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Review

Recent Developments in the Application of *Gallus domesticus* Eggshells for the Biosorption of Dyes and Heavy Metals

Clint Sutherland *, Beverly S. Chittoo

Project Management and Civil Infrastructure Systems, The University of Trinidad and Tobago, San Fernando Campus, Trinidad and Tobago (W.I.); E-Mails: clint.sutherland@utt.edu.tt; beverly.chittoo@utt.edu.tt

* **Correspondence:** Clint Sutherland; E-Mail: clint.sutherland@utt.edu.tt

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Abstract

Global efforts to develop low-cost solutions for the treatment of contaminants in wastewater continue unabated. The conversion of eggshells, a waste material, into a high-value product can be economical and environmentally sustainable. The recent developments in applying eggshells towards the biosorption of contaminants are presented. Eggshells effectively remove pollutants such as metal cations, metal anions, and reactive, basic, and direct dyes. Promising advances in modifying eggshells, elucidating the critical operational parameters, and optimizing the biosorption process have been reported. To this end, the modeling of biosorption kinetics, equilibrium, thermodynamics, and mechanisms are discussed. Also, a 3-stage category is proposed to better classify the biosorbent preparation efforts. The pseudo-second-order model was reported to represent biosorption kinetics best, implying that chemisorption may be a key attachment mechanism in most instances. The Langmuir model best represented the equilibrium data, inferring monolayer sorption on homogenous surfaces. Most studies reported that the uptake mechanism was physisorption or chemisorption. Despite these strides, the application of eggshell biosorption remains mostly at the laboratory testing stage. Thus, key points from recent developments and recommendations for future inquiry are presented.

Keywords
Eggshells; biosorption; heavy metal; dye; biosorbent preparation

1. Introduction

The increase in the discharge of effluents from anthropogenic activities such as population growth, industrialization, urbanization, manufacturing, and agriculture has amplified the degradation of groundwater and surface waters globally. According to Ali *et al.* [1], heavy metals and dyes are the most common pollutants emitted in wastewater among the various contaminants. Textile, leather, electroplating, galvanizing, metallurgical, paint, and other metal processing and refining industries generate considerable volumes of effluents, which often contain significant amounts of toxic heavy metals, including Cd, Cu, Zn, Ni, and Pb [2, 3]. Additionally, fertilization and the use of pesticides and livestock manure can also result in heavy metal contamination [4]. Heavy metals are difficult to remove from wastewater due to their high solubility, mostly in the dissolved state, their bonding with organic matter and other ions potentially persisting in either mixed or chemical forms in the water and their low concentrations [5]. Furthermore, unlike organic contaminants, heavy metals are non-biodegradable. This, coupled with their persistent nature, results in the accumulation of heavy metals in the food chain. Unlike organic pollutants, heavy metals are non-biodegradable. This, coupled with their persistent nature, results in the accumulation of heavy metals in the food chain, posing a significant danger to human health. Chronic exposure to common heavy metals such as cadmium can result in anemia, insomnia, kidney damage, bladder and prostate cancers, and osteoporosis [6]. Furthermore, it may lead to gastric cancer, breast cancer, lung cancer, and renal cancer [7]. Arsenic has been associated with severe health effects, including bladder, lung, and skin cancers [8]. Lead toxicity can lead to impaired blood synthesis, hypertension, severe stomach aches, and brain and kidney damage [9].

Dyes are one of the major pollutants present in effluent discharged from significant industries such as paper, leather, textile and paint [10]. It is estimated that 700,000-1,600,000 metric tonnes of dyes are generated annually, and about 280,000 tonnes enter natural water bodies every year from effluent discharge [11, 12]. According to Rápó and Tonk [13], the textile industry is responsible for approximately 54% of dye effluents in the environment, while the dyeing industries contribute 21%. The paper and pulp industries contribute 10%, the tannery and paint industries contribute 8%, and the dye manufacturing industry is responsible for the remaining 7%. Disposal of untreated dye-containing effluent into water bodies may cause several environmental problems. It may disrupt photosynthetic activities in aquatic ecosystems, increase turbidity in surface waters, produce mutagenic effects on marine organisms, and limit downstream beneficial uses such as drinking water and irrigation [13, 14]. Further, excessive exposure to dyes may lead to mild to severe toxic effects on human health, including headaches, dizziness, body fatigue, skin irritation, respiratory problems, seizures and an increased risk of cancer [15, 16]. Accordingly, studies into removing heavy metals and dyes from wastewater are at the forefront of environmental research.

Various technologies, including reverse osmosis, precipitation, electro-dialysis, adsorption, coagulation and flocculation, electrocoagulation, filtration, and ion exchange, have been explored to remove these pollutants from water and wastewater [17, 18]. Due to its insensitivity to toxic

pollutants, ability to attain low concentration levels, high efficiency, ease of operation at large scale, low cost, and recycling potential, adsorption is one of the most capable processes for the removal of inorganic and organic contaminants from wastewater [19, 20]. Activated carbon-based adsorbents such as commercial activated carbon and activated carbon from waste materials like rice husk, coconut husk and orange peel have been extensively reported in the literature as effective decontaminants [17, 21]. Their outstanding sorption performance is generally attributed to their characteristics, including internal pore morphology, pore volume, chemical structure, porosity and presence of functional groups from their source material, and activation. However, a significant drawback of the large-scale application of activated carbon-based adsorbents is their high cost [22].

Published literature shows several studies have been conducted to find alternative materials for commercial adsorbents. Due to their characteristics and added benefits, including being readily available, inexpensive, biodegradable, and eco-friendly, various agro-based waste materials have been used to absorb heavy metals and dyes [23]. Some of them include mango bark [24], mango leaves [25], orange peel, pomegranate peel, banana floret [26], sugar cane bagasse [27], rice husk [28], groundnut shells [29], coffee husk [30], sawdust [31], watermelon seed hulls [32], cocoa shells [33] and eggshells [34]. According to Waheed *et al.* [35], eggshell wastes are primarily generated from egg processing plants, chicken hatcheries, food service industries, bakeries, households, and food manufacturing companies. These sources collectively contribute to a significant amount of waste eggshells. In 2018 alone, global egg production was approximately 120 million tonnes [36]. The weight of an eggshell is approximately 11% of the total egg weight; therefore, this would have resulted in approximately 13 million tonnes of eggshell waste [37, 38]. According to Steiger *et al.* [34] and Waheed *et al.* [35], the enormous amount of eggshell food waste generated annually is generally disposed of in landfills, leading to environmental and economically challenging problems. Mashangwa *et al.* [39] explained that the porosity of eggshells makes them a promising biosorbent. The authors explained that eggshells comprise three layers, the cuticle on the outer surface, a spongy or calcareous layer, and an inner lamellar or mammillary layer. The calcareous and mammillary layers comprise more than 90% of the eggshell material. These two layers are arranged in such a way that there are many circular pores. According to Yusmartini *et al.* [40], each eggshell contains between 10000 and 20,000 pores. It is also significant that eggshells mainly comprise calcium carbonate (94%), with just 1% calcium phosphate, 1% magnesium carbonate, and 4% organic matter [41]. Considering the high calcium carbonate content, it is expected that eggshells may behave like known sorbents that also contain this compound, such as calcareous soil or calcite and due to the presence of calcium ions, it is expected that biosorption by eggshells will occur by ion exchange [42, 43].

This review examines the adsorption of heavy metals and dyes from aqueous solutions utilizing eggshells. Studies published within the last decade were sourced from international electronic databases, including Scopus, Google Scholar, PubMed, Web of Science, and ScienceDirect. The search employed keywords such as adsorption, eggshell, heavy metals, dyes, and regeneration, using AND/OR operators in the titles and abstracts. In recent years, the preparation of eggshells for biosorption has gone beyond mere washing and grinding. Current studies reveal that advanced treatments, such as physical, chemical, thermal, and functionalization, can improve eggshell contaminant selectivity and performance. This state-of-the-art review stands out as it precisely brings to the forefront the improvements to be gained by advanced preparation techniques. To this end, the study consolidates scattered research. It identifies key issues essential for process up-

scaling and development, such as the impact of solution pH on the interactions and mechanisms of adsorption modeling and eggshell regeneration. Specifically, this review looks at (i) the application of eggshell biosorption and its development during the past decade, (ii) the methods of preparation and modification of eggshells for the sorption of heavy metals and dyes, and (iii) the mechanisms that may influence the biosorption of various metals and dyes by eggshells. This comparative approach aims to highlight effective methods and current gaps, thereby facilitating the design of future studies.

2. Biosorption by Modified and Unmodified Eggshells

2.1 Chemically Modified Eggshells

Basaleh *et al.* [44] explored the removal of Pb (II) from solution using chemically treated eggshells modified using $KMnO_4$. The study's scope was restricted to single-contaminant synthetic solutions, which limits its comparison to real-world, multi-contaminant environments. Eggshells were washed, dried, and ground to a size between 0.04-0.10 mm. The biosorbents were modified by soaking the eggshells in varying concentrations of $KMnO_4$ (0.1-0.4 M) for 6 to 48 hrs. Finally, the specimens were washed and dried at 80°C in an oven. Reaction mixtures comprised 50 mL of Pb (II) (25-175 mg/L) solution, the biosorbent dose from 2.5-10.0 mg, pH from 2.0-9.0, agitation at 200 rpm, and temperature from 25-60°C. The optimum pH was 5.0, and equilibrium was attained within 60 min. Chemical modification by $KMnO_4$ increased the BET surface area from 2.57 to 90 m^2/g. The pore volume was also increased from 0.0047 to 0.35 cm^3/g. Experimental analysis of parameters, including pH, temperature, and adsorbate dose, were meticulously outlined. The pseudo-second-order model best modeled Kinetic studies, while the Langmuir isotherm best-modeled equilibrium data. The maximum sorption capacity was found to be a staggering 690.0 mg/g. This marked sorption performance should be validated through experiments with competing ions. This could significantly impact sorption capacity and selectivity in wastewater with multiple ions. The authors attributed the significant biosorption performance to the formation of manganese oxide on the surface of the sorbent. According to Hokkanen *et al.* [45], $KMnO_4$ is a potent oxidizing agent. Thus, when it reacts with reducing environments such as the calcium carbonate in eggshells, it reduces, resulting in manganese oxide, which can be precipitated on the surface of the adsorbent. Various studies, including those by Basaleh et al. [44] and Flores-Guia et al. [46], reported that manganese oxides are advantageous for adsorption as they increase the surface area and active sites on the adsorbents. Thermodynamic analysis revealed that the biosorption reaction was spontaneous, favorable, and endothermic and the sorption mechanism was chemisorption.

Adeniji *et al.* [47] reported on the biosorption of methylene blue in a single-contaminant synthetic solution by unmodified, citric acid- and sodium hydroxide-treated poultry eggshells. The authors determined that the optimum pH for biosorption was 8.0 for untreated eggshells and 12.0 for NaOH- and citric acid-treated eggshells. However, this significant shift in optimum pH suggests potential limitations in practical applications, where pH adjustment may be challenging. Equilibrium experiments were best represented by the Langmuir equation and revealed that at 25°C, the maximum methylene blue biosorption was 39.7, 90.9 and 20.5 mg/g for unmodified, sodium hydroxide- and citric acid-treated eggshells, respectively. This indicates that NaOH treatment enhanced methylene blue biosorption. FTIR analysis of the biosorbents revealed the presence of OH and NH functional groups, which the authors ascribed to aromatic or aliphatic origin within the

fibre protein network of the biosorbent. The authors observed that the OH and NH sites were eliminated following NaOH treatment. They attributed this to the possible formation of other active sites, which may have enhanced adsorption. According to Basaleh et al [44], the alkaline conditions induced by NaOH treatment may have deprotonated the calcium carbonate in the eggshells, forming hydroxyl groups on the surface. Furthermore, it may have caused eggshell protein degradation, leading to amine group formation. Hydroxyl groups may have offered extra adsorption sites, while amine groups likely facilitated adsorption through electrostatic interactions, enhancing adsorption. When treated with citric acid, OH and NH sites were preserved without the formation of other active sites. The reaction kinetics were best represented by the pseudo-second-order equation. Thermodynamic analysis showed the reaction was non-spontaneous and non-feasible. Further, analysis of the standard entropy revealed the citric acid-treated specimen exhibited decreased randomness, while the unmodified and NaOH-treated specimens exhibited increased chaos. The nature of the biosorption process involving citric acid specimens was endothermic, while the unmodified and NaOH-treated specimens were exothermic.

2.2 Calcinated Eggshells

Eletta *et al.* [48] reported on the sorption of cyanide using calcinated eggshells. To prepare the sorbent, the authors first soaked, washed and sun-dried the eggshells to remove the membrane. This was followed by crushing, washing and drying in an oven for 6 hrs at a temperature of 120°C. The specimens were then calcinated for 4 hrs at 900°C, hydrated, dehydrated and finally re-calcinated for 4 hrs at 600°C to increase the surface area. Reaction mixtures comprised cyanide concentrations from 0.01 mol/L to 0.05 mol/L, calcinated eggshell doses from 5.0 to 9.0 g and a mixing speed of 350 rpm. Experimental analysis showed the point of zero charge of the sorbent to be 8.6, and thus, at pH values below 8.6, the surface of the sorbent would be positively charged. XRD and FTIR analysis verified that, as a result of the calcination process, the $CaCO_3$ was successfully converted to CaO. The pseudo-second-order equation best represented the sorption kinetics. The time to reach equilibrium was found to be 40 min. Equilibrium studies revealed the Langmuir isotherm to represent the sorption process best. The model produced a maximum sorption capacity of 3.3 mg/g at a corresponding pH of 7.0 and a temperature of 30°C. The study did not critically assess how this capacity might be affected by varying environmental factors or competing ions in real wastewater. While the calcination process improved sorption properties, the cost-effectiveness or scalability of this intensive preparation for practical applications warrants further investigation. Kristianto *et al.* [49] reported on Ni (II) sorption using unmodified and calcined eggshells. The sorbent specimen was prepared by first washing, drying and sieving the eggshell to produce a size of 0.15 mm. The specimen was then calcinated at 850°C for 4 hours. The FTIR analysis of calcined eggshell displayed bands at 3637 and 2355 cm^{-1}, indicating the presence of OH in $Ca(OH)_2$. Peaks observed around 1410, 1062, and 657 cm^{-1} suggest the transformation of carbonate into CaO. This change in structure could impact the sorbent's stability and reusability; however, the authors did not examine how this transformation affects the material's durability or effectiveness over multiple sorption cycles. Batch reaction mixtures were prepared at a pH varying from 2.0-9.0, temperature from 25-40°C and an initial concentration from 10 to 60 mg/L. The optimum pH was determined by experiments to be 6.0. Equilibrium data analysis revealed a remarkable increase in maximum sorption capacity, with unmodified eggshells achieving 13.5 mg/g and calcined eggshells reaching

769.2 mg/g. The Langmuir model best represented the equilibrium data. Al-Ghouti and Salih [50] studied the biosorption of boron by unmodified and calcinated eggshells. The eggshell was calcinated at a temperature of 800°C for 4 hrs. The optimum sorption was reported at a pH of 6.0, a sorbent dose of 0.05 g and an agitation speed of 150 rpm. The reported maximum sorption capacities of unmodified and calcinated eggshells were 42.2 and 31.1 mg/g, respectively. It is noted that the unmodified sorbent performed better for boron uptake. This unexpected result suggests that calcination may have altered surface properties that hindered boron sorption, possibly due to changes in functional groups or pore structure. The Freundlich isotherm best represented the equilibrium data. The authors reported the presence of carbonyl and calcium oxide on the sorbent surface, which they attributed to being responsible for boron sorption. Thermodynamic analysis reported the reaction to be spontaneous and exothermic. Ashour and Tony [51] reported on the removal of Fe (II) and Fe (III) by natural and calcinated eggshells from single-contaminant synthetic solutions. The pseudo-second-order equation best-modeled batch kinetic data. The Langmuir equation best represented the equilibrium data. The maximum sorption capacity for Fe (II) by unmodified and calcinated eggshells was 165.6 and 181.3 mg/g, respectively. The maximum sorption of Fe (III) by unmodified and calcinated eggshells was 105.4 and 129.7 mg/g, respectively. The authors reported that the time to reach equilibrium was 120 min.

Rapo *et al.* [52] investigated the removal of Remazol Brilliant Violet-5R dye using calcinated eggshells. The study was limited to single-contaminant synthetic solutions, restricting its applicability to real-world scenarios involving complex, multi-contaminant environments. The biosorbent was prepared by washing, drying, and crushing the eggshells to obtain a particle size of less than 0.16 mm. The specimen was then calcinated to a maximum of 1000°C for 4 hrs. Reaction mixtures comprised initial concentrations from 20-100 mg/L, biosorbent doses from 0.5-2.0 g/L, pH from 2.0-11.0 and temperature from 20-40°C. Differential thermal analysis (DTA) curve showed that decomposition of the sample occurred at 728.6°C, which the authors attribute to the loss of organic compounds. The pore volume and surface area of the calcinated sorbent determined by the Dollimore–Heal and BET methods were found to be 0.015 cm^3/g and 3.0 m^2/g, respectively. After biosorption, an apparent reduction in both pore volume (0.012 cm^3/g) and surface area (1.7 m^2/g) was reported. The analysis of parameters, including pH, bioconcentration factor, temperature, adsorbent dose, and adsorbate dose, were meticulously outlined. The optimum temperature, sorbent dose and pH were determined to be 20°C, 1.5 g/L and 6.0, respectively. Kinetics and equilibrium studies were best represented by the pseudo-second-order model and Langmuir isotherm, respectively. A maximum sorption capacity of 17.0 mg/g was reported. The biosorbent preparation process involved calcination up to 1000°C, which, while effective in altering the material properties, is energy-intensive and may not be feasible for large-scale applications. The authors do not discuss the economic or environmental implications of this high-temperature treatment, which raises questions about the sustainability of the approach. Thermodynamic analysis revealed that the amount of biosorbed dye decreased as the temperature increased. The reaction was reported to be spontaneous and endothermic. The absence of desorption data limits evaluating the biosorbent's reusability—a crucial factor for practical applications.

2.3 Pandanus amaryllifolius Roxb. Impregnated Eggshells

Xin and Ngadi [53] reported on Cr (VI) biosorption using eggshells impregnated with *Pandanus amaryllifolius Roxb*. The authors prepared the biosorbent by first washing and then drying in an oven for 24 hrs at 40°C. Finally, the specimen was ground into a powder and sieved to a particle size of 0.1 mm. Pandanus impregnation was done using 200 g of 3 cm leaves, which were initially dried for 24 hrs at 105°C followed by grinding and sieving to a size of 0.15 mm. The leaves were soaked in ethanol for 24 hrs to allow extraction, after which the permeate was heated at 80°C for 24 hrs to remove the ethanol. Finally, eggshell (0.1 g) was added to 50 mL of extracted pandan oil for 24 hrs followed by filtration, washing and drying at 110°C. BET analysis revealed a surface area of 1.61 m^2/g and 0.46 m^2/g for unmodified and modified eggshells. Batch experimentation was performed by varying the adsorbent dose from 0.3–1.0 g, initial Cr (VI) from 0.8–8.0 mg/L, pH from 4.0-8.0 and temperature from 25-70°C. The parameters and sorption behavior analysis, including reaction time, pH, characterization studies, temperature, adsorbent dose, and adsorbate dose, were meticulously outlined. Eggshell-pandan sorbent achieved maximum biosorption after a contact time of 140 min, adsorbent dose of 0.5 g, temperature of 50°C and pH of 4.0. Kinetic analysis was adequately assessed using the pseudo-first order, pseudo-second order, and intraparticle diffusion models. Equilibrium data was evaluated using the Langmuir, Freundlich and Temkin models. The sorption kinetics were best modeled by the Lagergren pseudo-first-order model. Equilibrium data followed the Freundlich isotherm. The batch experiments covered a wide range of parameters, but the reported maximum sorption capacity of 0.2 mg/g is notably low, which suggests limited efficacy compared to other biosorbents. Thermodynamic studies indicated that the process was spontaneous, feasible, and endothermic, with increased randomness at the interface. However, while the calculated thermodynamic parameters (negative Gibbs free energy, positive enthalpy, and positive entropy) provide valuable insights, the absence of desorption studies limits understanding of the sorbent's reusability and long-term stability. Additionally, the study's restriction to single-contaminant solutions further limits its applicability to real-world, multi-contaminant environments where competitive adsorption could affect performance.

2.4 Magnetic Eggshells

Ajab et al. [54] investigated the removal of Cr (VI) from solution using a magnetic bio-composite eggshell and provided a detailed account of the biosorbent's preparation and experimental conditions. To create the biosorbent, the authors first washed, dried and crushed the eggshells. Then, $FeCl_3 \cdot 6H_2O$ (3.1 g) and $FeSO_4 \cdot 7H_2O$ (2.1 g) were dissolved in distilled water (40 mL). Eggshell (10.0 mg) was added to the solution and stirred for 30 min, then cooling and filtering. The residue was finally washed and dried at 102°C for 24 hrs. Batch experiments revealed that optimum conditions occurred at a pH of 2.0, a temperature of 20°C and a time to reach equilibrium of 30 min. The ideal pH of 2.0 may pose practical challenges, as real-world effluents often have varying pH levels, and additional acidification might be required, which could introduce costs and complexity. The study meticulously outlined the analysis of sorption behavior parameters, including point of zero charge, pH, material characterization, desorption, temperature, adsorbent dose, and adsorbate concentration. Separation of the biosorbent was initiated by applying a magnetic field. The point of zero charges of the magnetized eggshell was pH 8.0. The pseudo-first-order equation represented the kinetic data well. The Langmuir equation produced a maximum sorption capacity

of 12 mg/g. Thermodynamic analysis revealed the reaction to be exothermic and spontaneous, reducing disorder at the interface. A modest case for the magnetic bio-composite eggshell as a reusable Cr (VI) sorbent was proposed. The authors successfully desorbed Cr (VI) ions using 0.1 M HCl. However, the number of adsorption/desorption cycles was not reported. Notably, the authors tested the biosorbent with real-world leather tanning effluent (initial concentration of 20 mg/L), achieving a Cr (VI) removal rate of 72%, which adds practical relevance to the study.

2.5 Chitosan-Modified Eggshells

Kocabas and Satir [55] explored the removal of Brilliant Blue R dye using an eggshell-chitosan biosorbent, providing a detailed study that includes batch adsorption, desorption, competing ions, and column experiments. This comprehensive approach offers insights into potential real-world applications. To develop the biosorbent, a mixture of powdered eggshell and chitosan (1:1.5) was homogenized in acetic acid (5%). The resulting solution was injected into a NaOH (500 ml; 0.5 M) solution. The specimens were finally washed, dried and ground to a size below 0.15 mm. Characterization using SEM revealed the surface of the biosorbent to be rough, porous and heterogeneous. Reaction mixtures comprised of pH values varying from 1.0-10.0, a biosorbent dose of 0.2–8.0 g/L, a reaction time of 5-90 min, and temperatures of 25, 35, and 45°C. Kinetic investigations using multiple models found the reaction best followed the pseudo-second-order equation. At an optimum pH of 2.0, a biosorbent dose of 2.0 g/L, and a temperature of 25°C, the Langmuir equation revealed a maximum capacity of 11.1 mol/g. However, the highly acidic optimal pH might be impractical for actual wastewater treatment due to the need for additional pH adjustments, which could complicate application in diverse effluent environments. Variation in competing ions was studied using NaCl within the 0.02-0.50 mol/L range. Results revealed a marked decrease in biosorption capacity for salt concentrations beyond 0.1 mol/L. The authors attributed this to the accumulation of other ions in solution competing for the active sites. This finding highlights potential limitations when treating wastewater containing high salinity or competing ions. The thermodynamic analysis found the reaction to be spontaneous and endothermic and that it occurred with increased randomness. Despite lacking detail on the specific eluent used, Desorption studies demonstrated the biosorbent's reusability, showing only a 24% reduction in adsorption efficiency after seven cycles. This reusability is promising for practical application, but further studies on long-term durability and cost-effectiveness are warranted. Column experiments with real wastewater at an initial concentration of 25 mg/L and pH 2.0 achieved a capacity of 11.4 mg/g at a flow rate of 0.5 mL/min, reinforcing the material's potential utility in real-world scenarios.

2.6 Unmodified Eggshells

Tonk *et al.* [56] investigated the removal of Cd (II) ions by eggshells. The authors provided a detailed description of biosorbent preparation, including washing to remove impurities and drying for 24 hrs at 80°C. Finally, the specimens were crushed, milled and sieved to a size of 0.3 mm. Experimental batch studies were conducted with initial Cd (II) concentration varying from 11.0 to 157.0 mg/L, a biosorbent dose of 10.0 g/L, and an agitation speed of 200 rpm. The study outlined the analysis of sorption behavior parameters, including material characterization, bioaccumulation factor, reaction time, and adsorbate concentration. The bioaccumulation factor was calculated to be 10 times higher at lower Cd (II) concentrations, indicating a favorable process at low Cd (II) levels.

Kinetic data was analyzed using multiple models, with findings suggesting that the sorption process followed the pseudo-second-order model. Equilibrium data were best described by the Langmuir isotherm, showing a maximum monolayer capacity of 7.1 mg/g. However, the low sorption capacity might limit the eggshell's applicability in high-concentration Cd (II) environments without modifications or complementary treatments. The Temkin and Dubinin-Radushkevich isotherm analyses attributed the removal mechanism to physical sorption, which implies potential reversibility and ease of desorption but might also indicate weaker binding interactions. EDS analysis confirmed the sorption of Cd (II). Further, SEM and TEM analysis revealed modifications to the eggshell surface after biosorption in irregular-shaped agglomerates, which the authors attributed to ion exchange on the sorbent. Khelifi *et al.* [57] experimented with applying eggshells to biosorption Ni (II) ions from a single-contaminant synthetic solution. The eggshell was first washed, followed by drying for 24 hrs at 105°C, and finally crushed and sieved. Batch laboratory experiments were conducted by varying contact time from 5 to 120 min, initial Ni (II) concentration from 10 to 50 mg/L, adsorbent dose from 2.0 to 10.0 mg/L, and temperature from 20 to 50°C. Optimum biosorption was obtained at a pH of 5.6, a biosorbent dose of 10 g/L, a temperature of 50°C, and a contact time of 120 min. The authors opined that the greater removal experienced at higher temperatures resulted from particle acceleration, which increased intraparticle diffusion. Notably, the study lacked kinetic modeling and thermodynamic analysis, both essential for understanding adsorption mechanisms and predicting the feasibility of the biosorption process under different operational conditions. The study identified the Freundlich isotherm as the best fit for equilibrium data, suggesting a heterogeneous adsorption surface. However, the maximum adsorption capacity (2.3 mg/g at 20°C, based on the Langmuir model) was relatively low, which may limit its applicability in high-concentration Ni (II) remediation scenarios. While the authors noted that this capacity aligns with other low-cost biosorbents, they did not discuss potential improvements or the feasibility of the practical application, especially in the presence of competing ions commonly found in industrial wastewater. Mashangwa *et al.* [39] reported on the biosorption of Cd (II), Cu (II), Zn (II), and Ni (II) by unmodified eggshell. To prepare the eggshells, the authors initially washed and dried the sorbents at 150°C for 3 hrs. This was followed by grinding and finally sieving to a size between 0.08 and 0.2 mm. The reaction solutions had a pH ranging from 2.0 to 10.0 and a temperature of 24°C. Also, it is noteworthy that all experiments were conducted without agitation. The authors reported that optimum sorption conditions occurred at a contact time of 360 min and an adsorbent dose of 7.0 g. Eggshells comprise, in large part, $CaCO_3$, which results in the disassociation of Ca^{2+} in water and the creation of ion exchange sites on the sorbent. At pH values above neutral, the resulting negative charge of the sorbent creates conditions favorable to the sorption of heavy metals. Consequently, the authors selected a pH of 7.0 for experimentation, as it is environmentally prudent to release neutral effluent. Using an initial metal concentration of 100 mg/L, it was reported that the sorption efficiency for lead, nickel, copper and zinc were 97, 94, 95 and 80%, respectively. These results indicate that eggshells may have a selective affinity towards certain metals, a factor that could be further explored in competitive sorption studies. Abbas *et al.* [36] presented a comprehensive study on removing bismuth from untreated eggshells. The analysis of parameters, including pH, temperature, competing ions, adsorbent dose, and adsorbate dose, were meticulously outlined. Desorption studies were not reported. To prepare the biosorbent, the eggshells were first washed, dried for 10 hrs at 40°C, and finally crushed and sieved to a size of 0.45 micrometers. The authors concluded that the functional groups responsible for the sorption of bismuth included

carboxyl, aliphatic hydrocarbons, aromatic rings, amino and phenolic hydroxyl. The maximum biosorption capacity was reported to be 891.3 mg/g and was best represented by the Langmuir equation, suggesting monolayer adsorption and indicating homogeneous sorption sites on the eggshell surface. The authors also studied the effects of coexisting ions. They reported that in the presence of Mg (II) (100 mg/L) and Zn (II) (100 mg/L), the removal capacity significantly decreased to 326.6 and 379.2 mg/g, respectively. Thermodynamic analysis revealed the biosorption process to be endothermic. The lack of desorption studies limits understanding of the biosorbent's reusability and the feasibility of applying it to large-scale wastewater treatment systems.

3. Properties of Biosorbent and Biosorption Systems

3.1 Biosorbent Characteristics

Biosorbents' physical and chemical characteristics are crucial to elucidating the mechanisms and ultimately optimising the design of biosorption systems. Some more influential characteristics include specific surface area, pore volume, pH_{PZC} of the biosorbent surface and biosorbent composition. The specific surface area, as determined by BET analysis, displayed unmodified, calcinated, and chemically modified eggshell values of 1.61 [53], 3.0 [52], and 90.0 m^2/g [44], respectively. This review shows eggshells modified using $KMnO_4$ exhibited a remarkably high specific surface area and a correspondingly high biosorption capacity. An increase in specific surface area has been reported to make active sorption sites more easily available [58, 59]. Reported values of pore volume for unmodified and calcinated eggshells were 0.0047 [44] and 0.015 cm^3/g [52], respectively. An increase in pore volume can increase the accessibility of sorbates to sites within the sorbent. Further, Ofomaja and Naidoo [60] successfully demonstrated that an increase in pore volume favored external mass transfer rates. The point of zero charges for unmodified, magnetized, and calcinated eggshells was reported at a pH of 6.6 [50], 8.0 [54], and 8.6 [48], respectively. Thus, for pH values above the pH_{pzc}, the surface of the sorbent would be predominantly negatively charged (favouring cations), and below, the surface would be predominantly positively charged (favouring anions). Al-Ghouti and Salih reported the density of unmodified eggshells [50] to be 1.16 g/mL. However, Sathiparan [23] highlighted that sorbent grinding operations can influence eggshells' BET surface area and true density. In the reviewed literature, the primary constituent components of eggshells were resolved by EDS and XRF analysis. Authors have reported that carbon can range in values from 21.3 to 39.5%, oxygen can range from 41.1 to 55.6%, and calcium in the form of $CaCO_3$ from 14.35 to 27.05% [49, 50, 56]. The variation of these components may be attributed to factors such as genotype, age of the hen, and feeding [61, 62].

3.2 Biosorption Experimental Design

The application of modeling techniques to optimize the biosorption process has seen increased use in the past years. The use of single-variable optimization can be complex when simulating biosorption processes. The advantage of current modeling and statistical techniques is the saving of time and cost, as well as the ability to capture effects and interactions among process variables. Basaleh *et al.* [44], successfully applied response surface methodology-central composite design (RMS-CCD) to the $KMnO_4$-eggshell modification process. The authors tested multiple modifying agents and used RSM for experimental design and to assess the impact of the modifications.

Independent factors adopted were concentration and time, while the removal efficiency was selected as the dependent factor. The goodness of fit of the developed predictive models was assessed using analysis of variance (ANOVA). Eletta *et al.* [48] also employed the RSM-CCD to optimize cyanide biosorption by calcinated eggshells. The authors used biosorbent dose and concentration as independent and removal efficiency as the dependent variable. The developed polynomial model was also assessed using ANOVA. Al-Ghouti *et al*. [50] used factorial and completely randomized design for their experimental design. The authors evaluated the effect of pH using ANOVA single factor. They also successfully used ANOVA two-factor with replications to assess the relationship between initial concentration and temperature.

3.3 Biosorbent Preparation

As global development continues unabated, there have been increases in the release of conventional and emergent pollutants into our ecosystem. To keep pace, biosorption researchers continuously discover new and improve existing biosorbents. In this review, the preparation of eggshell biosorbents is categorized into three stages, as outlined in Figure 1. The reviewed literature showed that stage 1 preparation typically involved washing the eggshells with distilled water and drying them within the range of 40-150°C for a period ranging from 3-24 hrs. Stage 2 preparations, such as calcination, are performed within the range of 500 to 1000°C, with the decomposition of the eggshells reported to occur at 728.6°C by Rapo *et al.* [52]. Oxidizing agents such as $KMnO_4$ were successfully used to modify eggshells [44]. Ajab *et al.* [54] created a magnetized eggshell sorbent capable of separating using a magnetic field. Successful stage 3 preparation was reported by Kocabas and Satir [55] for creating a chitosan-eggshell composite and Xin and Ngadi [53] for eggshells impregnated with pandanus.

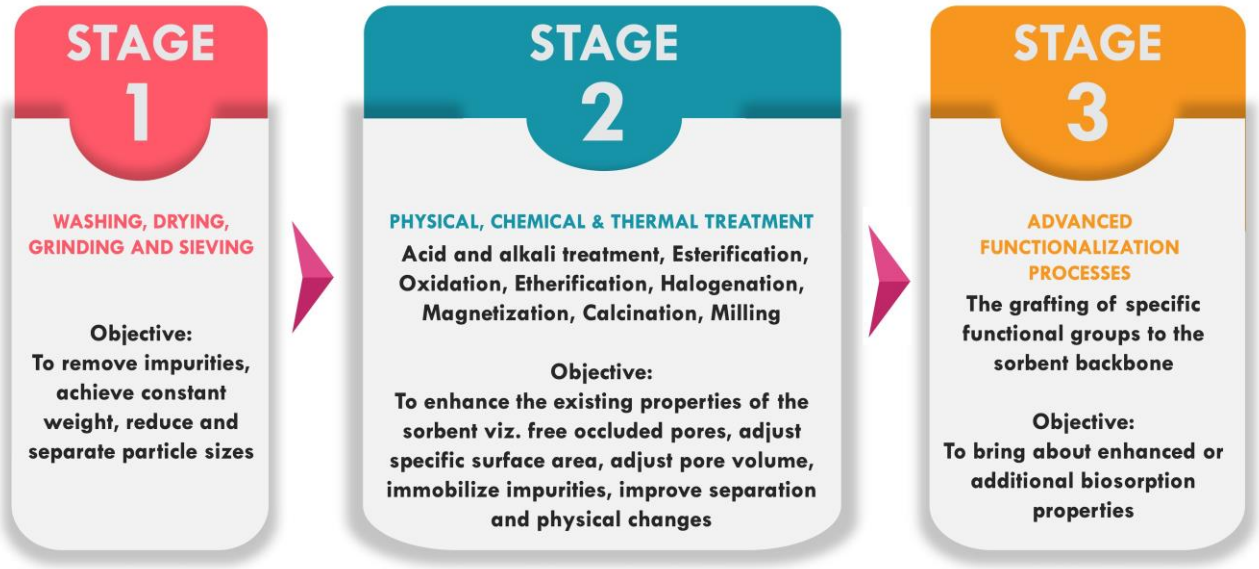

Figure 1 Stages of biosorbent preparation.

4. Elucidating the Performance of Eggshell Biosorption

Over the past seven years, several studies have focused on altering eggshells' physical and chemical characteristics. This endeavor has seen an improvement in sorbate-sorbent separability

through magnetization via the incorporation of Fe salts and improved sorption capacity through chemical (e.g., acid and alkali modifications) and thermal (e.g., calcination) treatment. Kristianto *et al.* [49] reported on the calcination of eggshells to produce a biosorbent with a marked increase in Ni (II) uptake; however, the sorption of boron experienced a reduction in uptake after calcination treatment [50]. Chemical modification through NaOH successfully increased methylene blue's sorption capacity. However, acid treatment revealed a significant decrease below that of unmodified eggshells (Table 1). The biosorption of Bi^{3+} was reported by Abbas *et al.* [36] and was shown to possess a biosorption capacity of 891.3 mg/g. The exceptional performance compares well to other reported sorbents such as *Streptomyces rimosus* (38.9 mg/g) reported by Fathi *et al.* [63] and macrocyclic functionalized hydrogel (9.8 mg/g) reported by Omondi *et al.* [64]. Kristianto *et al.* (2019) [49] showed that by calcinating eggshells, the sorption capacity for Ni (II) was increased by more than 50 times that of unmodified eggshells. Exceptional biosorption performance was also reported by Basaleh *et al.* [44] for the removal of Pb (II) by $KMnO_4$-modified eggshells (690.0 mg/g) and Ashour and Tony [51] for the removal of Fe^{3+} (129.7 mg/g) and Fe^{2+} (181.3 mg/g).

Table 1 Maximum sorption capacity attained through biosorption by modified and unmodified eggshells.

Biosorbent	**Contaminant**	**pH**	**Maximum capacity (mg/g)**	**Ref.**
Unmodified eggshells	Nickel	5.6	2.3	[57]
Unmodified eggshells	Cadmium	5.7	7.1	[56]
Unmodified eggshells	Bismuth	8.0	891.3	[36]
Calcinated eggshells	Cyanide	7.0	3.3	[48]
Calcinated eggshells	Nickel	6.0	769.2	[49]
Unmodified eggshells	Nickel	6.0	13.5	[49]
Calcinated eggshells	Boron	6.0	31.1	[50]
Unmodified eggshells	Boron	6.0	42.2	[50]
Calcinated eggshells	Iron (II)	-	181.3	[51]
Unmodified eggshells	Iron (II)	-	165.6	[51]
Calcinated eggshells	Iron (III)	-	129.7	[51]
Unmodified eggshells	Iron (III)	-	105.4	[51]
Pandanus impregnated eggshells	Chromium (VI)	5.0	0.2	[53]
Magnetic eggshells	Chromium (VI)	8.0	12.0	[54]
Unmodified eggshells	Copper (II)	5.0	94.59	[65]
Unmodified eggshells	Co (II)	6.0	6.90	[66]
Chicken eggshell powder	Lead (II)	5.0	25.19	[67]
Chicken eggshell powder-doped iron (III) oxide-hydroxide	Lead (II)	5.0	42.74	[67]
$KMnO_4$-modified Eggshells	Lead (II)	5.0	690.0	[44]

Calcinated eggshells	Remazol brilliant violet-5R	6.0	17.0	[52]
Citric acid-modified eggshells	Methylene blue	12	20.5	[47]
NaOH-modified eggshells	Methylene blue	12	90.9	[47]
Unmodified eggshells	Methylene blue	8.0	39.7	[47]
Chitosan-modified eggshells	Brilliant blue R	2.0	11.4	[55]
Sodium alginate-modified alkali-activated eggshell/Fe_3O_4 nanoparticles	Crystal violet	8.0	332.6	[68]
Unmodified eggshells	Malachite green	6.0	243.2	[69]
Nano-magnetic eggshell modified graphene	Methyl red	4.0	10.98	[70]

5. Mechanisms of Biosorption

In the reviewed literature, the biosorption mechanisms by unmodified and modified eggshells were generally elucidated using characterization, kinetic, equilibrium, and thermodynamic analysis. Table 2 provides a summary of the mechanistic insights reported across different studies. Kinetic studies predominantly identified the pseudo-second-order model as the best fit for biosorption data, suggesting that the rate-limiting step may involve chemisorption processes. For example, several studies that investigated the adsorption of heavy metals, such as Cu (II) [65] and Pb (II) [67], by unmodified eggshells reported strong adherence to this model, indicating that the interaction between the metal ions and the eggshell surface was not solely governed by physical diffusion. The Langmuir model dominated among the equilibrium models, implying monolayer adsorption. However, several studies found that the Freundlich isotherm model also conformed well to the sorption data, which suggests that monolayer biosorption and heterogeneous surface conditions may coexist under the used experimental conditions. Again, according to the table, there was no discernable difference between metal and dyes regarding the optimal equilibrium model. The Langmuir model's predominance suggests that, under the studied conditions, biosorption likely occurs at specific active sites on the eggshell surface without interactions between adsorbed molecules. However, the frequent use of the Freundlich isotherm model in other studies suggests that biosorption may also occur on heterogeneous surfaces, where sites vary in affinity and binding strength. This is particularly evident in studies involving modified eggshells by Praipipat *et al.* [67], where adding functional groups created a more complex sorption surface. Characterization studies, including SEM, FTIR, and XPS, provided further insights into the eggshell surface structure and functional groups responsible for biosorption. Tonk *et al.* [56] demonstrated that TEM and SEM images taken before and after Cd (II) ion adsorption revealed surface structure modifications on eggshell waste attributed to ion exchange reactions occurring during the process. This evidence supports the notion of a multi-mechanistic adsorption process involving both physical and chemical interactions. Thermodynamic analysis generally indicated that the biosorption processes were spontaneous, as evidenced by negative Gibbs free energy values (ΔG). However, the enthalpy values (ΔH) varied across studies, indicating that the sorption processes could be either endothermic or exothermic depending on the adsorbate type and experimental conditions. Ashour and Tony [51], demonstrated that the adsorption of Fe (III) by calcinated eggshells exhibited endothermic behavior,

suggesting that higher temperatures enhance sorption by possibly increasing the mobility of ions. Conversely, Adeniji *et al.* [47] observed exothermic behavior for the adsorption of methylene blue by NaOH-modified eggshells, implying that lower temperatures are favorable for the dye adsorption, possibly due to the nature of dye-sorbent interactions, which may rely more on electrostatic attractions. Where reported, authors generally attributed the mechanism of uptake for both dye and metal to physical adsorption [49, 50, 52] and the involvement of electrostatic interactions [36, 54] or chemisorption [44, 47, 65] and, to a lesser extent, ion exchange [53, 54, 56].

Table 2 Elucidation of eggshell biosorption mechanisms.

Biosorbent	Contaminant	Kinetic Model	Equilibrium Model	Thermodynamics	Mechanisms	Ref.
Unmodified eggshells	Nickel	-	Freundlich	Endothermic	-	[57]
Unmodified eggshells	Cadmium	Pseudo-second order	Langmuir	-	Physical sorption and ion exchange	[56]
Unmodified eggshells	Bismuth	Pseudo-second order	Langmuir	Endothermic	Electrostatic interaction and cation exchange	[36]
Calcinated eggshells	Cyanide	Pseudo-second order	Langmuir	-	-	[48]
Calcinated eggshells	Nickel	-	Langmuir	Exothermic	Physical sorption	[49]
Unmodified eggshells	Nickel	-	Langmuir	Exothermic	Physical sorption	[49]
Calcinated eggshells	Boron		Freundlich	Spontaneous and exothermic	Physical sorption	[50]
Unmodified eggshells	Boron		Freundlich	Spontaneous and exothermic	Physical sorption	[50]
Calcinated eggshells	Iron (II)	Pseudo-second order	Langmuir	Endothermic	-	[51]
Unmodified eggshells	Iron (II)	Pseudo-second order	Langmuir	Endothermic	-	[51]
Calcinated eggshells	Iron (III)	Pseudo-second order	Langmuir	Endothermic	-	[51]
Unmodified eggshells	Iron (III)	Pseudo-second order	Langmuir	Endothermic	-	[51]
Pandanus Impregnated eggshells	Chromium (VI)	Pseudo-first order	Freundlich	Spontaneous, feasible and endothermic	Physical and chemical ionic interaction	[53]
Magnetic eggshells	Chromium (VI)	Pseudo-second order	Langmuir	Spontaneous and exothermic	Electrostatic interaction and ion exchange	[54]

Unmodified eggshells	Copper (II)	Pseudo-first order	Langmuir	Spontaneous and exothermic	Chemisorption	[65]
Unmodified eggshells	Co (II)	Pseudo-first order	Langmuir	-	Physical sorption	[66]
Chicken eggshell powder	Lead (II)	Pseudo-first order	Langmuir	-	Chemisorption	[67]
Chicken eggshell powder-doped iron (III) oxide-hydroxide	Lead (II)	Pseudo-first order	Freundlich	-	Physical sorption	[67]
KMnO4-modified eggshells	Lead	Pseudo-second order	Langmuir	Spontaneous, feasible and endothermic	Chemisorption	[44]
Calcinated eggshells	Remazol brilliant violet-5R	Pseudo-second order	Langmuir	Spontaneous and exothermic	Physical sorption	[52]
Citric acid-modified eggshells	Methylene blue	Pseudo-second order	Langmuir	Endothermic	Chemisorption	[47]
NaOH-modified eggshells	Methylene blue	Pseudo-second order	Langmuir	Exothermic	Chemisorption	[47]
Unmodified eggshells	Methylene blue	Pseudo-second order	Langmuir	Exothermic	Chemisorption	[47]
Chitosan-modified eggshells	Brilliant blue R	Pseudo-second order	Langmuir	Spontaneous and endothermic	-	[55]
Unmodified eggshells	Malachite green	Second-order polynomial equation	Freundlich	-	Physical adsorption, microprecipitation and alkaline fading	[69]
Nano-magnetic eggshell modified graphene	Methyl red	Pseudo-second order	Langmuir - Freundlich	Spontaneous, feasible and endothermic	-	[70]

6. Regeneration and Recyclability of Eggshell Adsorbents

A thorough analysis of the reviewed literature revealed minimal investigation into the regeneration and recyclability of eggshell adsorbents. HCl, EDTA and HNO_3 were generally reported as the most efficient eluent for the desorption of these heavy metals from unmodified and modified eggshell adsorbents, and desorption efficiency was directly related to the eluent concentration. Ajab *et al.* [54] explained that under acidic conditions, the metal ions were substituted by protons, causing the functional groups of the adsorbents to become protonated. Consequently, the

adsorbents released metal ions. Mohammed *et al.* [71] found that ground and nano-sized eggshells could be effectively reused four times with a marginal reduction in efficiency, making them very promising Cu (II) adsorbents. Praipipat *et al.* [67], showed that in the release of Pb (II) ions from chicken eggshell powder-doped iron (III) oxide-hydroxide, a 0.5 M HNO_3 solution resulted in only 15% reduction in adsorption after 5 cycles. Tabidi *et al.* [66] achieved only 7.5% reduction in adsorption efficiency after 4 cycles using HNO_3 (concentration not reported) for the release of Co (II) ions from unmodified eggshells. Acidic dyes such as reactive red 120 were effectively desorbed from eggshells using 0.1 M NaOH and revealed a marginal 7% reduction in adsorption after 5 cycles [72]. However, there is still a lack of studies on the recyclability of eggshell adsorbents, particularly involving dye adsorption. These areas with deficiencies present a significant barrier to industrial implementation, so it is recommended for future research emphasis.

7. Future Prospects and Current Challenges [Limitations]

Using eggshells as a biosorbent for contaminant removal has attracted substantial research attention, but key limitations hinder large-scale applications. Much of the research has focused on batch systems with single-ion synthetic solutions, which may not accurately represent the complex interactions seen in natural wastewater environments. Competing ions present in natural wastewater can significantly affect biosorption efficiency, highlighting the need for more studies that use natural wastewater to improve the understanding and optimization of eggshell biosorption in practical scenarios. While modifications to eggshells such as physical, chemical, thermal, and functional treatments have shown promise in enhancing adsorption capacity, these processes can be costly and may challenge scalability. Conducting cost-benefit analyses to assess various modification techniques, including the expenses associated with chemicals, energy, and reusability, would help determine their feasibility for broader applications. Additionally, securing a consistent supply of eggshell waste is essential for pilot and full-scale operations, which demand substantial quantities of biosorbent. Practical challenges also arise in both batch and column systems. In batch systems, separating eggshell particles after adsorption can be difficult. In column systems, the small particle size of powdered eggshell often leads to increased head loss, restricting flow rates and reducing efficiency. Research is needed to address these issues, such as developing methods for easier particle separation and optimizing particle size distribution for use in columns. Moreover, pharmaceuticals, pesticides, and personal care products (PPCPs) are increasingly found in water sources and pose significant environmental risks. Yet, studies on the effectiveness of eggshell biosorption for these contaminants are limited. Operational challenges, including the recovery of biosorbent material, potential leaching of contaminants, and post-saturation waste management, need careful consideration. Additionally, life cycle assessments (LCAs) and studies on reusability could provide valuable insights into the environmental sustainability of eggshell biosorbents. While eggshells present a promising eco-friendly biosorbent option, addressing these limitations through targeted research and innovation is essential for advancing their application from controlled experiments to practical, large-scale solutions.

8. Conclusions

Developments during the past decade into the application of modified and unmodified eggshells for the biosorption of metals and dyes were discussed in this review. We propose that the

preparation of biosorbents be categorized into 3 stages. The synthesis of biosorbents to target specific pollutants is a major step in developing eggshell biosorbents. The reviewed literature showed numerous authors taking the bold step of performing 2- and 3-stage biosorbent preparation techniques. As a result, they have recorded exceptional biosorbent performances. Increased biosorption rates and capacities may be accounted for by increased sorbate affinity through adjustments to sorbent area, volume, morphology, and functional groups. The use of tools like RSM is quite valuable in the design of experiments. The testing and modeling of operational parameters revealed that biosorption kinetics were well represented, in most instances, by the pseudo-second-order equation. The Langmuir model dominated the equilibrium models, implying monolayer adsorption onto homogeneous surfaces. Biosorption of both metals and dyes by eggshells was generally spontaneous. Biosorption of metals and dyes by eggshells was typically spontaneous, with particle size significantly enhancing the adsorption rate, particularly with nano-sized eggshell particles. However, a significant challenge in batch processes is the difficulty of separating eggshell particles after adsorption. In column systems, small particle sizes lead to increased head loss, limiting flow rates and efficiency. Comprehensive economic analyses should be conducted to evaluate the feasibility of eggshell-based biosorption, especially concerning large-scale modifications and eggshell sourcing. Addressing these issues is crucial for up-scaling applications. To advance the development of eggshell biosorbents, further research is needed on optimizing regeneration and reuse methods and conducting column studies at laboratory, pilot, and complete scales. Additionally, investigating the use of eggshell biosorbents to remove emerging contaminants, such as pharmaceuticals, is highly recommended to expand the range of potential applications.

Author Contributions

Both authors contributed equally to the conceptualisation and writing of the article.

Competing Interests

The authors have declared that no competing interests exist.

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