

Ecological Risk and Adsorption of Toxic Metals from Gbalahi Landfill Leachate using Chicken Eggshells as a Low Cost Adsorbent

J. Kan-Uge¹, E. H. Alhassan², A. B. Duwiejuah^{3*}, F. T. Iddrisu², and B. H. R. Gameli¹

¹ *Department of Environment and Sustainability Sciences, Faculty of Natural Resources and Environment, University for Development Studies, Tamale, Ghana*

² *Department of Fisheries and Aquatic Resources Management, Faculty of Biosciences, University for Development Studies, Tamale, Ghana*

³ *Department of Biotechnology and Molecular Biology, Faculty of Biosciences, University for Development Studies, Tamale, Ghana*

*Corresponding Author: abalu096@gmail.com

Abstract

Pollution is a world-wide talked about subject but little has been achieved in the 21st century in terms of improvement of aquatic environment, water quality and reducing human health risks. One of the most effective methods of removing toxic metals is adsorption. The study was to assess the ecological risk and efficacy of chicken eggshell as a low cost adsorbent for the removal of toxic metals from Gbalahi landfill leachate. Chicken eggshells (1 g, 2 g, 4 g, 6 g and 8 g) were added to 100 mg L⁻¹ each of the spiked ternary leachate (1 mg L⁻¹, 5 mg L⁻¹, 10 mg L⁻¹, 25 mg L⁻¹ and 50 mg L⁻¹) and agitated for 60 minutes at a constant temperature (25 °C). The leachates, and elutes were obtained and transported to the Ecological Laboratory of University of Ghana for initial analysis. The study revealed that 0.2060 mg L⁻¹ for cadmium (Cd), 0.0060 mg L⁻¹ for chromium (Cr), 0.0010 mg L⁻¹ for lead (Pb), 0.0012 mg L⁻¹ for mercury (Hg), 0.0024 mg L⁻¹ for arsenic (As) and 0.3410 mg L⁻¹ for nickel (Ni) were present in the leachate. The removal efficiencies for Cd, Hg, and Pb ranged from 98.67% to 99.99%, 99.89% to 99.99%, and 99.98% to 99.99%, respectively. Langmuir model ($0.46 \leq R^2 \leq 0.84$) showed a better fit for the adsorption of the toxic metals by chicken eggshells than Freundlich model ($0.26 \leq R^2 \leq 0.40$). Cadmium and nickel proved to be the metals with the highest level of toxicity. Chicken eggshells have a high adsorption efficiency in the landfill leachate. The pH of the leachates were favourable for the adsorption. The toxic metals in the leachate were within the low contamination and low-risk category indicating low ecological risks. Low-cost chicken eggshells can be used as an economically efficient material for the removal of cadmium, mercury and lead from landfill leachate. More adsorptive studies should be carried out using chicken eggshells as an adsorbent to remediate other wastewater in order to gain a broad knowledge on the adsorbent's applicability.

Keywords: Chicken eggshells, ecological risk, leachate, toxic metals, removal efficiency

Introduction

Water is a key resource for the presence of life on earth and to get access to clean water is life-threatening for humans and the ecosystem. However, during the last several decades, an ever-growing population, fast industrialisation, expanding urbanisation, and irresponsible use of natural resources have all had a severe impact on water quality (Vardhan et al., 2019). Despite its significant contribution to food security, untreated wastewater application poses a serious threat

to public health and the environment due to high pollutant concentrations and contaminant loads. These toxic metals are discharged into the water on a regular basis from a variety of natural and man-made sources. Average amounts of chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), arsenic (As), and cadmium (Cd) reported in surface water bodies in various locations across the world are considerably over the maximum permitted limits for drinking water (Kumar et al., 2021; Prasad et al., 2021). This represents a public concern. As toxic metals are not

biodegradable, they tend to bioaccumulate, which means that their concentration in living organisms increases with time (Kumar et al., 2020). They are also persistent, and due to biomagnification, they can impact a variety of species directly or indirectly.

Many metal ions are toxic or carcinogenic. They can cause organ damage in the lungs, kidneys, liver, prostate, esophagus, stomach, and skin, as well as neurodegenerative illnesses and diseases including Alzheimer's and Parkinson's disease, even at extremely low concentrations (Cabral Pinto et al., 2019). Metals may harm aquatic creatures as well (phytoplankton, zooplankton, and fish), accumulating in several organs, causing oxidative damage, endocrine disruption, and immune system depression, all of which can have an impact on survival and growth (Le et al., 2019). These metal species have a tendency to leach into groundwater, causing water pollution, preventing agricultural production owing to soil erosion, and causing significant health issues in animals and nearby human communities (Birn et al., 2018). Toxic metals effects as well as their possible ecological consequences, need the development of strategies to effectively remove them from the polluted environment. This approach should be cost-effective, environmentally friendly, selective, and sensitive enough to identify traces with high precision (Malik et al., 2019). Leachate from a landfill has the potential to pollute groundwater, surface waterways, and soil, damaging the environment and endangering human health (Di Maria and Sisani, 2017). Leachate streams that run straight into the aquatic environment have an acute and chronic influence on the ecosystem, which may be highly damaging and lead to a reduction in biodiversity and sensitive species populations (Mukherjee et al., 2015). The use of chicken eggshells as an adsorbent to extract toxic metals from wastewaters such as landfill leachates has a lot of promise (Beata et al., 2021). Chicken eggshells have been used to extract organic and inorganic harmful chemicals from wastewater (Beata et al., 2021). When compared to most modified

adsorbents, chicken eggshells are less expensive to acquire. Toxic metals would be removed from landfill leachate, which would benefit the environment and public health. Low-cost farm waste adsorbents such as chicken eggshells, can be used to achieve this.

Materials and Methods

Leachate sample collection

Leachate samples were taken from the Gbahali landfill ponds. The sample was fetched into polypropylene bottles and transported to the Spanish laboratory of the University for Development Studies. The hand gloves and polypropylene bottles used for the sampling of landfill leachate were thoroughly washed. The hand gloves safeguard the hand skin and avoid direct contact with the landfill leachate since it comprises toxic metals.

Adsorbent preparation and initial analysis of landfill leachate

Chicken eggshells were obtained from fast food joints and poultry hatchery close to the University for Development Studies. The chicken eggshells were rinsed in deionised water and broken into suitable pieces and properly air-dried for 48 hrs and then ground to powder using a laboratory motor and pistol and sieved out on a 100 μm mesh sieve. The 100 mL of the collected landfill leachate was sampled and filtered using Whatman's qualitative filter paper (with 125 mm \O particle retention size). The sample was then stored in 35 mL polythene bottle and transported to the Ecological Laboratory of the University of Ghana for analysis. This was done to determine the initial concentrations of cadmium, mercury, lead, chromium, arsenic, and nickel in the landfill leachate.

Preparation of leachate stock solution

To achieve 1 mg of each of the toxic metal, the molecular weight of mercury chloride (HgCl_2) (271.50), lead nitrate ($\text{Pb}(\text{NO}_3)_2$) (331.21) and cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) (236.42) were ascertained and divided by the atomic

weight of Hg (200.60), Pb (207.20), and Cd (122.41), respectively. The stock solution was prepared by dissolving precisely weighed 1.35 g of HgCl₂, 1.60 g of Pb (NO₃)₂, and 1.93 g of Cd (NO₃) into the landfill leachate to prepare a solution of 1000 mg/L concentration of the mixture (Cd, Hg, and Pb) in a 1000 mL volumetric flask of leachate. This was done in the Spanish laboratory at the University for Development Studies.

Spiking of landfill leachates using leachate stock solutions

The initial concentrations were relatively lower in levels except for cadmium and nickel. Due to this, the landfill leachate was spiked to the maximum contamination limits. A prepared leachate stock solution containing three toxic metals of interest due to their toxicity effect was used for the spiking of landfill leachate. The contamination limits for each toxic metal were 1 mg/L, 5 mg/L, 10 mg/L, 25 mg/L and 50 mg/L.

Adsorption experiment

The adsorption experiment was done at the Spanish Laboratory of the University for Development Studies, Nyankpala campus. One gram (1 g) of the eggshells was accurately weighed using an analytic electronic weighing scale (Sartorius Analytical Weighing Scale CP125 S) and then transferred into a conical flask. After that, 100 mL of the polluted leachate (1 mg/L plus the initial concentrations of the ternary mixture) (Table 1) was transferred into the conical flask. The same process was repeated for 5 mg/L, 10 mg/L, 25 mg/L, and 50 mg/L at their respective adsorbent dosage of 2 g, 4 g, 6 g, and 8 g (Table 1). The samples

were then placed on an orbital shaker (J.P SELECTA. S.A, ROTABIT) and agitated for 60 minutes. The samples were then filtered using Whatman filter paper (Ashless, circle, Cat No. 1442 125, 125 mm Ø) and transferred into a well-labelled 40 mL plastic bottle and carefully sealed. The elutes were then transported to the Ecological Laboratory of the University of Ghana for analysis.

All the adsorption experiments were performed at a pH range of 7.25 to 8.01 and temperature of 25 °C. The elutes obtained were transported to the Ecological Laboratory of the University of Ghana for analysis using Perkin Elmer PIN Accel 900T GRAPHITE Atomic Absorption

$$\text{Recovery (\%)} = \frac{\text{mean value}}{\text{added amount}} \times 100$$

Spectrophotometer (AAS) (Waltham, United States of America). The percentage recovery of standard for each metal was calculated as: and the recovery (%) obtained was 99.70%.

Calculation of adsorption efficiency of cadmium, mercury and lead

The equilibrium concentration of the adsorbent and the uptake of the toxic metal which is represented by the symbol Q_e for each toxic metal at each adsorbent dosage was calculated using equation 1. The removal efficiency (Q_e) was calculated as:

$$Q_e = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{Equ. (1)}$$

Where Q_e is the adsorption capacity, C_i is the initial concentration of the toxic metal, and C_f is the final concentration of toxic metals after adsorption.

TABLE 1
Toxic metal concentrations and varied dosages in the ternary solution for adsorption

| Toxic metal | Conc. (mg L ⁻¹) at 1 g | Conc. (mg L ⁻¹) at 2 g | Conc. (mg L ⁻¹) at 4 g | Conc. (mg L ⁻¹) at 6 g | Conc. (mg L ⁻¹) at 8 g |
|-------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Cadmium | 1.206 | 5.206 | 10.206 | 25.206 | 50.206 |
| Mercury | 1.001 | 5.001 | 10.001 | 25.001 | 50.001 |
| Lead | 1.001 | 5.001 | 10.001 | 25.001 | 50.001 |

Note: The initial concentrations were added to the spiked concentrations to achieve the contamination limits.

Langmuir and Freundlich Isotherms

Langmuir and Freundlich isotherm models were mathematically expressed based on their assumptions as follows: The Langmuir isotherm model was first described in the removal of the gas molecule onto an analogous solid surface (Khayyun and Mseer, 2019). This isotherm is often used to determine and know the maximum removal or adsorption capacity including the type of interaction between the metals and the adsorbent (Boukhelifi et al., 2020).

Ecological Risk Index (RI)

The ecological risk index (RI) was formulated by Hakanson in 1980, and was used to assess the leachate ecological risk of the toxic metals. The toxic level, ecological sensitivity, and total concentration of toxic metals were taken into consideration by the method of Kabala and Singh (2001). The possible ecological risk index was calculated following these steps below equations (1, 2 and 3):

$$C_f = \frac{C_m}{C_n} \dots\dots\dots \text{Eq 1}$$

$$E_r = T_r * C_f \dots\dots\dots \text{Eq 2}$$

$$RI = \sum E_r \dots\dots\dots \text{Eq 3}$$

where C_f is the contamination factor, C_m and C_n are the concentrations of each toxic element in the mobile and stable fractions, respectively, E_r and T_r were the potential ecological risk factor and the toxic response factor (30 for Cd, 40.5 for Hg, 5 for Pb, 2 for Cr, 5 for Ni and 10 for As) (Hakanson, 1980). The contamination factor, potential ecological risk index potential and ecological risk values (Table 2) were used to evaluate the risk of

toxic metal in the leachate.

Results and Discussion

Ecological risk of the toxic metals in the leachate

The concentration of cadmium in the leachate exceeded its limit making it toxic to the ecology which can pose even greater risks to the ecosystem (Tables 2 and 3). Cadmium toxicity mostly impacts growth and replication. Fungi are the most impacted soil microorganisms, and with modest contact to the metal in soil, there is selection for resistant types of microorganisms. Cadmium is toxic to a wide variety of microorganisms. The main effect is on the rate of growth. The majority of soil microorganisms have been damaged, with some species becoming extinct as a result of cadmium contamination. After a brief contact to the metal in the soil, resistant bacteria are chosen (Boateng et al., 2019). The concentration of lead in the leachate is lesser making it less toxic to the environment (Tables 2 and 3). The concentration of chromium in the sampled leachate is lower than its threshold which makes it less detrimental to the ecology. Chromium, unlike the other hazardous elements described, is vital to humans and animals in the form of Cr (III). Chromium is generally stable in air and clean water, but when it comes into contact with organic matter in biota, soil, or water, it is converted to the trivalent form (European Commission, 2002). The leachate concentration of nickel exceeded its limit making it toxic to the ecology. One of the most toxic heavy metals is nickel. The concentration of mercury in

TABLE 2
Grade of the C_p , E_r and RI

| C_f | E_r | RI | Ecological risk |
|------------------|----------------------|----------------------|----------------------------|
| < 1 | ≤ 40 | $RI \leq 150$ | Low contamination |
| $1 < C_f \leq 3$ | $40 < E_r \leq 80$ | $150 < E_r \leq 300$ | Moderate contamination |
| $3 < C_f \leq 6$ | $80 < E_r \leq 160$ | $300 < E_r \leq 600$ | Considerable contamination |
| $6 < C_f \leq 9$ | $160 < E_r \leq 320$ | $RI > 600$ | High risk |
| $C_f > 9$ | $E_r \geq 320$ | - | Very high contamination |

TABLE 3
Initial toxic metal concentration of landfill leachates

| Metal | Cadmium | Mercury | Lead | Chromium | Nickel | Arsenic | PERI |
|----------------------------------|---------|----------------------|-------------------------|-------------------------|--------|---------|-------|
| Mean conc. (mg L ⁻¹) | 0.206 | 0.0012 | 0.001 | 0.006 | 0.341 | 0.0024 | |
| StD | 0.002 | 1 x 10 ⁻⁴ | 0.00 | 0.001 | 0.001 | 0.0001 | - |
| WHO, 2011 | 0.003 | 0.001 | 0.010 | 0.050 | 0.020 | 0.010 | - |
| C _f | 0.206 | 0.005 | 1.43 x 10 ⁻⁵ | 6.67 x 10 ⁻⁵ | - | 0.0002 | 0.211 |
| E _r | 6.180 | 0.194 | 7.14 x 10 ⁻⁵ | 0.0001 | - | 0.002 | 6.376 |

the leachate is lower making it less toxic to the ecology. Its fluidity at room temperature is more noticeable, but it is more essential for the prospective exposure of man and the environment. Mercury, however, accumulates in higher plants, particularly perennials. In plants, the major impact is linked to the root (European Commission, 2002). The concentration of arsenic in the sampled leachate is lower than the other metals studied which makes it less detrimental to the ecology. Arsenic and several of its derivatives are extremely powerful toxins that can affect the environment.

The toxic metals in the leachate were within the low contamination of less than 1, low-

risk category (E_r < 40) and PERI < 150 indicating low ecological risks (Table 2). The contamination factor is generally used to assess the anthropogenic effects on the leachate quality. The C_f and E_r values for the toxic metals were Cr > Pb > As > Hg > Cd (Table 2). The leachate from the landfill site was practically uncontaminated by Cr, Pb, As, Hg and Cd (C_f < 1).

Adsorption efficiency of toxic metals in a ternary system by eggshells in landfill leachate
Adsorption efficiencies in the present study conducted at all dosages under varied concentrations in the ternary systems was presented in Table 4. The use of low-

TABLE 4
Adsorption of ternary metals by chicken eggshells in landfill leachate

| Metals | Dosage | Initial concentration | Percentage |
|--------|--------|---------------------------|------------|
| Cd | 1 g | 1.206 mg L ⁻¹ | 98.67% |
| | 2 g | 5.206 mg L ⁻¹ | 99.64% |
| | 4 g | 10.206 mg L ⁻¹ | 99.80% |
| | 6 g | 25.206 mg L ⁻¹ | 99.90% |
| | 8 g | 50.206 mg L ⁻¹ | 99.99% |
| Hg | 1 g | 1.001 mg L ⁻¹ | 99.89% |
| | 2 g | 5.001 mg L ⁻¹ | 99.98% |
| | 4 g | 10.001 mg L ⁻¹ | 99.99% |
| | 6 g | 25.001 mg L ⁻¹ | 99.99% |
| | 8 g | 50.001 mg L ⁻¹ | 99.99% |
| Pb | 1 g | 1.001 mg L ⁻¹ | 99.98% |
| | 2 g | 5.001 mg L ⁻¹ | 99.98% |
| | 4 g | 10.001 mg L ⁻¹ | 99.99% |
| | 6 g | 25.001 mg L ⁻¹ | 99.98% |
| | 8 g | 50.001 mg L ⁻¹ | 99.99% |

cost chicken eggshells will significantly contribute to recovering toxic metals from the environment via adsorption processes. The removal of cadmium from the environment is essential as it is considered toxic to the natural environment and human health. The removal efficiency of cadmium by chicken eggshells was $\geq 98.67\%$. This depicts a very high adsorption efficiency of eggshells. High rate of adsorption of the cadmium in the ternary system is attributed to the varying pores and heterogeneous surface of the ground chicken eggshells which aid in the adsorption. A similar study by Tizo et al. (2018) reported how the surface area influenced the high rate of adsorption in wastewater.

The chicken eggshells were able to adsorb $\geq 99.89\%$ of the mercury ions. This demonstrates a very high adsorption efficiency by the chicken eggshells. The eggshells can bind toxic metal ions and various actinides from aqueous solution (Chen et al., 2013). The cuticle on the outside surface, a spongy (calcareous) layer, and an interior lamellar (or mammillary) layer, all of which are organised in a three-layered structure, make up the eggshell (Lunge et al., 2012).

Lead is considered to be one of the most toxic metals that find its way into the environment. This study shows the percentage of the lead being removed from the landfill leachate was $\geq 99.98\%$. The adsorption capacity of the chicken eggshells did show an increase in all of the batch experiments due to the high affinity of chicken eggshells for toxic metal ions that did fully occupy the binding sites. As some experimental factors such as contact time, the dosage of chicken eggshells, pH, and

temperature considered by this study favoured the ions adsorption in the landfill leachate sample obtained for the experiment.

An increase in the dosage of adsorbent with its respective increase in concentration showed complete adsorption. This is because, as the adsorbent increases, the number of active sites at the surface also increases, this aids the interaction between the ions in the adsorbate with the adsorbent (Çay et al., 2004). The results indicate that increasing the adsorbent dose resulted in a higher percent of removal of the cadmium in the landfill leachate. Chicken eggshells also contain calcium, magnesium, copper, iron, manganese, molybdenum, sulphur and many more other useful elements (Elabbas et al., 2016).

pH and temperature for toxic metals in ternary system

pH values recorded ranged from 7.25 to 8.01 for the toxic metals in ternary systems (Table 5). The toxic metal ions interacted with the lignin on the surface of the adsorbent via an ion exchange mechanism, resulting in an increased adsorption at higher pH levels (Celik and Demirbas, 2005). The pH of a solution influences adsorption via the adsorbent's surface charge, degree of ionisation, adsorbent speciation, and in certain circumstances, even changing the adsorbent's surface charge (Cay et al., 2004; Alghandi et al., 2019). Adsorption at the surface of the adsorbent is also affected by changes in the adsorptive behaviour of the adsorbent's accessible functional groups when the pH of an aqueous solution rises (Duwiejuah, 2017). Also, temperature is an important parameter in determining adsorption

TABLE 5
pH for toxic metals in ternary systems at varied dosages

| Metals | Concentration (mg L ⁻¹) | pH |
|--------------|-------------------------------------|------|
| Cd : Hg : Pb | 1.206 : 1.001 : 1.001 | 7.25 |
| Cd : Hg : Pb | 5.206 : 5.001 : 5.001 | 7.73 |
| Cd : Hg : Pb | 10.206 : 10.001 : 10.001 | 7.98 |
| Cd : Hg : Pb | 25.206 : 25.001 : 25.001 | 7.75 |
| Cd : Hg : Pb | 50.206 : 50.001 : 50.001 | 8.01 |

efficiency. At high temperatures, the mobility of metal ions is improved (Waswar, 2010). However, there is the likelihood of damaging the structure and surface sites of the adsorbent.

Langmuir and Freundlich adsorption isotherms

Langmuir adsorption isotherm was used to describe how cadmium, lead and mercury interacted with chicken eggshell active sites (surface) in the landfill leachate. Cadmium showed a maximum adsorption capacity of 6.03×10^{-6} mg g⁻¹ which was lower as compared

to 11.10 mg g⁻¹ reported by Naema and Omar (2019). The study had K_L of 2.74×10^{-2} mg L⁻¹ as compared to 1.13 mg L⁻¹ reported by Naema and Omar (2019), R_L for cadmium in the study was 1.27 and a coefficient of determination (R^2) of 0.46 (Figure 1). The R_L for cadmium was 1.27 which implies the nature of the adsorption by eggshells was favourable because the R_L is greater than 1 (Ayawei *et al.*, 2017). Cadmium had the lowest coefficient of determination. For mercury, the maximum adsorption capacity in the ternary system was 1.25×10^{-7} mg g⁻¹ and an adsorption equilibrium (K_L) of

TABLE 6
Adsorption isotherm modelling of the results of the ternary systems

| Ion | Langmuir parameter | | | | Freundlich parameter | | | |
|-----|---------------------------------|-----------------------------|-------|-------|----------------------|-------|-----------------------------|-------|
| | Q_{max} (mg g ⁻¹) | K_L (mg L ⁻¹) | R_L | R^2 | $1/n$ | N | K_F (mg g ⁻¹) | R^2 |
| Cd | 6.03×10^{-6} | 2.74×10^{-2} | 1.27 | 0.46 | 0.81 | 1.24 | 28.21 | 0.26 |
| Hg | 1.25×10^{-7} | 8.69×10^{-4} | 1.01 | 0.83 | -4.84 | -0.21 | 1.64×10^{17} | 0.43 |
| Pb | 5.00×10^{-7} | 1.02×10^{-3} | 1.01 | 0.84 | -1.84 | -0.54 | 7.07×10^7 | 0.40 |

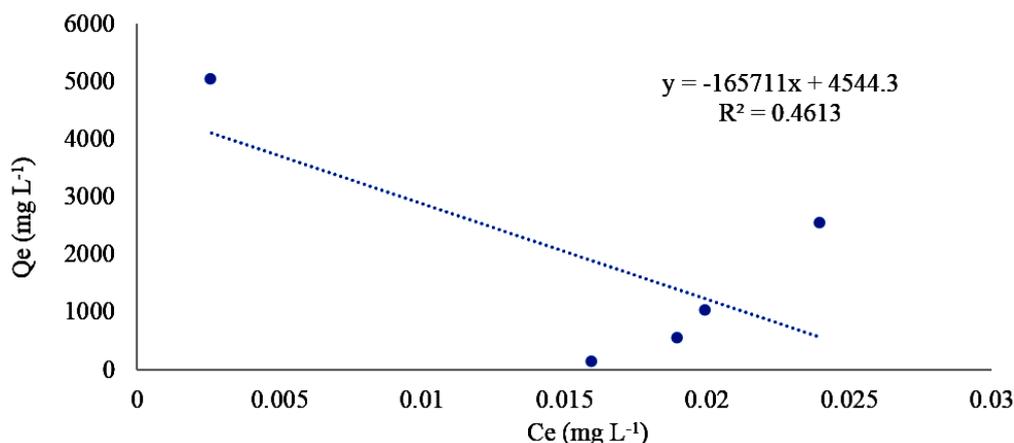


Fig. 1 Langmuir isotherm graph for the adsorption of cadmium in landfill leachate by ground chicken eggshells in the ternary system (Dosage: 1 g, 2 g, 4 g, 6 g, and 8 g; solution volume: 100 mL; contact time: 60 min; Temp.: 25 °C; rotational speed: 14.8 ± 1 U/min)

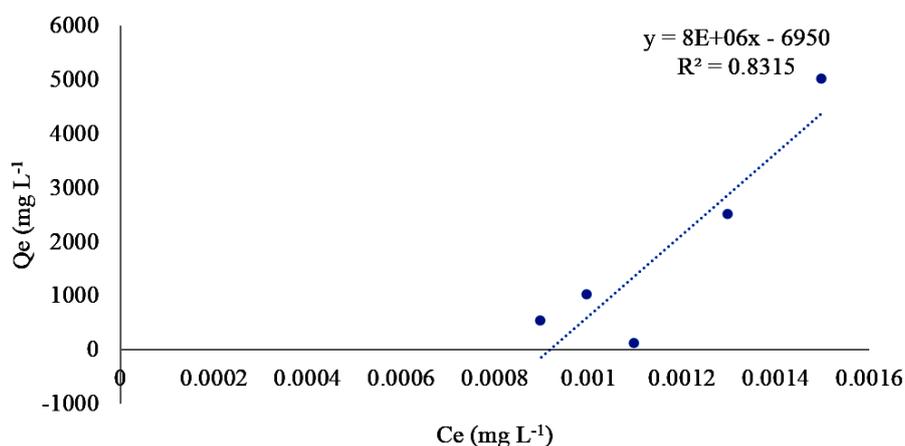


Fig. 2 Langmuir isotherm graph for the adsorption of mercury in landfill leachate by ground chicken eggshells in the ternary system (Dosage: 1 g, 2 g, 4 g, 6 g, and 8 g; solution volume: 100 mL; contact time: 60 min; Temp.: 25 °C; rotational speed: 14.8 ± 1 U/min)

$8.69 \times 10^{-4} \text{ mg L}^{-1}$ (Table 6). R_L for mercury in the study was 1.01 and a correlation coefficient (R^2) of 0.83 (Figure 2). In a similar study by Alamillo-López et al. (2020) in an attempt to have a maximum adsorption capacity using chicken eggshells, the authors had 1.51 mg g^{-1} but in the present study, mercury recorded a K_L lower than 7.41 mg L^{-1} compared to what Alamillo-López et al. (2020) had. The R_L of mercury was 1.01 implying that the adsorption was favourable (Ayawei et al., 2017). The Langmuir isotherm is the best fit for mercury. Also in the study, it was shown that lead had a maximum adsorption capacity in the ternary system as $5.00 \times 10^{-7} \text{ mg g}^{-1}$ and an equilibrium (K_L) of $1.02 \times 10^{-3} \text{ mg L}^{-1}$ (Table 6). The R_L for lead was 1.01 and a coefficient of determination (R^2) of 0.84 (Figure 3). The maximum adsorption capacity of the lead was $5.00 \times 10^{-7} \text{ mg g}^{-1}$ as compared to 3.90 mg g^{-1} as reported by Alamillo-López et al. (2020). The adsorption energy (K_L) for lead in the present study was $1.02 \times 10^{-3} \text{ mg L}^{-1}$ as compared to 2.07 mg L^{-1} reported by Alamillo-López et al. (2020). The present study indicated that R_L of lead was 1.01 implying the adsorption was favourable (Ayawei et al., 2017,) and also a chemical process. The R^2 obtained for lead was 0.84 which indicates that the best fit model was Langmuir isotherm.

The Freundlich isotherm offers an expression that enables the description of heterogeneous surfaces of adsorbent and the exponentially

distributed active sites on them and their energies (Ayawei et al., 2017). The $1/n$ (is the adsorption intensity) values obtained for the toxic metals in the ternary system for cadmium, mercury, and lead were 0.81, -4.84, and -1.84, respectively (Table 6). The $1/n$ of -4.84 and -1.84 for mercury and lead which were negative, signify normal adsorption by heterogeneous media where high energy sites were occupied first, before adsorption at lower energy sites. However, $1/n$ values for Cd, Hg and Pb were below 1 which indicates that a normal adsorption has occurred. The $1/n$ shows the heterogeneous nature of the surface of biochar and how energy is relatively distributed (Dada et al., 2012). Also, the N values of the cadmium, mercury, and lead in the ternary system were 1.24, -0.21 and -0.54, respectively (Table 6). For cadmium, the N value obtained was 1.24 which indicates the strongest relationship between the adsorbate and adsorbent. Naema and Omar (2019) obtained an N value of 0.10 for cadmium.

The K_F (mg/g) values for cadmium, mercury, and lead were 28.22, 1.64×10^{17} , and 7.07×10^7 , respectively (Table 6). The K_F is a Freundlich constant that shows adsorption capacity of the adsorbent. The K_F recorded for the adsorption process was 1.64×10^{17} and 7.07×10^7 for mercury and lead, respectively. Large Freundlich constant (K_F) implies that the contaminants (Hg and Pb) were strongly adsorbed on the adsorbent (eggshells). The

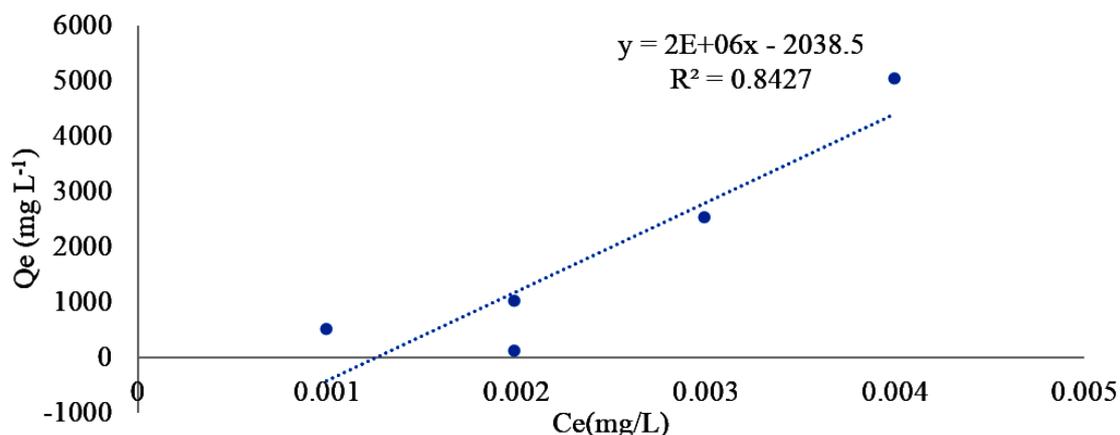


Fig. 3 Langmuir isotherm graph for the adsorption of lead in landfill leachate by ground chicken eggshells in the ternary system (Dosage: 1 g, 2 g, 4 g, 6 g, and 8 g; solution volume: 100 mL; contact time: 60 min; Temp.: 25 °C; rotational speed: $14.8 \pm 1 \text{ U/min}$)

present study recorded 28.21 mg g⁻¹ for cadmium as compared to 2.42 mg/g⁻¹ reported by Naema and Omar (2019). The Freundlich

adsorption isotherm R² values for cadmium, mercury and lead were 0.26, 0.43, and 0.40, respectively (Table 6, Figures 4-6) which

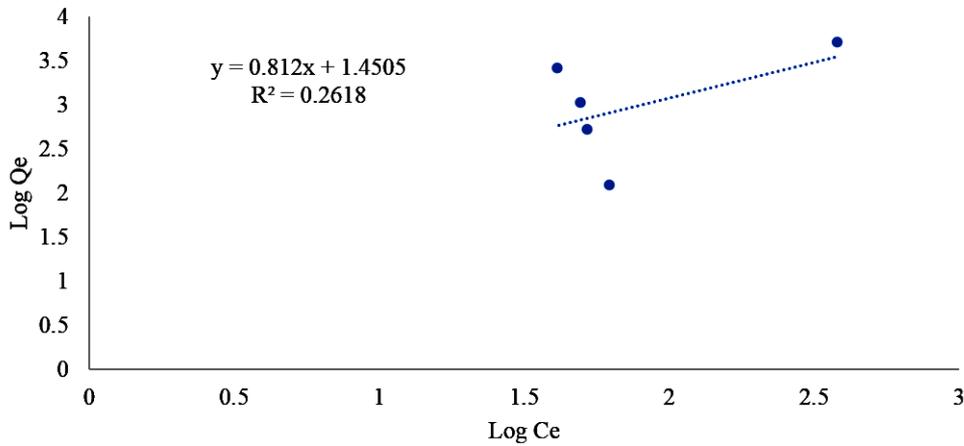


Fig. 4 Freundlich isotherm graph for the adsorption of cadmium in landfill leachate by ground chicken eggshells in the ternary system (Dosages: 1 g, 2 g, 4 g, 6 g, and 8 g; solution volume: 100 mL; contact time: 60 min; Temp.: 25 °C; rotational speed: 14.8 ± 1 U/min)

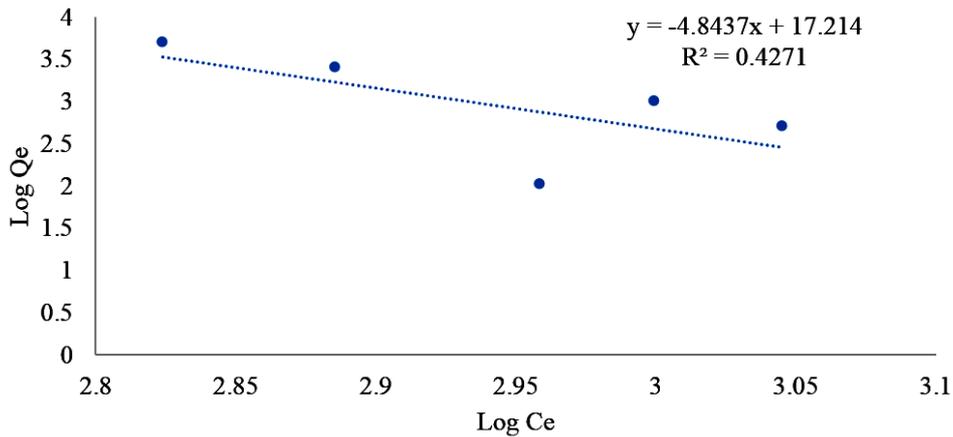


Fig. 5 Freundlich isotherm graph for the adsorption of mercury in landfill leachate by ground chicken eggshells in a ternary system (Dosages: 1 g, 2 g, 4 g, 6 g, and 8 g; solution volume: 100 mL; contact time: 60 min; Temp.: 25 °C; rotational speed: 14.8 ± 1 U/min)

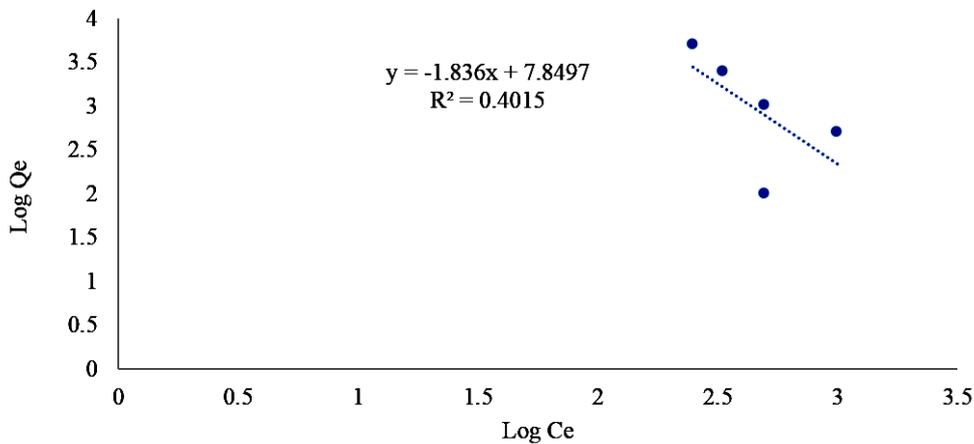


Fig. 6 Freundlich isotherm graph for the adsorption of lead in landfill leachate by ground chicken eggshells in a ternary system (Dosages: 1 g, 2 g, 4 g, 6 g, and 8 g; solution volume: 100 mL; contact time: 60 min; Temp.: 25 °C; rotational speed: 14.8 ± 1 U/min)

suggest the Freundlich isotherm did not well describe the adsorption process.

Conclusion

The removal efficiency of cadmium, mercury and lead from a landfill leachate by chicken eggshells adsorbent was very high and effective. The Langmuir adsorption isotherm well described the experimental results and gave the best fitness of the data for the three toxic metals. The toxic metals studied in the leachate were within the low contamination and low-risk category indicating low ecological risks. Ground chicken eggshell can be utilised as an effective and inexpensive adsorbent for toxic metals removal, particularly in landfill leachate, allowing the remediated wastewater to be utilised for other water-related activities in the environment. Similar adsorptive experiments should be carried out with different contact times, temperatures, and metal concentrations. The ground chicken eggshells can be applied at rate of 1 g, 2 g, 4 g, 6 g and 8 g dependent on adsorbate concentration for effective removal.

Acknowledgements

The authors wish to extend their special thanks to Mr. Abdul-Aziz Bawa and Mr. Saeed Abdullah for their assistance during the experiment in Spanish Laboratory of the University for Development Studies and Mr. Prince Owusu of the Ecological Laboratory, University of Ghana, for the analysis of the samples.

Conflict of interest

The authors declare that there are no conflicts of interests.

References

- Agrawal, V. R., Vairagade, V. S. and Kedar, A. P.** (2017). Activated carbon as an adsorbent in advance treatment of wastewater. *Journal of Mechanical Engineering*, **14(4)**:36 – 40.
- Alamillo-López, V. M., Sánchez-Mendieta, V., Olea-Mejía, O. F., González-Pedroza, M. G. and Morales-Luckie, R. A.** (2020). Efficient Removal of Heavy Metals from Aqueous Solutions Using a Bionanocomposite of Eggshell/Ag-Fe. *Catalysts*, **10(7)**: 727; <https://doi.org/10.3390/catal10070727>
- Alghandi, A. A., Al-Odayni, A., Saeed, S. W., Al-Kahtani, A., Alharti, A. F. and Aouak, T.** (2019). Efficient adsorption of lead (II) from aqueous phase solutions using polypyrrole-based activated carbon. *Materials*, **12(12)**:1 - 16.
- Ayawei, N., Ebelegi, A. N. and Wankasi, D.** (2017). Modelling and interpretation of adsorption isotherms. *Journal of Chemistry*. **2017**: 1 - 11. <https://doi.org/10.1155/2017/3039817>.
- Beata, C. G., Grześkowiak, T., Szymański, A., Zgola-Grześkowiak, A. and Frankowski, R.** (2021). Alkylphenols and alkylphenol ethoxypolates their impact on living organisms, biodegradation, and environmental pollution. In *Biodegradation, Pollutants and Bioremediation Principles* (pp. 1-32).
- Birn, A. E. A., Shipton, L., Schrecker, T. and Shipton, L.** (2018). Canadian mining and ill health in Latin America: a call to action. *Canadian Journal of Public Health*, **109(5-6)**: 786–790. [10.17269/s41997-018-0113-y](https://doi.org/10.17269/s41997-018-0113-y).
- Boateng, T. K., Opoku, F. and Akoto, O.** (2019). Heavy metal contamination assessment of groundwater quality: a case study of Oti landfill site, Kumasi. *Applied Water Science*, **9(2)**:1 - 15.
- Cabral Pinto, M. M. S., Marinho-Reis, P., Almeida, A., Pinto, E., Neves, O., Inácio, M., Gerardo, B., Freitas, S., Simões, M.R., Dinis, P. A., Diniz, L., da Silva, E. F. and Moreira, P. I.** (2019). Links between cognitive status and trace element levels in hair for an environmentally exposed population: A case study in the surroundings of the estarreja industrial area. *International Journal of Environmental Research and Public Health*, **16(22)**: 4560; <https://doi.org/10.3390/ijerph16224560>

- Cay, S., Uyanik, A. and Ozasik, A.** (2004). Single and binary component adsorption on copper (II) and cadmium (II) from aqueous solution using tea industry waste. *Separation and Purification Technology*, **38(3)**:273 - 280.
- Celik, A. and Demirbas, A.** (2005). Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. *Energy Sources*, **27(11)**:1167 - 1177.
- Chen, G., Shan, R., Shi, J. and Yan, B.** (2013). Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. *Bioresource Technology*, **171**:428 - 432.
- Dada, A. O., Olalekan, A. P., Olatunya, A. M. and Dada, O. J. I. J. C.** (2012). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, **3(1)**:38 - 45.
- Di Maria, F. and Sisani, F.** (2017). A life cycle assessment of conventional technologies for landfill leachate treatment. *Environmental Technology & Innovation*, **8**:411 - 422.
- Dwiejuah, A. B.** (2017). Eco-friendly biochars for the adsorption of heavy metals from aqueous phase. MPhil Thesis. University for Development Studies, Ghana. Retrieved from www.udsspace.uds.edu.gh.
- Elabbas, S., Ouazzani, N., Mandi, Berrekhis, F., Perdicakis, M., Pontvianne, S., Pons, M. N., Lopicque, F. and Leclerc, J. P.** (2016). Treatment of highly concentrated tannery wastewater using electrocoagulation: influence of the quality of aluminum used for the electrode. *Journal of Hazardous Material*, **319**:69 - 77.
- European Commission** (2002). Heavy metals in waste. Department for Environment, Food & Rural Affairs, February, pp 1 - 83.
- Freundlich, H. M. F.** (1906). Uber die adsorption in losungen. *Zeitschrift für Physikalische Chemie (Leipzig)*, **57**:385 - 470.
- Hakanson, L.** (1980). An ecological risk index for aquatic pollution control a sedimentological approach. *Water Research*, **14**:975 - 1001.
- Kabala, C. and Singh, B. R.** (2001). Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *Journal of Environmental Quality*, **30**:485 - 492.
- Khayyun, S. T. and Mseer, A. H.** (2019). Comparison of the experiment results with the Langmuir and Freundlich models for copper removal on limestone adsorbent. *Applied Water Sciences*, **9**:170.
- Kumar, A., Cabral-Pinto, M., Kumar, A., Kumar, M. and Dinis, P. A.** (2020). Estimation of risk to the eco-environment and human health of using heavy metals in the Uttarakhand Himalaya, India. *Applied Sciences*, **10**:1-18. <http://dx.doi.org/10.3390/app10207078>.
- Kumar, A., Jigyasu, D. K., Kumar, A., Subrahmanyam, G., Mondal, R., Shabnam, A. A., Cabral Pinto, M. M. S., Malyan, S. K., Chaturvedi, A. K., Gupta, D. K., Fagodiya, R. K., Khan, S. A. and Bhatia, A.** (2021). Nickel in terrestrial biota: Comprehensive review on contamination, toxicity, tolerance and its remediation approaches. *Chemosphere*, **275**: 129996. <http://dx.doi.org/10.1016/j.chemosphere.2021.129996>.
- Le, T. T. N., Le, V. T., Dao, M. U., Nguyen, Q. V., Vu, T. T., Nguyen, M. H., Tran, D. L. and Le, H.S.** (2019). Preparation of magnetic graphene oxide/chitosan composite beads for effective removal of heavy metals and dyes from aqueous solutions. *Chemical Engineering Communications*, **206**:1337 - 1352. <http://dx.doi.org/10.1080/00986445.2018.1558215>.
- Lunge, S., Thakre, D., Kamble, S., Labhsetwara, N. and Rayalua, S.** (2012). Alumina-supported carbon composite material with exceptionally high DE fluoridation property from eggshell waste. *Journal of Hazardous Materials*, **237**:161 - 169.
- Malik, L. A., Bashir, A., Qureshi, A. and Pandith, A. H.** (2019). Detection and removal of heavy metal ions: a review.

- Environmental Chemistry Letter*, **17**:1495 – 1521.
- Mukherjee, S., Mukhopadhyay, S., Hashim, M. A. and Sen Gupta, B.** (2015). Contemporary environmental issues of landfill leachate: assessment and remedies. *Critical Reviews in Environmental Science and Technology*, **45(5)**: 472 - 590.
- Naema, S. Y. and Omar, M. E.** (2019). Removal of Cd (II) from aqueous solution using egg shell as low cost sorbent. *SSRG International Journal of Applied Chemistry*, **6**:1 -11.
- Prasad, S., Yadav, K. K., Kumar, S., Gupta, N., Cabral-Pinto, M. M. S., Rezaia, S., Radwan, N., Alam, J.,** (2021). Chromium contamination and effect on environmental health and its remediation: A sustainable approaches. *Journal of Environmental Management*, **285**:112174. <http://dx.doi.org/10.1016/j.jenvman.2021.112174>.
- Tizo, M. S., Blanco, L. A. V., Cagas, A. C. Q., Cruz, B. R. B. D., Encoy, J. C., Gunting, J. V., Arazo, R. O. and Mabayo, V. I. F.** (2018). Efficiency of calcium carbonate from eggshells as an adsorbent for cadmium removal in aqueous solution. *Sustainable Environment Research*, **28(6)**:326 – 332.
- Vardhan, K. H., Kumar, P. S. and Panda, R. C.** (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *Journal of Molecular Liquids*, **290**: 111197. <http://dx.doi.org/10.1016/j.molliq.2019.111197>.
- Wasewar, L. K.** (2010). Adsorption of metals onto tea factory waste: a review. *International Journal of Research and Reviews in Applied Sciences*, **3(3)**:303 - 322.