Adsorption of Toxic Metals from Landfill Leachate onto Guinea Fowl Eggshells in the Era of Green Chemistry

Abudu Ballu Duwiejuah,* Elijah Yinigani Ayine, and Joseph Payne

One of the best and most affordable ways to remove harmful metals from water is by adsorption. This study investigated the efficiency of guinea fowl (*Numida meleagris*) eggshells as a low-cost adsorbent for cadmium (Cd) and nickel (Ni) removal from landfill leachate. In replicas, 100 mL wastewater was added to each of the weighed adsorbent dosages (1 g, 1.5 g, 2 g, 2.5 g, 3.0 g, and 3.5 g) in a flat-bottom flask and agitated for 60 minutes at pH of 7.82 and temperature 24 °C. The adsorption efficacy of cadmium and nickel by guinea fowl eggshells were 90.5% to 96.5% and 96.1% to 99.3%, respectively. The maximum adsorption capacity of cadmium was 4.89×10^{-2} mg/g and an adsorption equilibrium (K_L) 22.74 mg/L. The Langmuir isotherm model was better fitted to the results of the experiment than the Freundlich isotherm model.

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Contact information: Department of Biotechnology, Faculty of Biosciences, University for Development Studies, Tamale, Ghana;
** Corresponding author: aduwiejuah@uds.edu.gh*

INTRODUCTION

Poor landfill management results in the production of toxic leachate, which has a substantial negative influence on the nearby freshwater and groundwater. The aqueous effluent produced by solid waste as a result of its physical, chemical, and biological modification in landfills is known as leachate. Among the several elements that make up landfill leachate, heavy metals are non-biodegradable, capable of lowering the quality of surface and groundwater, and hazardous to biological systems even at low concentrations (Parvin and Tareq 2021).

Pollution of natural water with toxic metals has increased due to the expansion of industrial growth and development (Agboola *et al.* 2021). This causes environmental problems, including risks to human health. Toxic metals are non-biodegradable and toxic, and their presence in wastewater is a significant cause for concern (Isa *et al.* 2020). Also, Cd^{2+} and Ni^{2+} are found in wastewater such as agricultural sources, electroplating, metallurgical, mining, tanneries, and painting (Sultana *et al*. 2022). Cd^{2+} and Ni^{2+} are accumulative and toxic even at low concentrations, and they are potentially carcinogenic to living organisms (Allaoui *et al*. 2021). Most toxic ions offer a substantial threat to human health, as they can lead to serious illnesses and a variety of disorders when consumed in excess.

The insufficient removal of the Cd^{2+} and Ni^{2+} during water treatment is another concern of the environment, and the efficiency of treatments employed by the industries makes it more problematic. Not all chemical and physical separation processes are efficient for removal of these contaminants from an aqueous solution (Ramos *et al*. 2022). The existing methods of treatments are costly and regularly end up generating secondary contaminants (Sultana *et al*. 2022). This prompts the need for effective processes and simple techniques that are economically viable, environmentally efficient, and do not generate secondary contaminants. Among these, the process of adsorption stands out owing to its low cost, adsorbate recovery possibility, and operational simplicity (Ramos *et al*. 2021).

It was in the early ‘90s that the concept of green chemistry was developed by the United States Environmental Protection Agency (US-EPA); this concept has attracted great attention (Mukherjee 2022). In the era of green chemistry, pollution control is achieved by methods and technologies that are eco-friendly, less costly, simple to use, and effective. The concept of green chemistry leads to the search for new technologies and processes that from the very beginning cut short or prevent environmental contamination by reducing the chemical wastes volumes and their toxicity, using inoffensive or safer materials (Mukherjee 2022). This science is presently in an explosive growth and developmental stage. Green chemistry has emerged as a novel avatar to solve environmental pollution in order to secure the future (Anastas and Williamson 1996). In summary, green chemistry aims to design, produce, and use efficient, safe, effective, and more ecologically benign chemical processes and products, leading to environmental pollution control.

Eggshells offer numerous advantages in the green chemistry concept as adsorbents. These include affordability, eco-friendliness, and not requiring special preparations. The manufacturing industry has a severe problem of high heavy metal concentrations in wastewater. Eggshells, which are generated by the food and poultry industries with approximately 110 billion tonnes global annual production, have been considered a waste that ends up in landfills (Jannat *et al.* 2022). Guinea fowl eggs are one of the most consumed and enjoyed foods mostly in Africa and especially in Northern Ghana. Despite the fact that guinea fowl are supposed to have originated in Africa, global production has grown quickly in recent years. Under semi-intensive conditions, guinea fowl can be successfully raised with little effort (Yildirim 2012). Guinea fowl eggshells is an unappreciated waste; when improperly disposed, it becomes a public health and environmental concern and can contribute to proliferation of harmful microbes (Ayodele *et al*. 2021).

Eggshell contains 90 to 98% calcium carbonate ($CaCO_3$) (Setiawan *et al.* 2018; Jannat *et al.* 2022). It has been reported to contain 94% $CaCO_3$, 4% organic matter, 1% magnesium carbonate, and 1% calcium phosphate by weight (Ahmad *et al.* 2012) making calcium more highly bioavailable for easier adsorption than the commercially available limestone (Setiawan *et al.* 2018; Jannat *et al.* 2022). Mammillary cores, which are organic aggregates rich in sulphated proteoglycans and are present on the outside of eggshells, have the potential to bind calcium and serve as places where calcite crystals develop (Peigneux *et al.* 2020). The eggshell potentially can be applied in recycling, including treatment of wastewater.

Eggshells have economic value as an adsorbent (Lee *et al*. 2022). Additionally, metal ions and other actinides from diluted water solution might be bound by eggshells (Chen *et al.* 2013). Aside the cuticle on the outside, a spongy layer, and an inner lamellar layer are all ceramic components that make up the eggshell's distinctively three-layered structure (Lunge *et al.* 2012). Eggshells have a high calcium carbonate concentration, which potentially makes them a good adsorbent for the treatment of water and soils polluted by metallic ions (Lee *et al*. 2022). Eggshells therefore have emerged as a suitable candidate in the search for readily available, cost-effective, non-toxic, and versatile material as potential adsorbent to remove contaminants from water (Mittal *et al*. 2016).

Considerably toxic metals including arsenic, cadmium, chromium, copper, lead, manganese, and mercury could be removed using eggshells. Elabbas *et al.* (2016) explored the removal of Cr(VI) ions from wastewater using crushed hen eggshells. Baláž *et al.* (2015) examined a batch adsorption system of Cd(II) removal capacity in wastewater using crushed eggshell. Park *et al.* (2007) studied the comparative Cr and Cd removal from electroplating wastewaters.

The eggshell's porosity makes it a desirable material to utilize as a green source of adsorbent. In the adsorption of toxic metals from landfill leachate, chicken eggshells, guinea fowl eggshells, groundnut husk, rice husk, and others may be used. In this study, guinea fowl eggshells were used as a low-cost and green source adsorbent for cadmium and nickel adsorption from landfill leachate.

EXPERIMENTAL

Landfill Leachate Collection

Leachate was collected from Gbahili landfill site in Tamale, Northern Region, Ghana. Samples were collected into polypropene bottles, labelled, and transported at ice temperature.

Guinea Fowl Eggshells Preparation

The eggshells obtained from guinea fowl hatcheries in Tamale, Ghana were washed in deionised water, broken into suitable pieces, and sun dried for 48 h. Broken eggshells were ground into powder using a mortar and pestle and sieved using a 100 µm mesh sieve.

Experimental Setup

The landfill leachate sample was filtered with Whatman filter paper and analysed for the cadmium and nickel concentrations. The pH of the leachate from the landfill was measured using pH meter. A dosage of 0.5 g of powdered guineafowl eggshells (adsorbent) was added to 100 mL of landfill leachate in a conical flask and agitated for 60 minutes using an orbital shaker (Rotabit orbital shaker with 20 rpm to 230 rpm rotational speed) at a speed of 50 rpm. Repeated experiments were done for 1 g, 1.5 g, 2 g, 2.5 g, 3.0 g, and 3.5 g adsorbent dosages at pH of 7.82 and a temperature of 24 °C. The adsorbent-landfill leachate solutions were filtered using Whatman filter paper (125 mm Ø) and transferred into a 35 mL plastic bottles.

Adsorption Efficiency of Guinea Fowl Eggshell of Cadmium and Nickel

The removal efficiency (*i.e.*, adsorption capacity) was calculated as follows,

$$Q_e\,(\%) = \frac{C_o - C_e}{M} \times V \times 100 \quad (1)$$

where Q_e is the adsorption capacity, C_o is the initial concentration of Cd or Ni, C_e is the final concentration of Cd or Ni after adsorption, *M* is the amount or dosage of guinea fowl eggshells, and *V* is the volume of the solution.

Adsorption Isotherm Modelling

Adsorption isotherm models were used to show the relationship in the equilibrium state between the amount of cadmium and nickel solution on guinea fowl eggshell. To represent monolayer adsorption with the adsorbent surface, the Langmuir isotherm has been used (Sikdar *et al.* 2020).

The Freundlich model has been used to represent adsorption on heterogeneous surfaces adsorbents (Jeppu and Clement 2012). Hence, the study aims to estimate the affinity, understand the adsorption mechanism and properties of adsorbent surface with the adsorbate, and analyse the experimental conditions and the adsorption capacity relation (Hu and Zhang 2019). The Langmuir isotherm (Eq. 2) and its linear form Eq. 3) were used as follows,

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (3)$$

where q_e denotes the quantity of metal ions (Cd and Ni) adsorbed per gram of the guinea fowl eggshell at equilibrium (mg/g), C_e denotes the adsorbate equilibrium concentration (mg/L), q_m denotes the maximum monolayer coverage capacity (mg/g), K_L denotes Langmuir constant (L/mg). The q_m values were determined from the intercept and slope of the Langmuir plot of C_e *versus* q_e.

The Langmuir isotherm model important features were computed in terms of equilibrium parameter R_L, which is a dimensionless constant denoted as equilibrium parameter or separation factor, calculated as follows,

$$R_L = \frac{1}{1+K_L C_o} \quad (4)$$

where C_o denotes the adsorbate initial concentration. When the $R_L = 1$ is linear, $R_L > 1$ is considered to be unfavourable, $R_L = 0$ is irreversible, and when $0 < R_L < 1$, adsorption is favourable (Ayawei *et al*. 2017).

The Freundlich isotherm model is usually applied to describe the adsorption features of the heterogeneous surface. The Freundlich isotherm linear equation was expressed as follows,

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F\,, \quad (5)$$

where K_f denotes the Freundlich constant (mg/g), q_e denotes the amount of adsorbed metal gram of the guinea fowl eggshell at equilibrium (mg/g), C_e denotes the landfill leachate equilibrium concentration (mg/L), n denotes adsorption density, and $\frac{1}{n}$ denotes the adsorption intensity.

RESULTS AND DISCUSSION

Adsorption Efficiency of Toxic Metals by Guinea Fowl Eggshells in Landfill Leachate

Guinea fowl eggshells achieved cadmium adsorption efficiency of 90.51% to 96.49% at the different dosages (Table 1). The level of cadmium adsorption is attributed to the availability and number of vacant active sites due to varying pores and heterogeneous surface of the eggshells, which aided Cd adsorption. The availability and number of active sites can be enhanced by the dosage of adsorbent. Moreover, dosage and contact time of the adsorbent are a function of removal efficiency and materials cost (Londono-Zuluaga *et al*. 2019). It has been reported that the contact time necessary to achieve acceptable removal rate of heavy metal may vary from one minute (Rodríguez *et al*. 2012) to six hours (Sofiane and Sofia 2015). Guinea fowl eggshells possess irregular, porous, and rough surfaces, with granularity and a distribution of tubular holes. The pores contribute to the gas exchange between the interior and exterior environments (Rajoriya *et al*. 2021). By increasing the amount of surface area that can interact with the pollutants, this feature facilitates the adsorption process on the adsorbent. A study by Abatan *et al.* (2022) stated that Cd(II) adsorption increased from 44.0 to 71.4% and Cr(VI) from 44.8 to 61.0% when the dosage of adsorbent was increased in the range 5 to 25 g for each 100 mg/L of the solution. The efficiency of adsorption of the adsorbent in an inactive amount drops with increasing target concentration. A study also used 1.0 g of eggshell, which was sufficient to remove high fractions of 95.6% of Cr^{3+} and 99.8% of Cd^{2+} (Zonato *et al.* 2022). Kalmykova *et al.* (2008) observed that the efficiency of adsorption of cadmium was 97.3% on sphagnum peat for a concentration of 100 ppb and declined to 86.6% when the Cd concentration was increased to 5000 ppb, which caused the sites of adsorption to reach saturation. Also, adsorption efficiency dropped significantly when the initial ions concentration was increased from 10 to 80 mg/L; the likely reasons are the saturation of the adsorbent active sites on the surface and the repulsive electrostatic force between the aqueous solution and the metal ions on the surface (Hassan *et al.* 2020).

Adsorption efficiency for nickel was 96.1% to 99.3%. This suggests that inexpensive guinea fowl eggshells can be utilised as an effective adsorbent to remove nickel from landfill leachate. The process of Ni^{2+} adsorption using eggshells is reported to reach adsorption equilibrium within 80 min (De Angelis *et al.* 2017). Considerably toxic metals including arsenic, cadmium, chromium, copper, lead, manganese, and mercury could be removed using eggshells. In a single factor, at a 24 h reaction time, copper concentration of 25 mg/L, 10 mg of adsorbent dose, and at 25 °C temperature, the efficiencies of adsorption of eggshell with a membrane and eggshell at pH 5 were 90.5% and 95.2%, respectively whilst at pH 5.9 the eggshell membrane was 73.3% (Chou *et al.* 2023). Elabbas *et al.* (2016) explored Cr(VI) ions removal from wastewater using crushed hen eggshells. Baláž *et al.* (2015) examined a batch adsorption system of Cd(II) removal capacity in wastewater using crushed eggshell. Park *et al.* (2007) studied the comparative Cr and Cd removal from electroplating wastewaters. These studies report the effective removal of Cr and Cd using eggshell as adsorbent.

The initial ion concentration of an aqueous solution has a prominent effect on the process of adsorption, as an increase in this concentration results in an increase in the ion load of the species adsorbed (Hassan *et al.* 2020). Mezenner and Bensmaili (2009) and Hosseini *et al.* (2022) showed that adsorption involves reactions on the surface, and with the passage of time, the sites of adsorption on the surface of adsorbent gradually decrease.

The surface repulsion effect prevents adsorption by empty residual sites of adsorption on the surface. Adsorption occurs quickly at the initial stage and slows down as the sites of adsorption decrease; thus, the time affects the rate of adsorption (Hosseini *et al.* 2022).

The pH value recorded was 7.82 and the temperature recorded was 24 °C for the toxic metals in landfill leachate. The ionic state of the functional groups in a biomaterial is influenced by the pH of a solution, and this relationship can be utilised to explain the adsorption of Cd and Ni. Insufficient focus has been placed on the concurrent effects of the pH level on the ionic species of metals that are found in the bulk solution. The dissociation constants associated with various types of acidic groups at adsorbent surfaces have received attention (Hubbe *et al.* 2011). At a pH more than 7, the surface will be mostly negative, favouring the connection of Cd^{2+} and Ni^{2+}, which are cations. At low pH values, removal of metal is restricted due to domination by hydrogen ions. This trend is likely owing to the competition between hydrogen and metal ions on the sites of adsorption. Hydrogen ion adsorption limits the attraction of metals. According to Moubarik (2015) at low pH values the surface charge is positive hence the adsorption of Cd is electrically unfavourable. Higher pH increases the negative charges on the eggshell surface, thus attracting the Cd cations and allowing its adsorption. According to Annane *et al.* (2021), the adsorption process of Cd ions on eggshells was optimised based on the adsorbent dose, initial pH, concentration, and contact time until saturation of the active sites.

Table 1. Adsorption of Metals by Guinea Fowl Eggshells in Landfill Leachate

Metals	Dosage (g)	Initial conc. (mg/L)	Percentage (%)
Cadmium	0.5	4.9	96.1
	1.0	4.9	94.6
	1.5	4.9	93.5
	2.0	4.9	94.4
	2.5	4.9	92.6
	3.0	4.9	90.5
	3.5	4.9	96.5
Nickel	0.5	9.6	96.1
	1.0	9.6	96.7
	1.5	9.6	97.4
	2.0	9.6	99.3
	2.5	9.6	99.3
	3.0	9.6	97.9
	3.5	9.6	99.0

Langmuir Adsorption Isotherm for Guinea Fowl Eggshells

The Langmuir adsorption isotherm was used to describe how cadmium and nickel interacted with guinea fowl eggshell active sites (surface) in landfill leachate. The maximum monolayer coverage adsorption capacity of cadmium was 4.89×10^{-2} mg/g with an adsorption equilibrium (K_L) of 22.74 mg/L (Table 2), which is related to the extent of interaction between the guinea eggshells surface (adsorption energy) and adsorbate. There is a strong interaction between the adsorbate and adsorbent if the K_L value is large, and smaller K_L value implies a weak interaction. The present study showed a weak interaction between the guinea eggshells and Cd, as the maximum monolayer coverage adsorption capacity was relatively small. The maximum adsorption capacity of Cd was less than 3.01, 3.80 and 10.37 reported by Zonato *et al.* (2022), Abatan *et al.* (2022) and Flores-Cano *et al.* (2013), respectively (Table 3). This present study showed 4.89×10^{-2} mg/g for cadmium and was lower than 11.10 mg/g reported by Naema and Omar (2019). This present study showed K_L of 22.74 mg/l, which was higher than 1.13 mg/L reported by Naema and Omar (2019). The R_L for cadmium was 0.19 with a coefficient of determination (R^2) of 0.0369 (Fig. 1). The R_L for cadmium was 0.19, which indicates the shape of the isotherm for adsorption by eggshells was favourable because the R_L was less than 1 (Ayawei *et al.* 2017). The R_L value for Cd adsorption was close to zero because Cd was present in the landfill leachate at a relatively high concentration.

For nickel, the maximum adsorption in the landfill leachate was 5.29×10^{-3} mg/g, with an adsorption equilibrium (K_L) of -5.18 mg/L (Table 2). The present study showed a weak interaction between the guinea eggshells and Ni, as the maximum monolayer coverage adsorption capacity was relatively low. As a larger value indicates a strong interaction between the adsorbent (guinea fowl eggshell) and adsorbate (Ni), whereas a weak interaction suggests a smaller value of Langmuir constant (Tran *et al.* 2019). The present study showed a maximum adsorption capacity of 5.29×10^{-3} mg/g for nickel, which was lower than the 13.5 mg/g reported by Kristianto *et al.* (2019). The present study found 5.18 mg/L for K_L which is lower than the 0.6 mg/L reported by Kristianto *et al.* (2019). The R_L for nickel was -2.30 with a coefficient of determination (R^2) of 0.7021 (Fig. 2). The calculated Langmuir separation factor (R_L) was -2.30 for Ni, indicating that the Langmuir isotherm may not be suitable indicators of the process of adsorption. The R_L negative values could be due to the low initial concentrations of metal in the industrial wastewater used.

Table 2. Adsorption Isotherm Modelling of the Results of Guinea Fowl Eggshell

Ion	Langmuir Parameters					Freundlich Parameters			
Metal	Q_{max} (mg/g)	K_L (mg/l)	R_L	R^2		$^1/_n$	N	K_F (mg/g)	R^2
Cd	4.89×10^{-2}	22.74	0.19	0.04		0.01	100	477.31	0.03
Ni	-5.29×10^{-3}	-5.18	-2.3	0.7		-0.03	-33.33	894.95	0.48

Table 3. Results of Similar Adsorption Studies

Adsorbent	Adsorbate	pH	q_{max}	Reference
Eggshell	Cd	6.00	3.80	Flores-Cano *et al.* 2013
Eggshell	Cd	6.00	10.37	Abatan *et al.* 2022
Eggshell	Cr	6.00	10.71	Abatan *et al.* 2022
Eggshell	Cd	7.50	3.01	Zonato *et al.* 2022
Eggshell	Cr	5.00	3.03	Zonato *et al.* 2022
Guinea fowl eggshell	Cd	7.82	4.89×10^{-2}	This study
Guinea fowl eggshell	Ni	7.82	-5.29×10^{-3}	This study

Freundlich Adsorption Isotherm for Guinea Fowl Eggshells

The $^1/_n$ value obtained for cadmium was 0.01, whereas the K_F (mg/g) value obtained for cadmium was 477. The N value obtained for cadmium was 100 (Table 2) and the R^2 value for cadmium was -0.0277 (Fig. 3). For nickel, the $^1/_n$ value obtained was -0.03, the K_F (mg/g) value was 894.95, the N value was -33.33 (Table 2) and the R^2 value was 0.4792 (Fig. 4). A description of heterogeneous adsorbent surfaces and the exponentially scattered active sites and energies on them is explained by the Freundlich isotherm (Ayawei *et al.* 2017). The K_F measures an adsorbent's capability for adsorption. The K_F recorded for the adsorption process was 477 and 895 for cadmium and nickel, respectively. The $^1/_n$ recorded for cadmium and nickel was 0.01 and -0.03, respectively, which indicates that the adsorption normal $^1/_n$ is less than 1 (Ayawei *et al.* 2017).

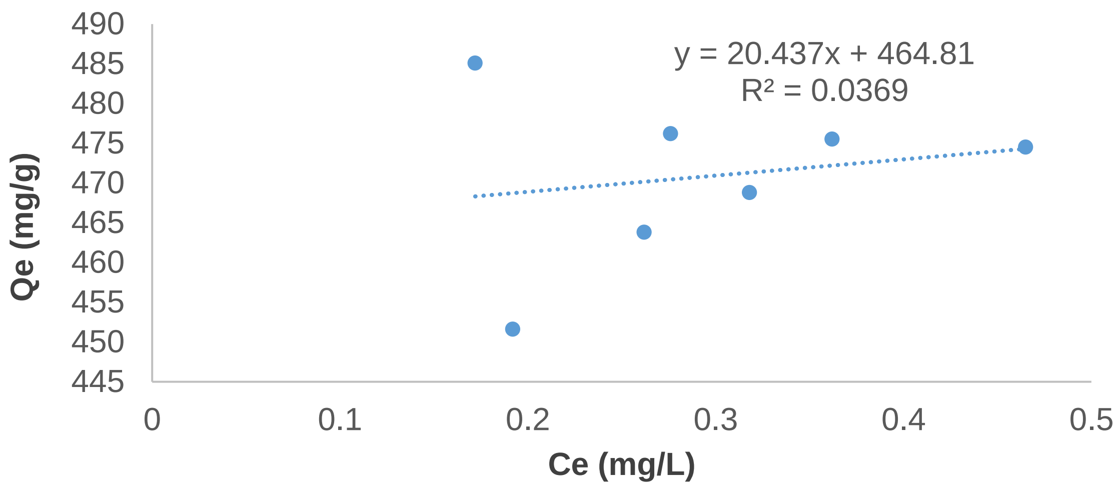

Fig. 1. Langmuir isotherm for the adsorption of cadmium in landfill leachate by guinea fowl eggshells

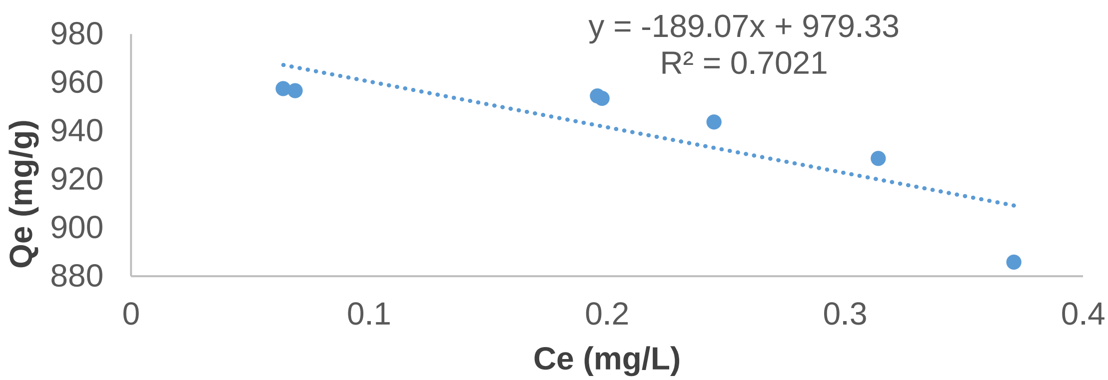

Fig. 2. Langmuir isotherm for the adsorption of nickel in landfill leachate by guinea fowl eggshells

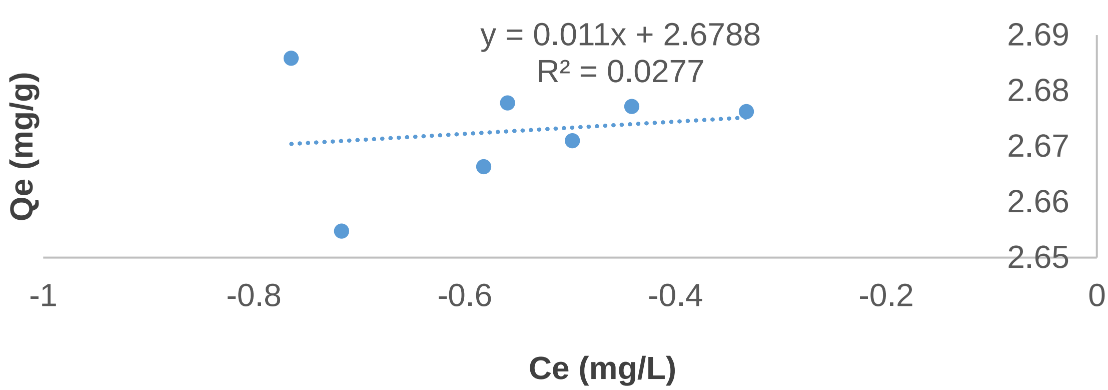

Fig. 3. Freundlich isotherm for the adsorption of cadmium in landfill leachate by guinea fowl eggshells

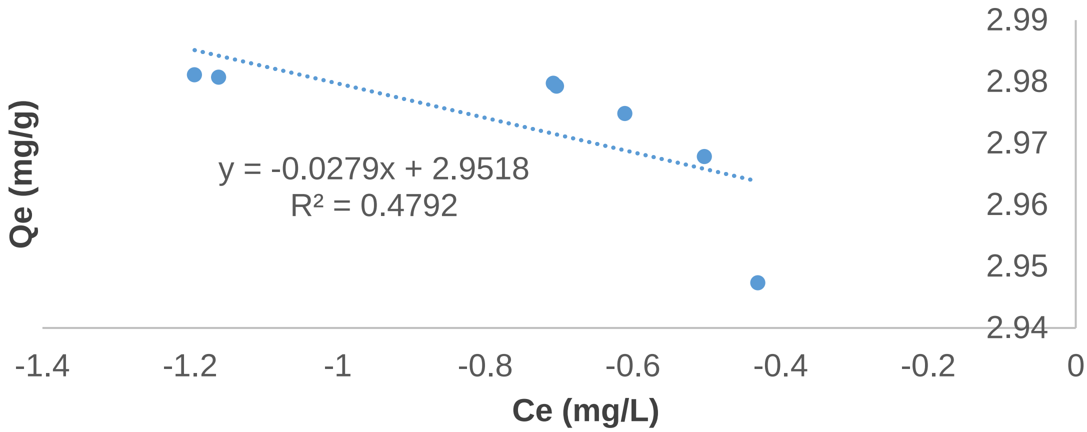

Fig. 4. Freundlich isotherm graph for the adsorption of nickel in landfill leachate by guinea fowl eggshells

CONCLUSIONS

Guinea fowl eggshells can be used for cadmium and nickel removal in landfill leachate, making this adsorbent a candidate for water remediation. The adsorption efficacies of cadmium and nickel by guinea fowl eggshells were 90.5% to 96.5% and 96.1% to 99.3%, respectively. The Langmuir isotherm suited the experimental results for cadmium and nickel. Guinea fowl eggshells can be used as a low-cost adsorbent for Ni and Cd removal from the leachate under certain conditions. Therefore, the conversion of guinea fowl eggshells in large volumes and at low-cost into green adsorbent can be applied for the adsorption of toxic metals in landfill leachate and wastewater. As a means of waste management through recycling waste and eco-friendly materials. The guinea fowl eggshell powder can adsorb higher concentrations of toxic metals from wastewater in practical application systems. Guinea fowl eggshells are readily available and inexpensive. More adsorptive research should be carried out using different eggshells as a low cost green adsorbent to remediate other toxic metals from the environment.

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Conflict of Interest

Authors have no conflicts of interest.

Data Availability Statement

The original contributions presented in the study are included in the article / supplementary material, further inquiries can be directed to the corresponding author.

Author Contributions

All authors contributed equally to the conceptualisation, drafting, and editing of the research article.

REFERENCES CITED

Abatan, O. G., Alaba, P. A., Oni, B. A., Akpojevwe, K., Efeovbokhan, V., and Abnisa, F. (2022). "Performance of eggshells powder as an adsorbent for adsorption of hexavalent chromium and cadmium from wastewater," *SN Applied Sciences* 2, 1996. DOI: 10.1007/s42452-020-03866-w

Agboola, O., Fayomi, O. S. I., Sadiku, R., Popoola, P., Alaba, P. A., and Adegbola, A. T. (2021). "Polymers blends for the improvement of nanofiltration membranes in wastewater treatment: A short review," *Materials Today: Proceedings* 43, 3365-3368.

Ahmad, R., Kumar, R., and Haseeb, S. (2012). "Adsorption of Cu^{2+} from aqueous solution onto iron oxide coated eggshell powder: Evaluation of equilibrium, isotherms, kinetics, and regeneration capacity," *Arab J Chem* 5(3), 353-359.

Allaoui, M., Berradi, M., Bensalah, J., Es-sahbany, H., Dagdag, O., and Ibn Ahmed, S. (2021). "Study of the adsorption of nickel ions on the sea shells of Mehdia: Kinetic and thermodynamic study and mathematical modelling of experimental data," *Mater. Today Proc*. 45(8), 7494-7500. DOI: 10.1016/j.matpr.2021.02.234

Anastas, P. T., and Williamson, T. C. (1996). "Green chemistry: An overview," in: *Green Chemistry: Designing Chemistry for the Environment*, ACS Symposium Series 626; American Chemical Society, Washington, DC, pp 1-17.

Annane, K., Lemlikchi, W., and Tingry, S. (2021). "Efficiency of eggshell as a low-cost adsorbent for removal of cadmium: Kinetic and isotherm studies," *Biomass Conversion and Biorefinery* 2021, 1-12. DOI:10.1007/S13399-021-01619-2

Ayawei, N., Ebelegi, A. N., and Wankasi, D. (2017). "Modelling and interpretation of adsorption isotherms," *Journal of Chemistry*, article ID 3039817.

Ayodele, O., Olusegun, S. J., Oluwasina, O. O., Okoronkwo, E. A., Olanipekun, E. O., Mohallem, N. D. S., Guimarães, W. G., Gomes, B. L. F. d. M., Souza, G., de, O., and Duarte, H. A. (2021). "Experimental and theoretical studies of the adsorption of Cu and Ni ions from wastewater by hydroxyapatite derived from eggshells," *Environ. Nanotechnology, Monit. Manag*. 15. DOI: 10.1016/j.enmm.2021.100439

Baláž, M., Bujňáková, Z., Baláž, P., Zorkovská, A., Danková, Z., and Briančin, J. (2015). "Adsorption of cadmium (II) on waste biomaterial," *J Colloid Interface Sci*. 454, 121-133.

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.

Chou, M. Y., Lee, T. A., Lin, Y. S, Hsu, S. Y, Wang, M. F, Li, P. H, Huang, P. H, Lu, W. C. and Ho, J. H. (2023). "On the removal efficiency of copper ions in wastewater using calcined waste eggshells as natural adsorbents," *Scientific Reports* 13, 437. DOI: 10.1038/s41598-023-27682-5.

De Angelis, G., Medeghini, L., Conte, A. M., and Mignardi, S. (2017). "Recycling of eggshell waste into low-cost adsorbent for Ni removal from wastewater," *J. Clean. Prod.* 164, 1497-1506. DOI: 10.1016/j.jclepro.2017.07.085.

Elabbas, S., Mandi, L., Berrekhis, F., Pons, M. N., Leclerc, J. P., and Ouazzani, N. (2016). "Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: Eggshell and powdered marble," *J. Environ. Manag.* 166, 589-595.

Flores-Cano, J. V., Leyva-Ramos, R., Mendoza-Barron, J., Guerrero Coronado, R. M., Aragón-Piña, A., and Labrada-Delgado, G. J. (2013). "Sorption mechanism of Cd (II) from water solution onto chicken eggshell," *Appl. Surf. Sci.* 276, 682-690.

Hassan, E. S. R. E., Rostom, M., Farghaly, F. E., and Abdel Khalek, M. A. (2020). "Bio-sorption for tannery effluent treatment using eggshell wastes; kinetics, isotherm and thermodynamic study," *Egypt. J. Pet.* 29, 273-278. DOI: 10.1016/j.ejpe.2020.10.002.

Hosseini, S. S., Hamadi, A., Foroutan, R., Peighambardoust, S. J., and Ramavandi, B. (2022). "Decontamination of Cd^{2+} and Pb^{2+} from aqueous solution using a magnetic nanocomposite of eggshell/starch/Fe_3O_4," *J. Water Process Eng.* 48, article 102911. DOI: 10.1016/j. jwpe.2022.102911.

Hu, Q., and Zhang, Z. (2019). "Application of Dubinin–Radushkevich isotherm model at the solid/solution interface: A theoretical analysis," *J. Mol. Liq*. 277, 646-648. DOI: 10.1016/j.molliq.2019.01.005

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources* 6(2), 2161-2287. DOI: 10.15376/biores.6.2.2161-2287

Isa, Y.M., Harripersadth, C., Musonge, P., Sayago, A., and Morales, M. G. (2020). "The application of eggshells and sugarcane bagasse as potential biomaterials in the removal of heavy metals from aqueous solutions," *South African Journal of Chemical Engineering* 34(1), 142-150.

Jannat, N., Al-Mufi, R. L., Hussien, A., Abdullah, B., and Cotgrave, A. (2022). "Influences of agro wastes on the physico-mechanical and durability properties of unfired clay blocks," *Cons. Build. Mater.* 318, 126011. DOI: 10.1016/j.conbuildmat.2021.126011.

Jeppu, G. P., and Clement, T. P. (2012). "A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects," *Journal of Contaminant Hydrology* 129-130, 46-53.

Kalmykova, Y., Strömvall, A. M., and Steenari, B. M. (2008). "Adsorption of Cd, Cu, Ni, Pb and Zn on Sphagnum peat from solutions with low metal concentrations," *J. Hazard. Mater.* 152, 885-891. DOI: 10.1016/j.jhazmat.2007.07.062.

Kristianto, H., Daulay, N., and Arie, A. A. (2019). "Adsorption of Ni (II) Ion onto calcined eggshells: A study of equilibrium adsorption isotherm," *Indonesian Journal of Chemistry*, 19(1), 143-150.

Lee, J. I., Kim, J. M., Yoo, S. C., Jho, E. H., Lee, C. G., and Park, S. J. (2022). "Restoring phosphorus from water to soil: Using calcined eggshells for P adsorption and subsequent application of the adsorbent as a P fertilizer," *Chemosphere* 287, article 132267. DOI: 10.1016/j.chemosphere.2021.132267

Londono-Zuluaga, C., Jameel, H., Gonzalez, R. W., and Lucia, L. (2019). "Crustacean shell-based biosorption water remediation platforms: Status and perspectives," *Journal of Environmental Management* 231, 757-762. DOI: 10.1016/j.jenvman.2018.10.096.

Lunge, S., Thakre, D., Kamble, S., Labhsetwar, N., and Rayalu, S. (2012). "Alumina supported carbon composite material with exceptionally high defluoridation property from eggshell waste," *Journal of Hazardous Materials* 237, 161-169.

Mezenner, N. Y., and Bensmaili, A. (2009). "Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste," *Chem. Eng. J.* 147, 87-96. DOI: 10.1016/j.cej.2008.06.024

Mittal, A., Teotia, M., Soni, R., and Mittal, J. (2016). "Applications of eggshell and eggshell membrane as adsorbents: A review," *J. Mol. Liq.* 223, 376-387.

Moubarik, A. (2015). "Valorization of olive stone and sugar cane bagasse by-products as biosorbents for the removal of cadmium from aqueous solution," *Food Res. Int.* 73, 169-175.

Mukherjee, P. (2022). "Green chemistry – A novel approach towards sustainability," *Journal of the Chilean Chemical Society* 66(1), 2021. DOI: 10.4067/S0717-97072021000105075

Naema, S. Y., and Omar, M. E. (2019). "Removal of Cd (II) from aqueous solution using eggshell as low cost sorbent," *SSRG International Journal of Applied Chemistry* 6, 1 - 11.

Park, H. J., Jeong, S. W., Yang, J. K., Kim, B. G., and Lee, S. M. (2007). "Removal of heavy metals using waste eggshell," *J. Environ. Sci.* 19(12), 1436-1441.

Parvin, F., and Tareq, S. M. (2021). "Impact of landfill leachate contamination on surface and groundwater of Bangladesh: A systematic review and possible public health risks assessment," *Applied Water Science* 11(6), 1-17.

Peigneux, A., Puentes-Pardo, J. D., Rodríguez-Navarro, A. B., Hincke, M. T., and Jimenez-Lopez, C. (2020). "Development and characterization of magnetic eggshell membranes for lead removal from wastewater," *Ecotoxicology and Environmental Safety* 192, article 110307.

Rajoriya, S., Saharan, V.K., Pundir, A.S., Nigam, M., and Roy, K. (2021). "Adsorption of methyl red dye from aqueous solution onto eggshell waste material: Kinetics, isotherms and thermodynamic studies," *Curr. Res. Green Sustain. Chem*. 4, article 100180. DOI: 10.1016/j.crgsc.2021.100180

Ramos, B., de, P., Perez, I. D., Aliprandini, P., and Boina, R. F. (2022). "Cu^{2+}, Cr^{3+}, and Ni^{2+} in mono- and multi-component aqueous solution adsorbed in passion fruit peels in natura and physicochemically modified: A comparative approach," *Environ. Sci. Pollut. Res*. DOI: 10.1007/s11356-021-18132-8

Ramos, B., de, P., Perez, I. D., Wessling, M., and Boina, R. F. (2021). "Metal recovery from multielementary electroplating wastewater using passion fruit powder," *J. Sustain. Metall*. 7(3), 1091-1101. DOI: 10.1007/s40831-021-00398-4

Rodríguez, M., Zalba, M., Goitía, M., Pugliese, A., Debbaudt, A., Agulló, E., Schulz, P., and Albertengo, L. (2012). "Calcareous chitin: A novel low-cost sorbent for cadmium (II)," *Latin Am. Appl. Res.* 42, 311 - 318.

Setiawan, B. D., Rizqi, O., Brilianti, N. F., and Wasito, H. (2018). "Nanoporous of waste avian eggshell to reduce heavy metal and acidity in water," *Sustain. Chem. Pharm.* 10, 163-167. DOI: 10.1016/j.scp.2018.10.002.

Sikdar, D., Goswami, S., and Das, P. (2020). "Activated carbonaceous materials from tea waste and its removal capacity of indigo carmine present in solution: Synthesis, batch and optimization study," *Sustain. Environ. Res.* 30, 1-16.

Sofiane, B., and Sofia, K. S. (2015). "Biosorption of heavy metals by chitin and the chitosan". *Der Pharma Chem.* 7, 54-63.

Sultana, M., Rownok, M. H., Sabrin, M., Rahaman, M. H., and Alam, S. M. N. (2022). "A review on experimental chemically modified activated carbon to enhance dye and heavy metals adsorption," *Clean. Eng. Technol*. 6, article 100382. DOI: 10.1016/j.clet.2021.100382

Tran, T. H., Okabe, H., Hidaka, Y., and Hara, K (2019). "Equilibrium and kinetic studies for silver removal from aqueous solution by hybrid hydrogels," *J. Hazard. Mater.* 365, 237-244.

Yildirim, A. (2012). "Nutrition of guinea fowl breeders: A review," *Journal of Animal Science Advances* 2(2), 188-193.

Zonato, R. O., Estevam, B. R., Perez, I. D., Ribeiro, V. A. S., and Boina, R. F. (2022). "Eggshell as an adsorbent for removing dyes and metallic ions in aqueous solutions," *Cleaner Chemical Engineering* 2, article 100023. DOI: 10.1016/j.clce.2022.100023.

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