied constituents.

The kinetic models of Thomas (Thomas 1944), Adams–Bohart (Bohart & Adam 1920), and Yoon–Nelson (Yoon & Nelson 1984) were applied to the experimental breakthrough data to determine the characteristic parameters of the column that are useful for process design. The linear forms of Thomas, Adams–Bohart, and Yoon–Nelson models are given in Equations (2)–(4), respectively, while the average percentage errors ($\varepsilon_\%$) that indicate the fit between the experimental and predicted values of $C/C_0$ are calculated according to Equation (5).

$$\ln \left( \frac{C_0}{C} \right) = \frac{K_{th} q_0 M_0}{Q} - K_{th} C_0 t$$

(2)

$$\ln \left( \frac{C}{C_0} \right) = K_{AB} C_0 t - K_{AB} N_0 \frac{Z}{u}$$

(3)

$$\ln \left( \frac{C}{C_0 - C} \right) = K_{YN} t - \tau K_{YN}$$

(4)

$$\varepsilon_\% = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{(C/C_0)_{exp} - (C/C_0)_{calc}}{(C/C_0)_{exp}} \right| \times 100$$

(5)
where $K_{Th}$ is the Thomas rate constant (mL/mg.min); $q_0$ is the adsorption capacity (mg/g); $K_{AB}$ is the Adam-Bohart kinetic constant (L/mg.min); $N_0$ is the saturation constant (mg/L); $Z$ is the column depth (cm); $u$ is the superficial velocity (cm/min); $K_{YN}$ is the Yoon–Nelson rate constant (1/min); $\tau$ is the time required for 50% adsorbate breakthrough (min); and $t$ is the breakthrough time (min). The subscripts exp and calc show the experimental and calculated values; and $N$ is the number of measurements. Using linear regression analysis on breakthrough curves, the Thomas parameters ($K_{Th}$, $q_0$) in Equation (2) were calculated from plotting $Ln(C_t/C_0) - 1$ vs. $t$, the Adams–Bohart parameters ($K_{AB}$, $N_0$) in Equation (3) were calculated from plotting $Ln(C_t/C_0)$ vs. $t$, and the Yoon–Nelson parameters ($K_{YN}$, $\tau$) in Equation (4) were calculated from plotting $Ln[C/(C_0 – C)]$ vs. $t$.

RESULTS AND DISCUSSION

Results of ES and CES characterization

Morphological aspects of both ES and CES are presented in Figure 2, whereas elemental composition is embedded as a table in this figure. The obtained results reveal that ES has an irregular particle shape with deep and wide cavities and interlacing fibers containing mainly CaCO$_3$ (97%), whereas CES comprises an irregular particle shape with a rough surface and scattered micropores containing mainly CaO (94%). After calcination, the particles are smaller in size and cemented together, which may be attributed to the fact that the calcined ES is in the oxide state, as evidenced by the presence of CaO. Similar observations were obtained by a previous work conducted on the same type of ES (Jaradat et al. 2022). These deep cavities, interlacing fibers, and micropores are observed by others as well, where each ES has been estimated to contain 7,000–17,000 pores (Mittal et al. 2016). The more developed pore structure of CES could provide higher surface area and consequently higher sorption capacity. Ahmad et al. (2021) reported an increase in the BET surface area of the raw eggshell from 0.56 m$^2$/g to 2.98 m$^2$/g after calcination at 800°C. Furthermore, CaO usually transforms into Ca(OH)$_2$ upon exposure to atmosphere (Zaman et al. 2018). The formation of hydroxide functional group in the form of Ca(OH)$_2$ during the process of calcination is a very common incident that may improve the sorption capacity (Zaman et al. 2018). The results of FTIR analysis performed on the raw ES and CES are presented in Figure 3. For ES, the major peaks are observed around 1,434 cm$^{-1}$, indicating the presence of carbonate minerals within the ES matrix (Awogbemi et al. 2020). Distinct peaks appearing at 876 cm$^{-1}$ and 709 cm$^{-1}$ should be associated with in-plane deformation and out-plane deformation modes, respectively, in the presence of CaCO$_3$, as confirmed by the observed, peaks at 2,517 cm$^{-1}$ and 1,796 cm$^{-1}$ (Awogbemi et al. 2020). The observed peaks at 3,299–3,504 cm$^{-1}$ indicate the presence of amines and amides in the eggshell membrane (Guru & Dash 2014). For CES, a sharp stretching band at 3,644 cm$^{-1}$ is observed, indicating the existence of hydroxyl group (OH$^-$) in the form of Ca(OH)$_2$ (Awogbemi et al. 2020). OH$^-$ group is vital in the adsorption process as it permits the formation of hydrogen bridges, which would cause the polar functional groups to be directed into the body of the adsorbent. This creates an important active site for adsorption to effectively occur (Mittal et al. 2016).

Leachate characterization

The properties of raw leachate used in the present work are presented in Table 2. The coefficient of variation (CV%) for all tested parameters is <20%, suggesting good consistency of the results. Generally, the collected landfill leachate samples are characterized by dark brown color, slightly alkaline pH (6.8), a high load of metallic contents, and high TSS concentrations (560 mg/L). PSD distinguishes three groups of particle sizes spanning from 0.3 to 3.0 μm, 4 to 20 μm, and 600 to 1,000 μm (Figure 4(a)). Density distribution curve shows that about 50% of particles are in colloidal size (<1 μm), whereas 95% do not exceed 20 μm. The relatively high values of EC (27.4 mS/cm) indicate the presence of inorganic materials in the samples (Kanmani & Gandhimathi 2013). The high level of Fe (44.7 mg/L) in the leachate sample indicates that Fe and steel scrap are dumped in the landfill (Kanmani & Gandhimathi 2013). Heavy metals (Zn, Pb, Cr, Cu, and Ni) were detected in all samples. Various waste is dumped at the Alakaider landfill site, such as batteries, fluorescent lamps, and Pb-based paints, which are not collected separately in Jordan, likely indicating the origin of these metals in leachate samples. The concentrations of Fe (44.7 mg/L), Pb (3.62 mg/L), Cu (4.67 mg/L), Zn (6.6 mg/L), Ni (1.84 mg/L), and Cr (1.34 mg/L) in the landfills’ leachates were high in all samples, exceeding the Jordanian standards for the maximum allowable discharge limits of industrial wastewater (JIEC) (Table 2), indicating severe contamination that poses direct threats of groundwater (GW) pollution with landfill materials. It has been reported that the GW resources near to Al-Akaider landfill site have already been affected by migration of heavy metals (Abu-Daabes et al. 2013). The concentrations of these metals in leachate samples of the Alakaider landfill site...
obtained in this work are close to those obtained by others for the same site (Abu-Daabes et al. 2013) and within the typical values reported for other sites (United Nations Environment Programme 2005) in developing countries (Table 2).

Jar test results
The removal efficiency of turbidity and TSS as a function of alum dose is shown in Figure 5. The intermolecular relationship between the turbidity and TSS is observed, as both increased initially and decreased thereafter with similar trends. The removal of turbidity and TSS increased with an increase in alum dosage until it reached the maximum value; then the removal started to decline. Maximum removal efficiencies of both turbidity (90%) and TSS (80%) are obtained at a dose
of 3.0 g/L, assigned here as an optimum dose. The coefficient of variation (CV%) for all tested parameters is <5%, suggesting good consistency of the results. Alum addition up to 3.0 g/L increased the particle size of suspended materials, enhancing the settling of suspended matter due to coagulation. At a dosage above the optimum value, removal efficiencies of both turbidity and TSS were decreased, which may be attributed to the restabilization of colloidal particles. This is verified by the results obtained from PSD analysis (Figure 4). Leachate treatment by coagulation at an optimum alum dose (3.0 g/L) resulted in disappearance of all particles having a size >3 μm, leaving only particles with small sizes (<3 μm) (Figure 4(b)). On the other hand, increasing the alum dose to 6.0 g/L resulted in restabilization of colloidal particles, as can be seen from Figure 4(c), where ~80% of particles are redistributed in the size range (0.1–3.0 μm), and the rest (20%) are >500 μm. The pH value was decreased slightly from 6.8 to 5.8 after alum addition, which may be attributed to the acidic character of AL₃⁺ cation. A preliminary experiment conducted to determine the optimum pH value revealed that the highest TSS and heavy metals removal was achieved at pH ≈ 6.0, which is consistent with the actual pH value of the solution after alum addition. Therefore, pH was not adjusted in all further experiments.

The results obtained from a further investigation at this optimum dose (3.0 g/L) showing the % removal of heavy metals are presented in Figure 6. The coefficient of variation (CV%) for all tested parameters is <5%, suggesting good consistency of the results. A notable reduction was observed for heavy metals by 80%, 77%, 76%, 73%, 56%, and 49% for Fe, Pb, Zn, Cu, Ni, and Cr, respectively. This may be attributed to the high binding affinity of these heavy metals, particularly Fe, Pb, Zn, and Cu,

**Figure 3** | FTIR spectra of ES and CES materials.

**Table 2 | Leachate composition at Al-Akaider landfill site**

| Parameter | Raw Leachate | CV % | JIEC standard limits | Al-Akaider [1] | Typical characteristics of leachate in developing countries [2] |
|-----------|-------------|------|----------------------|----------------|------------------------------------------------------------------|
| pH        | 6.8 ± 0.23  | 3.37 | 6.5–9.0              | 8.40 ± 0.16    | 4.5–9.0                                                          |
| EC        | 27.4 ± 4.3  | 15.6 | –                    | 86 ± 33        | –                                                                |
| TSS       | 360 ± 24    | 6.63 | 50                   | 200–2,000      | 6–2,700                                                          |
| Turbidity | 15,876 ± 2,165 | 13.6 | –                    | –              | –                                                                |
| Fe        | 44.7 ± 8.7  | 19.4 | 1.0                  | 50–1,200       | 3–2,100                                                          |
| Ni        | 1.84 ± 0.07 | 3.8  | 0.2                  | 2.88 ± 1.95    | 0.015–13                                                         |
| Cu        | 4.67 ± 0.84 | 18.0 | 0.2                  | 2.9 ± 2.2      | 4–1,400                                                          |
| Cr        | 1.34 ± 0.17 | 12.6 | 0.1                  | 6.88 ± 7.01    | 0.02–1.5                                                         |
| Cd        | ND          | –    | 0.01                 | 1.23 ± 1.82    | 0.0001–0.4                                                      |
| Pb        | 3.62 ± 0.42 | 11.6 | 0.1                  | –              | 8–1,020                                                          |
| Zn        | 6.6 ± 1.2   | 18.1 | 2                    | –              | 0.03–120                                                         |

All units are in mg/L except pH (SU), EC (ms/cm) and turbidity (NTU). [1] Abu-Daabes et al. (2013), [2] United Nations Environment Programme (2005).
**Figure 4** | PSD of raw leachate (a) and leachate pretreated by coagulation-flocculation at alum dosage of 3.0 g/L (b) and 6.0 g/L (c).

**Figure 5** | % Removal of turbidity and TSS at different alum doses.
toward colloids. This agreed well with the results obtained by other researchers (Baun & Christensen 2004), who claimed that the majority (>70%) of heavy metals in landfill leachate occur in colloidal or organic complexes. Several researchers had reached similar conclusions where adsorption, precipitation, and ion exchange all work to bind heavy metals to colloids (Metreveli & Frimmel 2007; Won et al. 2019). However, the obtained reduction by coagulation was insufficient to meet the discharge limits of heavy metals (Table 2), suggesting that further treatment is still needed.

**Column experiment results**

The flow rates to all columns were held constant (2.0 ± 0.045 mL/min) throughout the experiments (4,300 PV). Particle breakthrough curves in all columns are presented in Figure 7. As indicated from the breakthrough curves, the first evidence of particles breakthrough (C/C_{in} = 0.1) is observed after 1,000 and 1,300 PV in CES and GAC columns, respectively. From these points until the end of the experiment (4,300 PV), effluent TSS concentrations increased gradually, approaching 80% and 70% of their influent concentrations in CES and GAC columns, respectively. At these points, TSS effluent from these columns meets the TSS discharge limit (50 mg/L) of industrial wastewater (Table 2). Pretreatment of influent leachate with sand before the CES column prolonged the breakthrough time to >2,500 PV and resulted in significant improvement in the removal efficiency of TSS from 20% to 75% at the end of the experimental running time (Figure 7).

Breakthrough curves of all heavy metals investigated (Fe, Pb, Cu, Zn, Ni, Cr) in all packed bed columns are depicted in Figure 8. The progression of heavy metal concentrations in the effluent of the CES column is illustrated in Figure 8(a). The first evidence of obvious breakthrough of heavy metals in the CES column occurs after 1,000 PV, coinciding with the
breakthrough of TSS (Figure 7). At this point >90% of the influent concentrations of all heavy metals are removed by the CES column. An interesting observation obtained is that the initial breakthrough of TSS and all investigated heavy metals starts almost simultaneously (after 1,000 PV), which may be attributed to the binding affinity of these heavy metals toward PM. This suggests that PM may influence the transport of heavy metals through column media. Won et al. (2019) investigated the transport of Pb, Cu, Zn in a sand column experiment under kaolinite colloids and revealed that the presence of mobile kaolinite colloids retarded heavy metal adsorption in the sand and enhanced heavy metal transport. Similarly, a colloid-facilitated transport for heavy metals was observed in the presence of Na-bentonite (Metreveli & Frimmel 2007). As indicated from breakthrough curves, faster breakthrough is observed for Fe followed by Pb, Cu, Zn, Ni, and Cr, suggesting different binding

**Figure 8** | Heavy metals breakthrough curves in (a) CES column, (b) GAC column, (c) sand-CES column. \( Q = 2.0 \text{ cm/min}; \) \( 	ext{HLR} = 6.37 \text{ L/m}^2\text{min}; \) \( L = 7.0 \text{ cm}; \) \( 	ext{EBCT} = 11 \text{ min}. \)
affinities of these heavy metals toward particles in an order \( \text{Fe} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Cr} \), which agrees well with the results obtained by the jar test. In a competitive sorption experiment, Veeresh et al. (2003) observed that the affinity of metals toward soil particles, based on their partitioning coefficient (\( K_d \)) values, was \( \text{Pb} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Cd} \). As time progresses, breakthrough curves are more dispersed, and effluent concentrations increase continuously until the experiment's end (4,300 PV), where Fe, Pb, Cu, Zn, Ni, and Cr are removed by 50%, 55%, 60%, 52%, 46%, and 42%, respectively. The breakthrough curves of Cu, Zn, Ni, and Cr exhibit two distinct regimes. In the first regime, only a slight and gradual increase in their effluent concentrations is observed approaching 26%, 20%, 12%, and 8% of their influent concentrations at 3,700, 3,500, 3,300, and 3,000 PV for Cu, Zn, Ni, and Cr, respectively. In the second regime, a sudden considerable increase in their effluent concentrations is observed after these points until the end of the experiment (4,300 PV) approaching 40%, 47%, 55%, and 60%, respectively. This may suggest that these heavy metals initially broke through the CES column as colloid-associated part, while in the second regime the breakthrough may occur due to the elution of the dissolved fraction. The enhanced transport of heavy metals by colloids was observed by others (Metreveli & Frimmel 2007; Won et al. 2019). The Fe and Pb breakthrough curves exhibit only a gradual increase till the end of the experiment, approaching 50% and 45%, respectively, which may suggest that Fe and Pb break through the column as colloid-associated part while longer time is still needed to observe the breakthrough of the dissolved fraction. However, under the current applied hydrodynamic conditions, complete removal of the investigated metals in CES that satisfies the discharge limits (Table 2) was achieved before 1,500 PV (equivalent to 5 days of operational time) for Fe, Pb, and Cu, and before 3,000 PV (equivalent to 11 days of operational time) for Ni and Cr. After these points, effluent concentrations of these metals exceeded their discharge limits (Table 2), probably due to their association with PM. For Zn, the effluent concentration never approached its discharge limit (2.0 mg/L) during the experimental running time despite the elution of the dissolved fraction after 3,500 PV.

Similar trends are observed for heavy metals removal by GAC column experiment with a slightly better performance than that of CES column (Figure 8(b)). The initial breakthrough of all heavy metals starts simultaneously with TSS breakthrough (after 1,300 PV), suggesting their possible elution as colloid-associated part. After this point, the breakthrough curves of Fe, Pb, and Cu exhibited gradual increase till the end of the experiment with no evidence for a breakthrough of the dissolved fraction, since no sudden increase in their breakthrough curves is observed during the experimental running time. In contrast, Zn, Ni, and Cr breakthrough curves exhibited a sudden and notable increase after 3,700 PV, which may have happened due to the elution of the dissolved fraction.

The obtained results from CES and GAC column experiments indicate that CES can be competitive to GAC for heavy metals removal from landfill leachate. In both columns, PM enhanced the transport of all heavy metals as indicated from breakthrough curves. The breakthrough times at which the effluent concentrations of heavy metals exceeded the wastewater discharge limits (Table 2) occur due to their association with PM. This suggests that more efficient removal of PM will result in better column performance toward heavy metals removal, since a long time is required to observe the breakthrough of the dissolved fractions. This is verified by the results obtained from the second set of column experiments where the sand column is used prior to the CES column (Figure 8(c)). Using sand column prior to CES column resulted in delaying the breakthrough time of TSS from 1,000 PV to 3,000 PV, and increasing removal efficiency from 20% to 75% at the end of the column experiment. This in turn resulted in delaying the breakthrough times of all heavy metals. The first evidence of notable breakthrough of Fe and Pb occurs after 2,500 PV, coinciding with the breakthrough of TSS (Figure 7). At this point >95% of Fe and Pb are removed in this sand-CES column. No considerable or sudden increase in the effluent concentrations of Fe and Pb is observed after this point until the end of the experiment (4,300 PV), and their removal efficiencies remained >90%. Due to low concentrations of PM eluted through the sand-CES column, only a small fraction of Fe and Pb broke through the column as colloid-associated part, while longer time was needed for the dissolved fraction to break through. Cu, Zn, Ni, and Cr broke through the column initially after 3,000 PV, about the same time as the sudden increase in their breakthrough curves observed in previous CES column experiment (Figure 7(a)). This confirms that, at this time, Cu, Zn, Ni, and Cr broke through the column as dissolved fraction. Due to low effluent concentrations of TSS, only small binding sites are available on these particles, which were filled with Fe and Pb, leaving no space for other metals. Under the current applied hydrodynamic conditions, the effluent concentrations of Cu, Ni, and Cr exceeded their discharge limits nearly at the end of the experiment (4,000 PV). In contrast, the effluent concentrations of Fe, Pb, and Zn never exceeded their discharge limits during the entire column operational time. This indicates that PM removal by sand column resulted in better performance of CES toward removal of all investigated heavy metals. Besides, CES exhibited high binding affinity toward investigated heavy metals in an order Pb > Fe > Cu > Zn > Ni > Cr, since faster breakthrough is observed for Cr, followed by Ni, Zn, Cu, Fe, and Pb.
Similar results are obtained by Zhang et al. (2017), who used ES as an adsorbent in column mode experiment to remove heavy metals from acid mine drainage and found that ES has a great affinity toward heavy metals in an order Pb > Fe > Cu > Cd. Patel et al. (2020) studied the applicability of activated charcoal prepared from neem leaf powder (AC-NLP) for adsorption of heavy metals (Pb, Cu, Cd, Zn, Ni, and Cr) from synthetic wastewater using batch and column experiments. They found that AC-NLP is effective for heavy metals removal in an order Pb > Cu > Cd > Zn > Ni > Cr.

The adsorption capacities ($q_e$) of CES toward heavy metals calculated at the end of the column experiments (4,300 PV) increased considerably when using a sand column prior to CES column from 9.2 to 12.2, 1.0 to 1.26, 2.78 to 3.23, 4.65 to 5.22, 1.56 to 1.71, and 1.06 to 1.14 mg/g for Fe, Pb, Cu, Zn, Ni, and Cr, respectively. The adsorption capacities ($q_b$) of CES toward investigated heavy metals calculated at the breakthrough time ($t_b$) are summarized in Table 3. Comparisons of $q_b$ values obtained in this work with those reported by other researchers for various adsorbents are also presented in Table 3. The $q_b$ values obtained in our work are lower than those reported by others (Kalavathy et al. 2010; Lakshmipathy & Sarada 2015; Banerjee et al. 2018; Núñez et al. 2019) but with a much longer time to breakthrough, which is attributed to the lower influent concentration, lower HLR, and higher EBCT used in our work. At lower HLR, one could expect a higher sorption capacity due to longer contact time (Banerjee et al. 2018; Núñez et al. 2019). At the same time, increasing influent concentration was found to influence adsorption capacity (Kalavathy et al. 2010; Lakshmipathy & Sarada 2015; Banerjee et al. 2018; Núñez et al. 2019). Furthermore, it has been found that the leachate at the Al Akaiser landfill site is complex, containing high refractory organic matter (Jaradat et al. 2018), which probably affected the adsorption capacity of CES toward heavy metals. It is well known that the adsorption capacity may decrease because of the competition by natural organic matter with different organic contaminants through direct site competition and pore entrance blockage (Boukhili et al. 2013).

The column kinetic parameters were determined by applying Thomas, Adams–Bohart, and Yoon–Nelson models to the experimental breakthrough data of Cu, Zn, Ni, and Cr obtained from the sand-CES column experiment, where the effect of PM on their breakthrough was negligible (Figure 8(c)). Experimental breakthrough data of Fe and Pb were not used in this analysis since their breakthrough, during the column running time, occurs as associated phase with PM. The Thomas model, defined based on the Langmuir adsorption kinetics, describes the adsorption process where external and internal diffusion is not the limiting step and assumes negligible axial dispersion. The model does not constrain sorption by chemical reaction and is controlled by mass transfer at the surface (Thomas 1944). The Adams–Bohart model assumed that the adsorption rate is proportional to the fractional adsorption capacity possible on the surface of the adsorbent (Bohart & Adam 1920). The Yoon–Nelson model assumes that the rate of decrease in the adsorption probability of each adsorbate molecule is proportional to the adsorption capacity of the adsorbate molecules and the breakthrough probability of the adsorbent column (Yoon & Nelson 1984).

### Table 3 | Comparison of breakthrough times ($t_b$) and adsorption capacity ($q_b$) obtained in this work with the results of other researchers

| Adsorbent          | Dose (g) | Metal | $C_{in}$ mg/L | HLR L/m².min | EBCT min | $t_b$ | $t_s$ | $q_b$ mg/g | $q_s$ mg/g | Source               |
|--------------------|----------|-------|--------------|--------------|----------|-------|-------|-------------|-------------|---------------------|
| CES                | 25.5     | Fe    | 7.4          | 6.37         | 11       | 5.0 d | ..... | 3.93       | .....       | This study          |
|                    |          | Pb    | 0.76         |              |          | 5.5 d | ..... | 0.45       | .....       |                     |
|                    |          | Cu    | 1.96         |              |          | 5.8 d | ..... | 1.24       | .....       |                     |
|                    |          | Zn    | 3.2          |              |          | >15d  | ..... | 4.6        | .....       |                     |
|                    |          | Ni    | 1.07         |              |          | 11d   | ..... | 1.33       | .....       |                     |
|                    |          | Cr    | 0.724        |              |          | 11d   | ..... | 0.89       | .....       |                     |
| Clam shell (CS)    | 0.2      | Pb    | 30           | 15.3         | 0.65     | 0.25 h| 6.7 h | 42.5        | 13–28       | Núñez et al. (2019) |
| Waste              |          | C     |              | –32–64       | 1.6      | 3–8 h  | 13–20 h| 13–28       | 45.3        | Banerjee et al. (2018) |
| Pistachio shell    | 0.83     | Pb    | 500          | 12.7         | 3.92     | 1.25 h| 2.1 h | 45.3        | 26.9        | Lakshmipathy & Sarada (2015) |
| Watermelon on rind |          | Ni    | 100          | 20           | 9.8      | 7.0 h | 20 h  | 11.8        | 26.9        | Kalavathy et al. (2010)   |
|                    |          | Zn    |              | 2.5          | 7 h      | .....  |       |            |            |                     |

$q_b$: adsorption capacity (mg/g) obtained at the breakthrough time; $t_s$: saturation time at which $C/C_{in} > 0.9$; $q_s$: sorption capacity at saturation (mg/g).
All models’ parameters \((K_{Th}, q_0, K_{AB}, N_0, K_{YN}, \tau)\), calculated using linear regression analysis on breakthrough curves of Cu, Zn, Ni, and Cr, are presented together with the corresponding correlation coefficients \((R^2)\) in Table 4. The good values of \(R^2\) (0.97–0.99) obtained by all models do not necessarily indicate their validity in this investigation. This is further investigated by plotting the experimental points and the predicted breakthrough curves (Figure 9) with the calculated average percentage errors \((\varepsilon\%)\) (Table 4) for the findings of the best fitted model for the column system. It is clear from Figure 9 and \(\varepsilon\%\) values in Table 4 that there is a good agreement between experimental and predicted data in Thomas (Figure 9(a)) and Adams–Bohart (Figure 9(b)) models, suggesting the validity of these models for the removal of Cu, Ni, Zn, and Cr in this column system. This good accuracy \((\varepsilon\%\ <16.4\%)\) (Table 4) of Thomas and Adams–Bohart for Cu, Ni, Cu, and Cr sorption could be attributed to the incorporation of the critical parameters governing the sorption process, i.e., sorption capacity, external mass transfer coefficient, superficial velocity, and kinetic constants (Salamatinia et al. 2008). However, slight discrepancies between the experimental and predicted curves by Adams–Bohart model are observed when \(C/C_0\) exceeded 0.4, as in the case of Cr (Figure 9(b)). This suggest that the validity of Adams–Bohart model is limited to the low relative concentration region of data points, which is expected, since Adams–Bohart model is usually used to describe the initial part of the whole breakthrough curves (Zhang et al. 2017). Good fit to Adams–Bohart when \((C/C_0 < 0.4)\) indicates that the overall system kinetics is dominated by external mass transfer in the initial part of sorption column (Banerjee et al. 2018). In the only study conducted similarly to this work by using real wastewater in column mode experiment, Zhang et al. (2017) investigated the applicability of ES as alkaline sorbent to remove typical heavy metals from multicomponent acid mine drainage under various flow rates and bed depths. In their work, the Thomas model provided excellent fits to the whole breakthrough curves for all tested conditions, whereas Adams–Bohart adequately fitted the initial part of the breakthrough curve for multicomponent heavy metals solution containing Cd, Pb, Cu, Fe, and other constituents (Zhang et al. 2017). Although the Thomas and Adams–Bohart models exhibit good correlation with experimental data, their validity in this work is limited to the range of conditions used. Therefore, further investigation using synthetic wastewater spiked with various levels of heavy metals is important to better understand the adsorption mechanism of each heavy metal and to assess the removal efficiency of the CES under various controlled conditions such as various initial concentrations, various bed heights, and at relatively higher HLR to obtain complete breakthrough curves.

Despite the fact that these column experiments were run at a reasonably high loading rate (2.0 mL/min), the running time was inadequate for a complete heavy metal breakthrough in all packed columns under the imposed hydrodynamic circumstances. This suggests that heavy metals in landfill leachate exhibit a strong affinity toward both CES and GAC, which is

### Table 4 | Estimated parameter values of Thomas \((K_{Th}, q_0)\), Adams–Bohart \((K_{AB}, N_0)\), and Yoon–Nelson \((K_{YN}, \tau)\) models for the sorption process of Cu, Zn, Ni, and Cr on CES in sand-CES column

| Parameter | Cu         | Zn         | Ni         | Cr         |
|-----------|------------|------------|------------|------------|
| \(K_{Th}\) (L/mg.day) | 0.226 | 0.206 | 0.699 | 0.803 |
| \(q_0\) (mg/g) | 4.26 | 6.08 | 1.918 | 1.276 |
| \(R^2\) | 0.98 | 0.98 | 0.98 | 0.99 |
| \(\varepsilon\%\) | 14.9 | 16.4 | 15.2 | 3.7 |
| \(K_{AB}\) (L/mg.day) | 0.219 | 0.199 | 0.662 | 0.708 |
| \(N_0\) (mg/L) | 5.039 | 7.187 | 2.285 | 1.563 |
| \(R^2\) | 0.98 | 0.98 | 0.97 | 0.99 |
| \(\varepsilon\%\) | 14.5 | 15.2 | 15.7 | 7.18 |
| \(K_{YN}\) (1/day) | 0.444 | 0.646 | 0.745 | 0.619 |
| \(\tau\) (day) | 19.25 | 18.85 | 15.99 | 14.69 |
| \(R^2\) | 0.98 | 0.98 | 0.98 | 0.99 |
| \(\varepsilon\%\) | 15.7 | 67.3 | 16.4 | 38.9 |

Water Science & Technology Vol 84 No 12, 3829

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consistent with the results from other studies which suggested that in cases where the binding affinity of pollutants is powerful, retention factors can be high, resulting in longer times to observe the complete breakthrough (Zhang et al. 2017; Patel 2020). However, decreasing the hydrodynamic loading rate and increasing the EBCT would prolong the filter lifetime, resulting in better performance of CES (Núñez et al. 2019). Furthermore, the recommended HLR for onsite wastewater treatment ranges from 30 to 40 (L/m² .day) (US-Environmental Protection Agency 2002). The average HLR in this study was 6.37 L/m².min (corresponding to 9,170 L/m².day), which is 230 to 300 times greater than what is advised. The sorption achieved from the experiment is expected to rise if the advised HLR value is utilized because the prolonged contact time leads to a more extended period for heavy metals to break through (Banerjee et al. 2018; Núñez et al. 2019).

The process selection for the treatment of heavy metals from landfill leachate is greatly affected by presence of PM. In cases when heavy metals are mostly in the particulate-associated phase, a process similar to slow sand filtration may be efficient for the removal of PM and associated fraction of heavy metals. However, when heavy metals are mostly in dissolved phase, a filter media with high sorption capacity for heavy metals, such as GAC, would be needed. The CES as natural low-cost adsorbent would be effective for heavy metals removal from landfill leachate particularly if applied after slow sand filtration. The contaminated CES can be disposed of in incinerators or a landfill. However, the use of CES as low-cost adsorbent is attractive due to its contribution to the reduction of costs associated with the disposal of discarded eggshell waste and environmental protection.

CONCLUSIONS

This study demonstrates that CES could be utilized as an effective low-cost adsorbent for the removal of heavy metals from landfill leachate in a packed bed column system after pretreatment with coagulation/flocculation process.
Coagulation/flocculation process effectively reduced the turbidity (by 90%) and TSS (by 80%) when alum was applied at an optimum dose of 3.0 g/L. At this dose, concentrations of all investigated heavy metals were affected by particles removal and reduced by 50–80% in an order Fe > Pb > Zn > Cu > Cd > Ni > Cr, suggesting the same order of binding affinity of these metals toward particles. The results obtained from CES and GAC column experiments revealed that presence of PM enhanced the transport of heavy metals as evidenced from their earlier breakthrough compared to that in sand-CES column. Using sand column prior to CES column delayed the breakthrough time of TSS from 1,000 PV to 3,000 PV and increased the removal efficiency from 20% to 75% at the end of the column experiment. This, in turn, resulted in improving the performance of the CES column toward heavy metals removal; the removal efficiencies of Fe, Pb, Cu, Zn, Ni, and Cr increased from 50% to 92%, 55% to 93%, 60% to 87%, 53% to 76%, 45% to 65%, and 41% to 60%, respectively.

The validity of Thomas and Adams–Bohart models to the obtained experimental data is limited by the range of conditions used. Therefore, further investigation using synthetic wastewater spiked with various levels of heavy metals is important to better understand the adsorption mechanism of each heavy metal and to assess the removal efficiency of the CES under various controlled conditions such as various initial concentrations, various bed heights, and at relatively higher HLR to obtain complete breakthrough curves.

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AUTHORS’ CONTRIBUTIONS

J.A.Q. (Associate Professor) designed and conducted the experimental work, and wrote the manuscript. T.D.B. (Assistant Professor) and I.R. (Assistant Professor) helped with all sample collection and preparation and revised the manuscript.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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