



Article

Mechanistic Study of Pb^{2+} Removal from Aqueous Solutions Using Eggshells

Mohamed A. Hamouda ^{1,2,*} , Haliemeh Sweidan ¹, Munjed A. Maraqa ^{1,2}
and Hilal El-Hassan ¹ 

¹ Department of Civil and Environmental Engineering, United Arab Emirates University, P.O. Box 15551, Al Ain, UAE; hswaidan@uaeu.ac.ae (H.S.); m.maraqa@uaeu.ac.ae (M.A.M.); helhassan@uaeu.ac.ae (H.E.-H.)

² National Water Center, United Arab Emirates University, P.O. Box 15551, Al Ain, UAE

* Correspondence: m.hamouda@uaeu.ac.ae; Tel.: +971-3-713-5155

Received: 27 July 2020; Accepted: 4 September 2020; Published: 9 September 2020



Abstract: This study investigates the impact of eggshell particle size and solid-to-water (s/w) ratio on lead (Pb^{2+}) removal from aqueous solution. Collected raw eggshells were washed, crushed, and sieved into two particle sizes (<150 and 150–500 μm). Batch Pb^{2+} removal experiments were conducted at different s/w ratios with initial Pb^{2+} concentrations of up to 70 mg/L. The contribution of precipitation to Pb^{2+} removal was simulated by quantifying removal using eggshell water, whereas sorbed Pb^{2+} was quantified by acid digestion. Results indicated that eggshell particle sizes did not affect Pb^{2+} removal. High removal (up to 99%) of Pb^{2+} was achieved for low initial Pb^{2+} concentrations (<30 mg/L) across all s/w ratios studied. However, higher removal capacity was observed at lower s/w ratios. In addition, results confirmed that precipitation played a major role in the removal of Pb^{2+} by eggshells. Yet, this role decreased as the s/w ratio and initial concentration of Pb^{2+} increased. A predictive relationship that relates the normalized removal capacity of eggshells to the s/w ratio was developed to potentially facilitate the design of the reactor.

Keywords: Pb^{2+} removal; sorption; precipitation; waste recycling; removal mechanisms; solid-to-water ratio

1. Introduction

The presence of lead (Pb^{2+}) in industrial wastewater has become a noteworthy source of water pollution and poses a significant health hazard to humans [1]. Physiological damage to human kidneys, liver, brain, and nervous system can happen as a result of ingesting levels of Pb^{2+} higher than the body's tolerance [2]. In addition, elevated levels of Pb^{2+} in the human body have been shown to have negative health effects including fatigue, a decreased reproductive ability, problems in the digestive tract, and anemia [1,3]. In fact, sterility, stillbirths, and neonatal deaths are associated with constant exposure to Pb^{2+} [1]. Pb^{2+} poisoning is especially dangerous for children, as high levels of Pb^{2+} in the blood stream are associated with depression of brain development and cognitive skills [4–6]. Pb^{2+} poisoning can be contracted by humans through polluted drinking water, ingestion from food, inhalation of contaminated dust, or occupational exposure [1,2,4,6–9]. It can infiltrate and contaminate the water sources, and from there, contaminate every level of the food chain [1,2,10]. It has been difficult to scientifically specify a level under which Pb^{2+} is no longer associated with negative health effects, therefore many jurisdictions focus on the ability of treatment technologies to completely remove Pb^{2+} from water. The maximum acceptable concentration of Pb^{2+} in drinking water is becoming more stringent, with some jurisdictions assigning a level as low as 5 $\mu\text{g/L}$ [11], while the US EPA has set the maximum contaminant level goal for Pb^{2+} in drinking water at zero but an action level at 15 $\mu\text{g/L}$ [12].

Sources of Pb^{2+} in water originate mainly from industrial activities such as mining, smelting, printing, and metal plating. In addition, manufacturing of batteries, paints, alloys, ceramic glass, and plastics contribute to increased Pb^{2+} pollution in water bodies [1]. Wastewater from battery manufacturing contains, on average, a Pb^{2+} content of 0.5–25 mg/L [13–16]. Regulations for industrial effluent discharge or reuse vary considerably between different jurisdictions. Certain jurisdictions specify a maximum Pb^{2+} level for discharge of effluent wastewater into the environment; this level can be as low as 0.1 mg/L (Saudi Arabia and Oman) or as high as 1 mg/L (Tunisia) [17].

Several methods were proposed and investigated for the removal of Pb^{2+} from industrial wastewater including ion exchange, filtration and membrane processes, electro-dialysis, chemical precipitation, solvent extraction, and chemical coagulation [1,2]. In addition, electrocoagulation, membrane electrodialysis, and biosorption were also employed for Pb^{2+} removal [14]. A widely used method for Pb^{2+} removal from industrial wastewater is to precipitate Pb^{2+} with caustic soda at a pH 8.5–9.2 in the presence of Fe (III) salts, followed by the addition of a polyelectrolyte, which facilitates the flocculation of the Pb^{2+} precipitate. The effluent is further treated with sedimentation and filtration, after which the Pb^{2+} concentration is reduced to the legal allowable limit [16]. Sorption by activated carbon is also a convenient and efficient treatment method. However, the use of commercial activated carbon for sorption can be costly [18]. Therefore, there is an increasing need to re-use biowaste in wastewater treatment [19]. Many studies have focused their efforts on deriving substitute sorbents from waste materials, particularly agricultural waste [20]. This not only helps to reduce the cost of sorbents, but it also helps recycle agricultural waste. Waste materials that have been used for Pb^{2+} removal include: *Chlorella vulgaris*, chicken feathers reinforced with chitosan, cow bone, leather, coconut shell, peach and apricot stones, *Alocacée* shell, *Mimosaceae* husk, and *Burseraceae* sawdust [1,21–25].

Eggshells are an example of an agricultural waste that could be used for Pb^{2+} removal. In fact, the per capita consumption of eggs in the United Arab Emirates (UAE) was 8.3 kg in 2013 [26]. Previous research reported that eggshells consist of (weight %) calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%) [27]. Eggshells were studied for removal of various pollutants from water, including heavy metals such as copper, iron, cadmium, and Pb^{2+} [28–33]. Other work investigated the removal of dyes such as C.I. Reactive Yellow 205, methylene blue, and malachite green using eggshells [34–36]. However, few of these studies provided a detailed investigation of the mechanisms responsible for contaminant removal. It is plausible that, in addition to sorption, other removal mechanisms could be responsible for contaminant removal when using a naturally occurring material as a sorbent. Such mechanisms include ion exchange, as reported by Andersson et al. [37] for the removal of heavy metals from water onto the calcite surface, precipitation [38–40], or surface reactions [41]. However, only few studies investigated the impact of operation conditions (eggshell particle size and dose) on the mechanisms of Pb^{2+} removal. Nonetheless, existing literature on the use of eggshells for Pb^{2+} removal acknowledged that precipitation and sorption occurred [13,28,30,42]. However, the reviewed studies offer no quantification of the contribution of each mechanism, i.e., precipitation and sorption, which is an important aspect of process design.

Therefore, the objectives of this study were twofold: first, to identify the mechanisms responsible for the removal of Pb^{2+} from aqueous solutions using eggshells and to quantify the contribution of each of these mechanisms towards total removal. The authors were specifically interested in isolating the role of precipitation from surface attachment. While surface attachment may take different forms (i.e., sorption, ion exchange, complexation, etc.), for simplicity, it is referred to as sorption from here on. The second objective was to investigate the impact of the applied eggshells mass-to-solution volume ratio on Pb^{2+} removal. Results of this study provide novel and beneficial information for the design of eggshell reactors for optimal removal of Pb^{2+} , while also contributing to sustainable waste management by recycling eggshell material to treat wastewater.

2. Materials and Methods

A general framework for investigating and characterizing the use of biowaste materials for treatment and contaminant removal was previously published [19]. In this study, the framework is applied to carry out a mechanistic study of the removal of Pb^{2+} from aqueous solutions using eggshells (Figure 1).

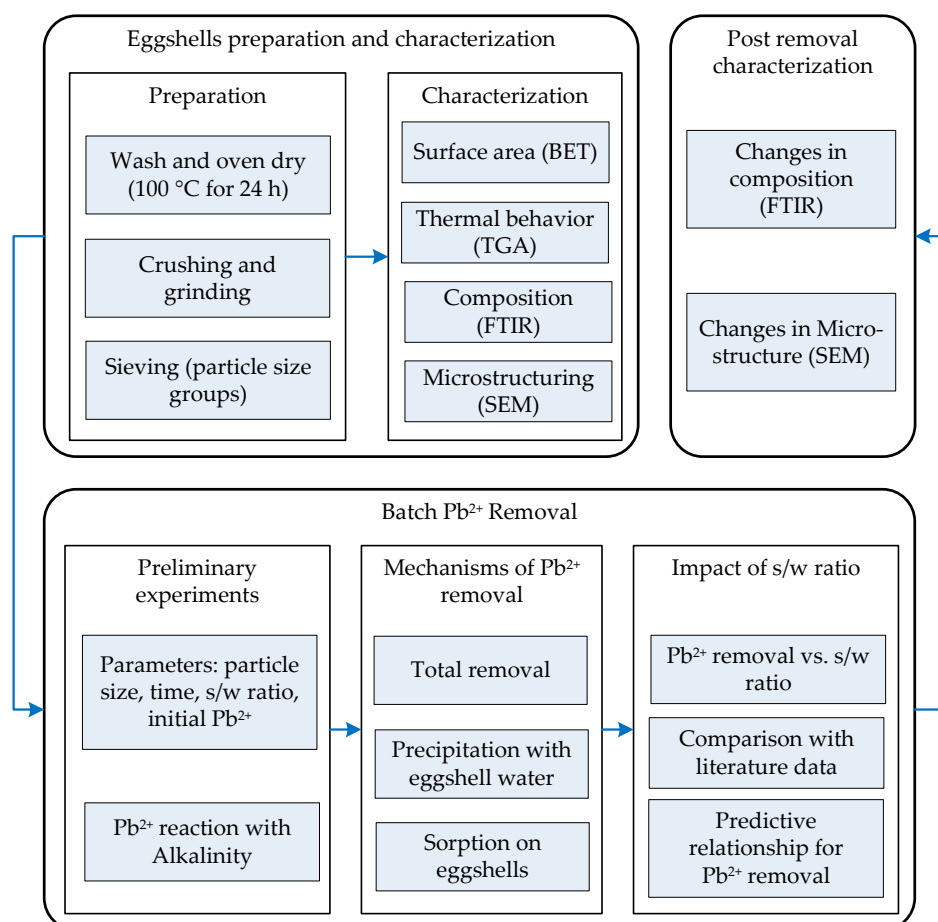


Figure 1. Summary of applied methodology.

2.1. Materials

Hanna Instruments 0.1M standard Pb^{2+} solution (HI4012-01) was used to prepare all Pb^{2+} solutions throughout this study. The required amount of standard Pb^{2+} solution was diluted in ultrapure water (Milli-Q® IQ 7000 Ultrapure, Merck, Darmstadt, Germany) as required to prepare the needed Pb^{2+} concentrations. In addition, H_2SO_4 (95–97% assay), ethanol (95% purity), phenolphthalein (Riedel-de Haën™, indicator grade, Honeywell International Inc., Charlotte, NC, US), and methyl orange powder (Fluka™, indicator grade, Honeywell International Inc., Charlotte, NC, US) were used for alkalinity measurements.

2.2. Preparation of Eggshells

Eggshells were collected from a local restaurant in the city of Al Ain, UAE. Two batches were collected from the restaurant across a period of two weeks; each batch contained the eggshells collected by the restaurant for the week. All batches of collected eggshells were then mixed and rinsed several times with deionized water to wash away any impurities. They were then dried at 100 °C for 24 h in a conventional drying oven (ULE 400, Memmert, Schwabach, Germany). The eggshells were then ground with a pulverizer (LC-53, Gilson Company Inc., Lewis Center, OH, USA). The distance between

the blades was set at about 0.7 mm to obtain particles in the range of 0.8–1.0 mm. This particle size was required to help physically remove the inner membranes. The eggshell inner membranes were then removed by soaking the eggshells in deionized water and mixing them, after which the inner membranes floated to the top and were physically removed. The eggshells were then rinsed several times to remove any residual membranes, dried again in the oven for 24 h at 100 °C, and further ground in the pulverizer. Subsequently, the obtained particles were sieved using stainless steel ASTM test sieves (Gilson Company Inc., Lewis Center, OH, USA). The resulting eggshells were classified into 4 groups depending on size, namely <150 µm, 150–500 µm, 500–800 µm, and >800 µm. The ground eggshells were stored in plastic sealable bags at room temperature until use.

2.3. Eggshells Characterization

The powdered eggshells were characterized to evaluate their potential performance for Pb²⁺ removal. Eggshell particles underwent nitrogen gas adsorption for characterization of their surface area and porosity. This was carried out with a Quantachrome Autosorb-1-C volumetric gas sorption instrument at 77K. Before measurements, samples were degassed at 150 °C for one hour. Further, Brunauer–Emmett–Teller (BET) theory was used to calculate surface area, and pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) model based on the desorption branch of the N₂ isotherms. Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) analyses were used to investigate the changes to the microstructure of eggshells as a result of Pb²⁺ removal, as will be discussed in detail in Section 2.8. Based on the results of eggshell particles characterization, it was decided to use only two particle sizes (<150 µm of d₅₀ = 75 µm and 150–500 µm of d₅₀ = 300 µm) in the Pb²⁺ removal experiments, as they had the highest surface area. In addition, the study focused on particle size 150–500 µm, which was thought to be more practical and feasible to scale to column studies.

2.4. Pb²⁺ Removal Experiments

For all Pb²⁺ removal batch experiments, Pb²⁺ solutions at the desired concentrations were prepared as stock solutions from which sample volumes of 50 or 100 mL were obtained. Specific amounts of crushed eggshell powder were added to the samples to achieve the desired solid-to-water (s/w) ratio. Samples were then subject to shaking in a water bath shaker (MaXturdy 18, Daihan Scientific Co., GANG-WON -DO, South Korea) at a temperature of 25 °C and rotational speed of 150 rpm. If required, they were filtered using syringe filters (Thermo Scientific™, PTFE, 0.45 µm, 25 mm). Measurements of Pb²⁺, Mg²⁺, and Ca²⁺ concentration in solution were taken by Varian ICP-OES 720 ES with standards by Chem-Lab™, Belgium. A Thermo Scientific™ Orion™ 3-star pH meter was used to carry out pH measurements. Alkalinity was measured by titration, according to method 2320 [43].

For all the experiments explained in the sections below, samples were analyzed in triplicate, and the coefficient of variation for Pb²⁺ concentration ranged from 0.3% to 8.4%. Average readings for the initial and final Pb²⁺ concentrations were used to calculate the capacity of removal (m in mg/g), regardless of the mechanism of removal, as shown in Equation (1): where V is the volume of solution used (L), M is the mass of eggshells used (g), C_0 is the initial Pb²⁺ concentration (mg/L), and C_e is the final (equilibrium) Pb²⁺ concentration (mg/L). The removal percentage of Pb²⁺ was also calculated using Equation (2).

$$m = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\text{Pb}^{2+} \text{ removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

2.5. Preliminary Investigation of Pb²⁺ Removal

A screening experiment was conducted to determine the adequate contact time (until equilibrium) and to demonstrate the potential of eggshells for Pb²⁺ removal. At an s/w ratio of 1:200, eggshells were

added to Pb^{2+} solutions of concentrations 0 to 70 mg/L for a contact time of 2 h. To help theorize the removal mechanisms involved, other parameters besides Pb^{2+} were monitored including pH, alkalinity, Ca^{2+} , and Mg^{2+} .

To investigate the potential precipitation of Pb^{2+} due to the presence of dissolved carbonates and bicarbonates, stock solutions of 1000 mg/L of Na_2CO_3 and NaHCO_3 were prepared and then left to react with Pb^{2+} in solution. One milliliter of the 1000 mg/L Na_2CO_3 stock solution was added to the 20 mg/L (0.19 meq/L) of Pb^{2+} solution and filled to the 100 mL mark in a volumetric flask. The resulting solution had a concentration of 10.07 mg/L (0.19 meq/L) Na_2CO_3 . Furthermore, 1.62 mL of the 1000 mg/L Na_2CO_3 solution was added to the 20 mg/L Pb^{2+} solution and filled to the 100 mL mark in a volumetric flask, leading to a solution of 16.2 mg/L (0.19 meq/L) NaHCO_3 . These solutions were then left for 2 h to observe any precipitation of Pb^{2+} by CO_3^{2-} or HCO_3^- . Resulting solutions were then filtered and the Pb^{2+} concentration, pH, and total alkalinity were measured before and after the addition of Na_2CO_3 and NaHCO_3 .

2.6. Effect of Particle Size and s/w Ratio on Removal of Pb^{2+}

In order to investigate the effect of eggshell particle size and s/w ratio on the removal of Pb^{2+} , 500 mL of Pb^{2+} solutions of 0 to 70 mg/L were prepared and their initial pH, Ca^{2+} , Mg^{2+} , and Pb^{2+} concentrations were measured. Then, 100 mL of each solution was added to 0.5 g of eggshells of particle size 150–500 μm , giving an s/w ratio of 1:200. The samples were shaken for 2 h then filtered. The filtrate was then analyzed for pH, alkalinity, Pb^{2+} , Ca^{2+} , and Mg^{2+} concentration. This process was also repeated for an s/w ratio of 1:100, 1:1000, and 1:2000 for eggshells of particle sizes 150–500 μm and <150 μm . This process is detailed in Figure 2.

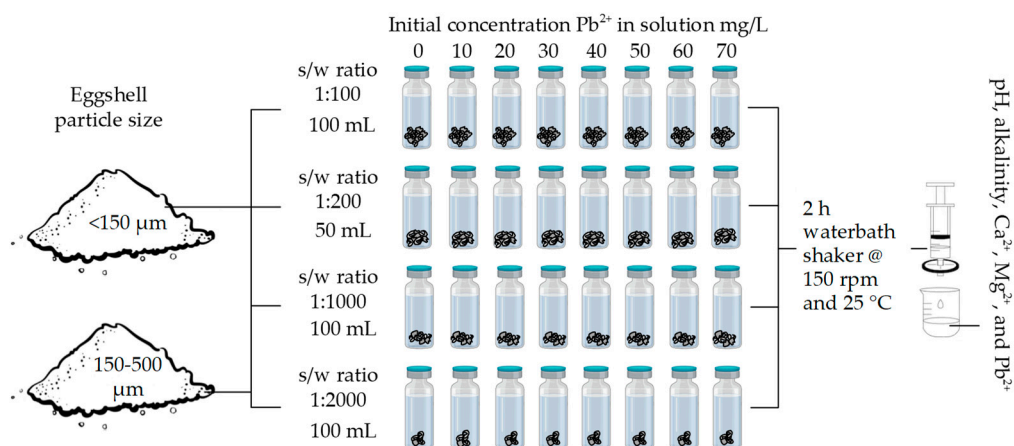


Figure 2. Experimental design for investigating the impact of solid-to-water (s/w) ratio and particle size on Pb^{2+} removal.

2.7. Differentiation between Removal of Pb^{2+} by Sorption and Precipitation

To elucidate the role of sorption versus precipitation in Pb^{2+} removal by eggshells, these mechanisms have to be isolated. To do so, eggshells used in the previous experiment (Figure 2) with an s/w ratio of 1:2000 and Pb^{2+} concentrations 0 to 60 mg/L were collected and separated from the solution with a sieve (number 120 mesh size 125 μm). The solution passing through the sieve was filtered through a 0.45 μm membrane, and a portion of the filtrate was used to rinse the eggshell particles to remove any Pb^{2+} precipitate on the surface. The eggshells were then dried in an oven at 60 $^{\circ}\text{C}$ for 16 h, and then subjected to ICP analysis after undergoing acid digestion according to method 3050B [44]. This was carried out to directly measure the amount of Pb^{2+} sorbed on the surface of the eggshells. The exact amount of Pb^{2+} sorbed was calculated using mass balance after accounting for the amount present in the water film originally surrounding the wet eggshells.

Another experiment was conducted to quantify the removal of Pb^{2+} by precipitation using eggshell extracts at different s/w ratios. A volume of 600 mL of eggshell water (ESW) with an s/w ratio of 1:200 was prepared using 150–500 μm eggshells. The mixture was mixed for 2 h in a water bath shaker at 150 rpm and 25 °C. The mixture was then decanted and filtered. The filtrate gave an ESW sample, which was used in the preparation of Pb^{2+} solutions. The pH, alkalinity, Ca^{2+} , and Mg^{2+} concentration of the ESW were measured. The ESW was then used to prepare 50 mL solutions of concentrations 0 to 70 mg/L Pb^{2+} . The solutions were mixed again for 2 h. Subsequently, they were filtered and analyzed for alkalinity, pH, Ca^{2+} , Mg^{2+} , and Pb^{2+} concentration. This process was repeated for the same eggshell size using an s/w ratio of 1:2000. This process is detailed in Figure 3.

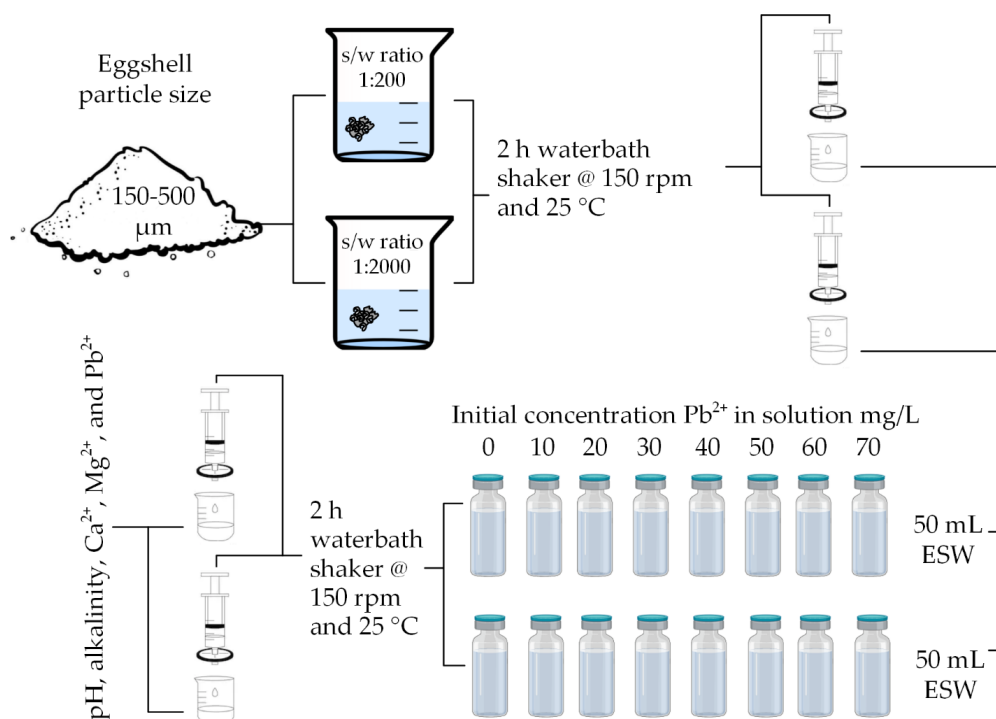


Figure 3. Experimental design for investigation of removal of Pb^{2+} in eggshell water (ESW).

2.8. Microstructure Characterization of Pb^{2+} Removal

FTIR and SEM analyses were used to investigate the changes in functional groups and morphology of selected eggshells post-exposure to Pb^{2+} and examine the removal mechanisms. FTIR spectroscopy was carried out on raw eggshells using a Shimadzu, IR-Prestige-21 spectrometer in transmittance mode at a resolution of 4 cm^{-1} from 500 to 4000 cm^{-1} . Similarly, it was performed on typical used eggshells after Pb^{2+} removal in a solution of 40 mg/L Pb^{2+} and an s/w ratio of 1:200. Samples were formulated by pulverizing eggshells into a powder, which was then sieved through an 80-micron sieve to remove coarse particles. Obtained powder samples were mixed with potassium bromide at a 3:1 ratio, by mass, and made into pellets for FTIR testing.

A JEOL-JSM 6390A scanning electron microscope was used to examine the morphology of eggshells with a particle size of 150–500 μm before and after Pb^{2+} removal. Pb^{2+} solutions of 20 mg/L at s/w ratios of 1:200 and 1:2000 were utilized. To separate the eggshells from the solution, the mixture was passed through a 125-micron sieve, rinsed with deionized water to remove any precipitated solids on the eggshell surface, and dried in the oven at 100 °C for 24 h. Samples were sputter-coated with a thin gold layer and examined in high-vacuum mode at 15 kV and magnification ranging from 100–1000.

3. Results and Discussion

3.1. Raw Eggshells Characterization

Removal of contaminants from solution by a biomass material depends on the material's surface area and accessibility to active sites [45]. Nitrogen adsorption curves were used to evaluate the surface area according to BET theory, while N_2 desorption curves were used to evaluate the pore size distributions based on the BJH model. The results are presented in Table 1 and Figure 4. As expected, the surface area was found to decrease with increasing eggshell particle size. It is worth noting that the BET surface area for eggshells was found to be comparable to the surface areas of other types of biomass used for sorption, as olive stones, tomato husks, and *Bacillus badius* (Table 1). In addition, the surface area of eggshells found in this study for particle size $<150\ \mu\text{m}$, $0.977\ \text{m}^2/\text{g}$, was similar to that reported by Tsai et al. [35] for eggshells of particle size $77\ \mu\text{m}$, $1.023\ \text{m}^2/\text{g}$. Figure 4 shows a representative curve for the nitrogen adsorption of eggshells of particle size $<150\ \mu\text{m}$; the eggshells follow a type II isotherm with negligible hysteresis. This indicates a lack of affinity between eggshells and N_2 molecules [35]. The N_2 adsorption isotherm signifies poor pore properties, owing possibly to a non-porous surface. Tsai et al. [35] also reached a similar conclusion when analyzing eggshells.

Table 1. BET and Langmuir surface area calculations of biowaste material at various particle size ranges.

Material	Size (μm)	Surface Area (m^2/g)	Pore Volume ($10^3\ \text{cm}^3/\text{g}$)	Pore Size (nm)	Reference
Eggshells	<150	0.977	3.544	14.8	This work
	150–500	0.056	-	-	This work
Eggshells	77.9	1.023	6.5	-	[35]
Olive stones	<1000	0.163	1.84	45.302	[46]
Tomato husks	75–150	0.68	0.0015	-	[47]

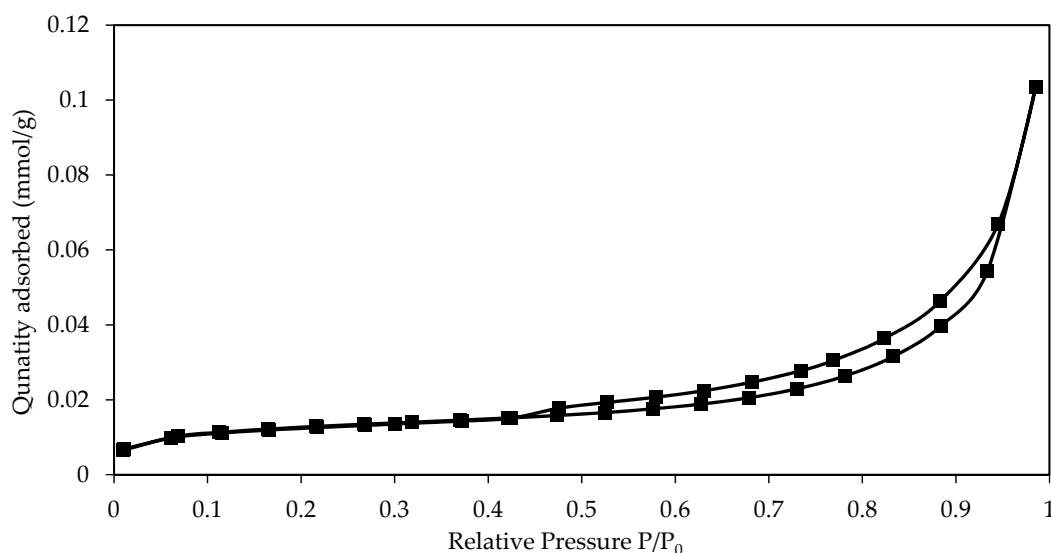


Figure 4. Nitrogen adsorption isotherm curves for eggshell powder of particle size $<150\ \mu\text{m}$.

The thermogravimetric analysis of raw eggshells has been examined in previous studies [48–50]. Such analysis highlights the change in eggshell powder mass with temperature and gives an indication of its composition. There is general agreement that the decomposition of raw eggshells with temperature has two regions of mass loss. In the first region, a minor mass loss (around 3%) indicates the decomposition of organic matter and occurs from 100 to $550\ ^\circ\text{C}$. Meanwhile, in the second region, a major mass loss (around 40%) takes place at higher temperatures up to $850\ ^\circ\text{C}$, signifying the decomposition of calcium carbonate [48–50].

3.2. Preliminary Pb^{2+} Removal Experiments

A screening experiment of removal with time indicated that Pb^{2+} removal happened over a short time period. The experiment was done using an initial Pb^{2+} concentration of 100 mg/L and s/w ratio of 1:100; measurements of Pb^{2+} concentration were taken at 30 min and every hour for 6 h. Little differences in removal were observed after 30 min of contact time. Therefore, to ensure equilibrium status is achieved, 2 h was chosen as the contact time for all further experiments. Another screening experiment was conducted to investigate the capacity of eggshells for Pb^{2+} removal at an s/w ratio of 1:200. The results indicated that eggshells showed a good potential for Pb^{2+} removal compared to previously investigated biowaste materials [1,23,46]. A removal capacity (m) of 8.18 mg/g (pH = 5.9) was found for an initial Pb^{2+} concentration of 70 mg/L, at which an equilibrium aqueous concentration of 29.5 mg/L was reached. During the analysis of Pb^{2+} solution after contact with eggshells, it was noticed that Ca^{2+} and Mg^{2+} were released into the solution by eggshells. Therefore, it was hypothesized that there could be other removal mechanisms, in addition to sorption, which could be responsible for the removal of Pb^{2+} . Previous studies have noted that Pb^{2+} precipitation due to reaction with carbonates could play a role in Pb^{2+} removal [51,52].

To confirm the potential precipitation of Pb^{2+} due to reaction with carbonates, an investigation was conducted to determine the extent of Pb^{2+} precipitation by reaction with CO_3^{2-} and HCO_3^- . $NaHCO_3$ and Na_2CO_3 were added to 20 mg/L Pb^{2+} solution. As expected, the pH and alkalinity of Na_2CO_3 and $NaHCO_3$ solutions decreased when added to a Pb^{2+} solution. Indeed, immediately after the addition of Na_2CO_3 , the pH was 8.29 and then decreased to 6.09, and alkalinity dropped from 14 to 11 mg/L as $CaCO_3$. Similarly, after the addition of $NaHCO_3$, the pH decreased from 7.31 to 5.94 and the alkalinity dropped from 16 to 5.6 mg/L as $CaCO_3$. The drop in alkalinity was accompanied by a drop in Pb^{2+} concentration from 23.66 to 0.75 and 2.53 mg/L for Na_2CO_3 and $NaHCO_3$ solutions, respectively. This indicates that alkalinity was consumed and Pb^{2+} was precipitated upon contact with CO_3^{2-} and HCO_3^- . These findings provide evidence that Pb^{2+} is precipitated by carbonates that are released by eggshells in solution.

3.3. Effect of Particle Size and s/w Ratio on Removal of Pb^{2+}

The method outlined in Section 2.6 was used to investigate the effect of s/w ratio and particle size on the eggshell capacity for Pb^{2+} removal. The results, presented in Figure 5, show that eggshell particle size generally did not have a measurable effect on the removal capacity, but a higher removal capacity was achieved with the smaller particle size (<150 μm) at high initial Pb^{2+} concentrations (>50 mg/L). This effect at a higher initial concentration of Pb^{2+} was observed in previous studies where m decreased with the increase in eggshell particle size [42], or with the increase in the particle size of calcite and aragonite [51]. Despite the large difference in the surface area of the two eggshell sizes used in this study (Table 1), a rather insignificant difference in the eggshell capacity for Pb^{2+} removal was noticed between the two sizes for initial Pb^{2+} concentrations below 50 mg/L (Figure 5). However, eggshell particle size could result in a significantly lower removal capacity for larger particles and higher initial Pb^{2+} concentration.

Furthermore, the removal capacity of eggshells decreases as the s/w ratio increases; at s/w ratios 1:1000 and 1:2000, the removal capacity is higher than that for ratios 1:100 and 1:200 (Figure 6). If the removal of Pb^{2+} is due to sorption, then a decrease in the eggshell removal capacity with the increase in the s/w ratio may be due to less effective mixing at a higher density of eggshells in the solution causing reduced accessibility to sorption sites. On the other hand, if the removal of Pb^{2+} is due to precipitation, then a decrease in the eggshell capacity with the increase in the s/w ratio could be due to a decreased dissolution of $CaCO_3$ per unit mass of eggshells at higher s/w ratios. In addition, if precipitation occurs on the eggshell surface (microprecipitation) then less sites become available for sorption. In this batch experiment mode, the highest removal capacity was found to be about 70 mg/g which occurred for particle size <150 μm at an s/w ratio of 1:2000 and an initial Pb^{2+} concentration

of about 60 mg/L. Furthermore, high percentage removals (up to 99%) were achieved for low Pb^{2+} concentrations (<30 mg/L) across all s/w ratios studied (not shown here). The low concentration of solute ensured high removal.

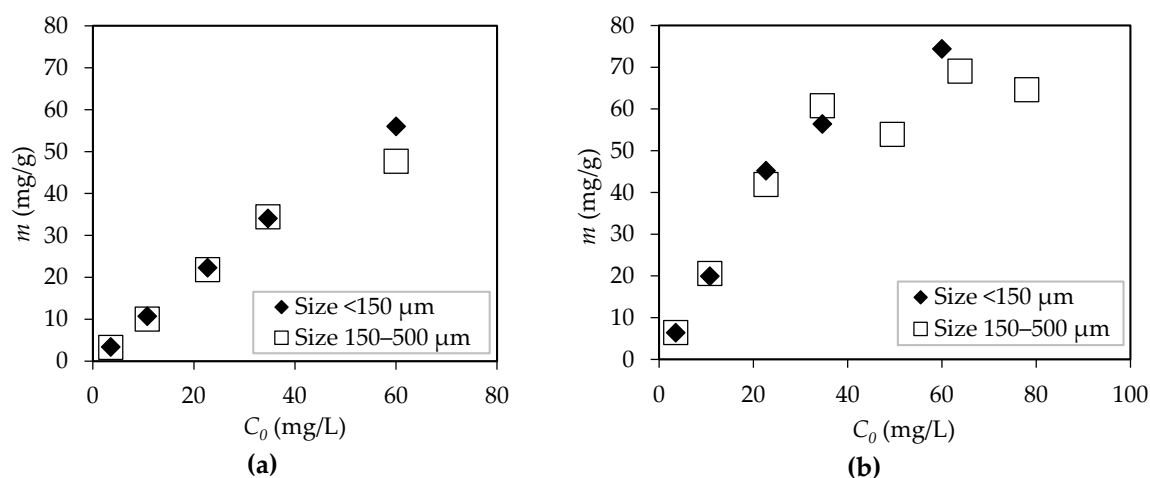


Figure 5. Removal of Pb^{2+} versus initial Pb^{2+} concentration for particle size 150–500 µm and <150 µm at (a) s/w ratio 1:1000 (pH increased from 5.49 (SD 0.25) to 8.64 (SD 0.64) for particle size <150 µm and from 5.49 (SD 0.25) to 6.92 (SD 0.67) for particle size 150–500 µm) and (b) s/w ratio 1:2000 (pH increased from 5.49 (SD 0.25) to 6.89 (SD 0.72) for particle size <150 µm and from 5.49 (SD 0.25) to 6.86 (SD 0.72) for particle size 150–500 µm).

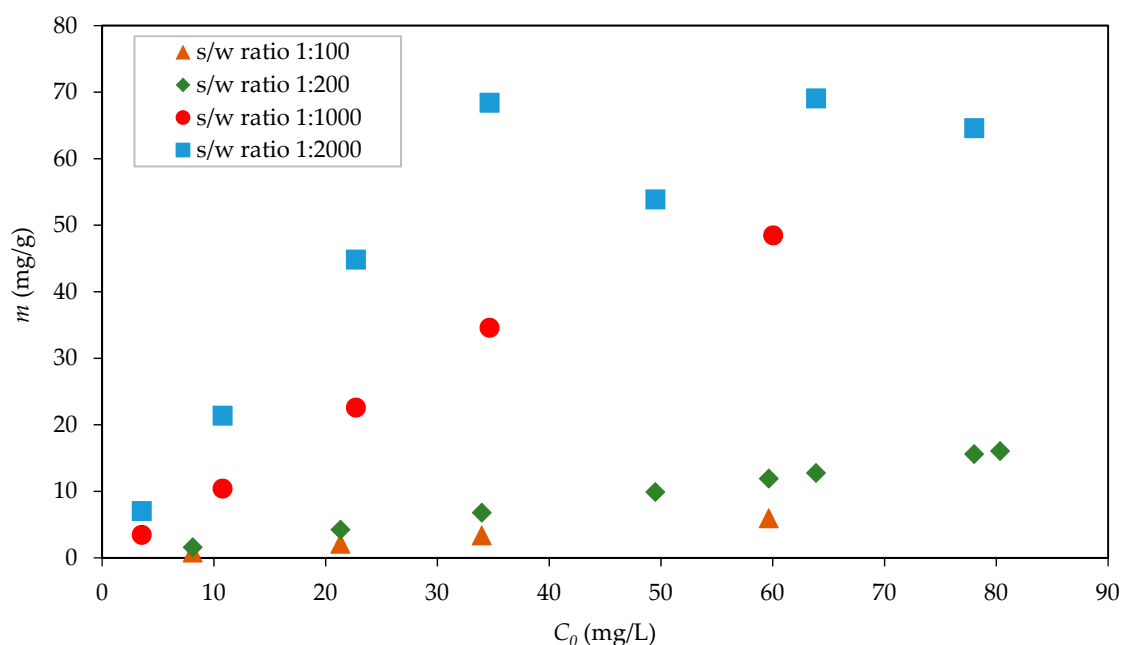


Figure 6. Removal capacity of eggshells for Pb^{2+} removal as a function of initial Pb^{2+} concentration and s/w ratio for particle size 150–500 µm (pH increased from 5.76 (SD 0.48) to 8.35 (SD 0.27) for s/w ratio 1:100; from 5.71 (SD 0.37) to 7.94 (SD 1.06) for s/w ratio 1:200; from 5.49 (SD 0.25) to 6.92 (SD 0.67) for s/w ratio 1:1000; and from 5.49 (SD 0.25) to 6.86 (SD 0.72) for s/w ratio 1:2000).

Previous studies (Table 2) showed variations in the capacity of eggshells employed for Pb^{2+} removal, with values as low as 0.12 mg/g [29] to as high as 156 mg/g [42]. Such variations could be due to differences in the experimental conditions employed, including differences in the initial concentration, particle size, and s/w ratio. However, these studies only included one s/w ratio in their investigation. As demonstrated in this study, the s/w ratio has a significant impact on the removal

capacity (m). To gain insight into the effect of s/w ratio, normalized removal capacity (m/C_0) is plotted versus s/w ratio as shown in Figure 7. Normalized capacity values for each s/w ratio used in this study were obtained from the slope of the best fit line with zero intercept of the corresponding data set presented in Figure 6. Data from previous studies [28–30,42] were superimposed for comparison purposes. Since these previous studies only included one s/w ratio in their investigation, an average value of the slope (m/C_0) was taken for each study. One study by Soares et al. [30] showed a decreasing trend of (m/C_0) with the increase in C_0 and therefore the selected data points (Figure 7) represent those before a plateau for removal capacity (m) was reached. The data of Figure 8 show a linear trend on a log–log scale.

Table 2. Eggshell capacity for removal of Pb^{2+} as reported by other studies.

Study	Eggshell Size (μm)	s/w Ratio	pH	C_0 (mg/L)	m (mg/g)
[42] ^a	750	1:500	5.0	523, 1045	156
[28]	<1000	1:40	5.5	10–150	2.24
[30] ^b	<500	1:100	5.0	100–1435	12.9
[29]	210–400	1:40	NA	3	0.12

^a Only the results for the 750 μm particle size are considered here. ^b Considered values represent those before a plateau for removal capacity was reached.

From Figure 7, it is clear that the impact of the s/w ratio is significant. The best fit relationship for the data in Figure 7 is given in Equation (3). The relation shows that the slope (m/C_0) is almost inversely proportional to the s/w ratio. Equation (3) is valid only in the range of the s/w ratio presented in Figure 8 and before the removal capacity of eggshells (m) reaches a plateau, and for particle size <1 mm.

$$\log(m/C_0) = -0.933 \log(s/w \text{ ratio}) - 2.9 \quad R^2 = 0.99 \quad (3)$$

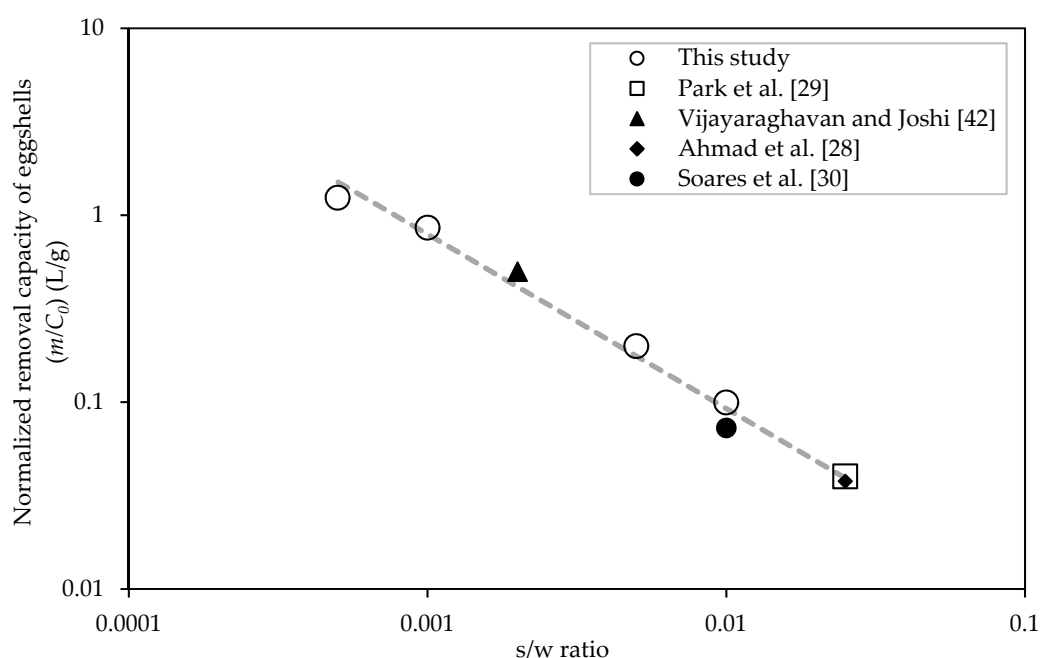


Figure 7. Comparison between normalized capacity of eggshells for Pb^{2+} removal (m/C_0) versus s/w ratio used in this study and previous studies.

The predictive relationship (Equation (3)) could be used in designing batch reactors utilizing eggshells for Pb^{2+} removal from wastewater. Specifically, this relationship could be used to optimize the design conditions and configuration of the batch reactors (single versus sequential batch reactors).

For example, based on Equation (3), 250 kg of eggshells would be required to reduce Pb^{2+} concentration from 55 to 1 mg/L with a reaction time of 2 h for 10 m³ of contaminated water if one batch reactor is used. However, if two or three batch reactors in series were to be used, the mass of eggshells would be reduced to 80 and 12 kg, respectively, with a reaction time of 2 h for each reactor. Thus, using multiple reactors in series reduces the required mass of eggshells and consequently reduces the mass of generated waste. However, the use of multiple reactors as compared to a single reactor would entail higher construction and operation costs. As such, Equation (3) could serve as a guide to reach an optimal system design subject to economic and environmental constraints.

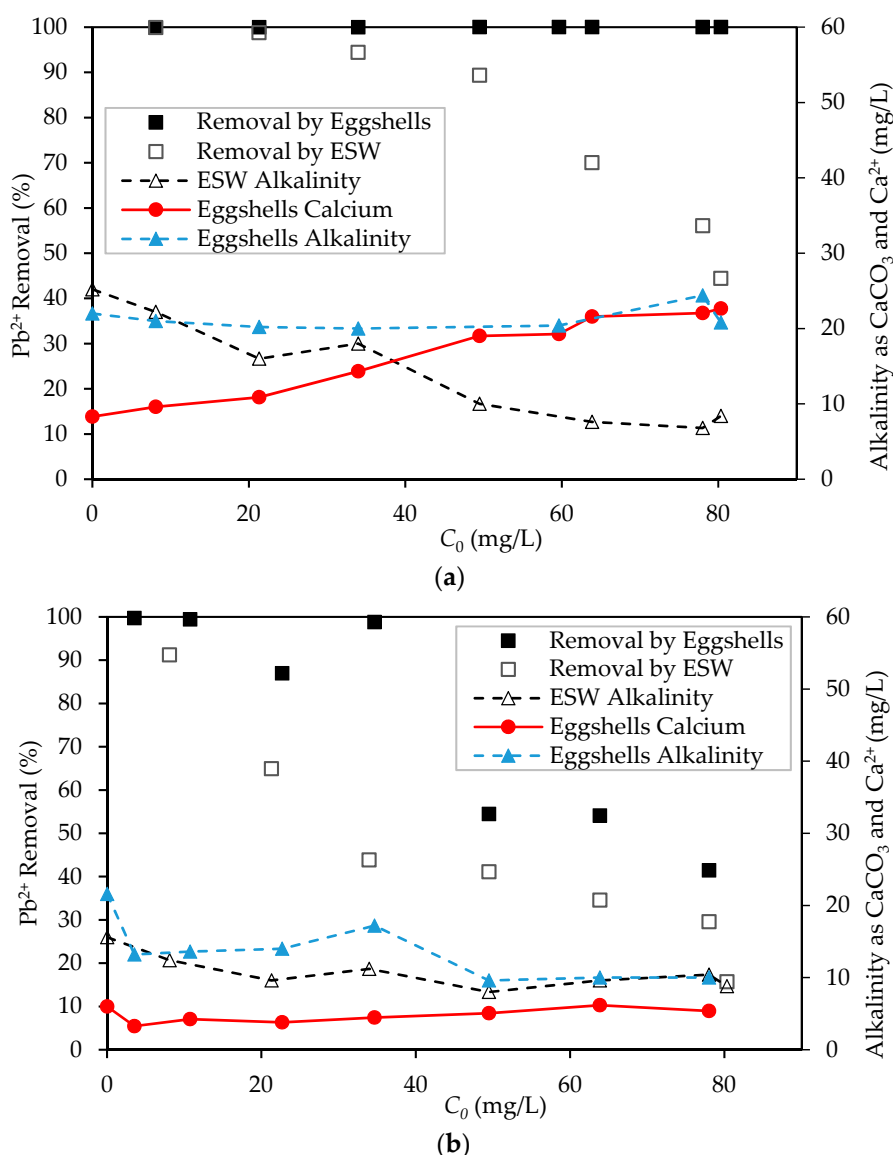


Figure 8. Comparison of percentage Pb^{2+} removal using eggshells of size 150–500 μm and ESW at (a) s/w ratio 1:200 (pH increased from 5.71 (SD 0.37) to 7.94 (SD 1.06) with eggshells, whereas with ESW the pH instantly drops from 9.36 (ESW only) to 6.18 (SD 0.75) right after mixing with lead solution) and (b) s/w ratio 1:2000 (pH increased from 5.49 (SD 0.25) to 6.86 (SD 0.72) with eggshells, whereas with ESW the pH instantly drops from 9.36 (ESW only) to 6.06 (SD 0.51) right after mixing with lead solution).

3.4. Differentiation between Removal of Pb^{2+} by Sorption and Precipitation

To study the removal of Pb^{2+} by precipitation, the method outlined in Section 2.7 was followed. The percentage of Pb^{2+} removal as a function of the initial Pb^{2+} in solution (C_0) is presented in Figure 8.

The figure compares the total Pb^{2+} removal obtained when eggshells were physically in solution and Pb^{2+} removal due to precipitation with eggshell water (ESW). Clearly, precipitation plays a major role in the removal of Pb^{2+} by eggshells. At a low initial concentration, Pb^{2+} removal could entirely be attributed to precipitation due to the presence of carbonates in the solution. However, the role of precipitation is reduced as the s/w ratio and initial concentration of Pb^{2+} become higher (Figure 8a). The difference between the removal in the two cases (eggshells and ESW) could be attributed to sorption. However, it was observed that aqueous Ca^{2+} in equilibrium with eggshells increased with the increase in initial Pb^{2+} concentration, while alkalinity remained almost constant (Figure 8a). The level of Ca^{2+} , in the case of ESW, remained the same at 8.3 and 7.5 mg/L for s/w ratios 1:200 and 1:2000, respectively, at all initial Pb^{2+} concentrations. Thus, comparison between Pb^{2+} removal with ESW versus that of eggshells may provide an underestimation of the extent of precipitation. Further, the increase in Ca^{2+} in the presence of eggshells was more pronounced at the high s/w ratio (Figure 8a) compared to that for the low s/w ratio (Figure 8b). Such a finding was accompanied by an almost constant alkalinity due to the continuous release of carbonates by eggshells. This could explain the higher difference between the removal of Pb^{2+} by eggshells and ESW at the high s/w ratio (Figure 8a).

To provide a better elucidation of the roles of different removal mechanisms. The authors resorted to direct quantification of the amount of sorbed Pb^{2+} by acid digestion. Precipitation was then calculated as the difference between total removal and percentage of Pb^{2+} sorbed on the eggshells. This quantification is presented in Figure 9, which distinguishes Pb^{2+} removed by sorption from that removed by precipitation at an s/w ratio of 1:2000. Though the percentage of Pb^{2+} removal declined with increasing initial Pb^{2+} concentration, precipitation continued to be more prominent than sorption up to an initial Pb^{2+} concentration of 60 mg/L, after which removal by precipitation significantly dropped (Figure 9a) and became almost similar to removal by sorption. On the other hand, the contribution of sorption to the percent removal was the same at different initial concentrations but slightly decreased after 60 mg/L. These findings are consistent with those of Ahmad et al. [28], who concluded that precipitation may become important for the removal of Pb^{2+} and Cu^{2+} by waste eggshells. It should be noted that some studies suggest that microprecipitation of Pb^{2+} by carbonates present in eggshells was followed by adsorption of the metal carbonates on the eggshell surface [30,42]. Thus, it is difficult to confirm that all the sorbed Pb was in the form of Pb^{2+} , as there could be some PbCO_3 remaining on the surface, which could result in an underestimation of the role of precipitation in Pb removal.

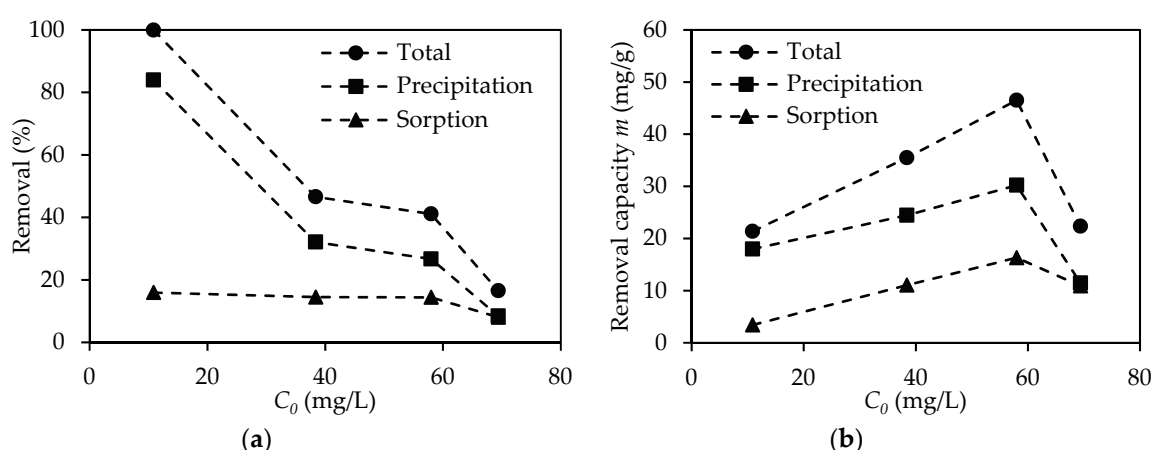


Figure 9. Removal of Pb^{2+} by sorption and precipitation versus initial Pb^{2+} concentration (size 150–500 μm and s/w ratio of 1:2000) expressed in (a) percent removal and (b) removal capacity.

Figure 9b shows the changes in removal capacity of eggshells as a function of initial Pb^{2+} concentration. The contribution of both sorption and precipitation to the removal capacity increased with the increase in the initial Pb^{2+} , but then both dropped after 60 mg/L. This behavior was also

observed for the total removal capacity at this s/w ratio (1:2000) and particle size (150–500 μm) as shown in Figures 5b and 6. The expectation is for the removal capacity (m) to reach a plateau value after a certain initial concentration, as shown for Pb^{2+} removal by eggshells in the work of Soares et al. (2016) and Cu^{2+} removal by eggshells in the work of Ahmad et al. (2012), in which the solution pH was maintained at a fixed value (at 5 and 5.5, respectively). However, in this study, the observed decline, rather than a plateau, in the removal capacity (m) could be attributed to a decrease in the available carbonates needed for the precipitation reaction, coupled with a decrease in the solution pH. The latter could be the reason why the observed removal capacity by sorption dropped as well.

3.5. Thermodynamic and Stoichiometric Analysis

Several Pb^{2+} solid phases could occur in the $\text{Pb-CaCO}_3\text{-H}_2\text{O}$ system including PbO , Pb(OH)_2 , PbCO_3 (cerussite), $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite), and $\text{Pb}_{10}(\text{OH})_6(\text{CO}_3)_6$ (plumbonacrite). PbO and plumbonacrite are thermodynamically stable at very high pH values ($\text{pH} > 12$) [53]. Pure $\text{Pb(OH)}_2(\text{s})$ is believed not to exist, but the basic salt, used to prepare the Pb solution, combined with aqueous Pb(OH)_2 could exist as a solid form at high pH [54]. In this study, the solution pH started at around pH 5.5 (only Pb^{2+} in the water) and increased to less than 9.0 after two hours from the addition of eggshells, making lead carbonate, in the form of cerussite or/and hydrocerussite, the more probable solid that could be formed. The chemical reactions describing the formation of cerussite and hydrocerussite along with their solubility product (K_{sp}) values [52] are



Thermodynamic analysis was conducted to investigate the possible formation of cerussite or hydrocerussite using the range of values of Pb^{2+} , CO_3^{2-} , and pH encountered in this study. Pb^{2+} ranged from 10 to 70 mg/L (4.8×10^{-5} to 3.3×10^{-4} mol/L) and alkalinity ranged from 10 to 40 mg/L as CaCO_3 . If all alkalinity is due to the release of CO_3^{2-} from the eggshells, then the molar concentration of CO_3^{2-} would range from 1×10^{-4} to 4.2×10^{-4} mol/L. The activity coefficients of Pb^{2+} and CO_3^{2-} were determined using the Debye–Huckel law as described by Snoeyink and Jenkins [55] and fell in the range of 0.77 to 0.89 (an average value of 0.83 was considered here for Pb^{2+} and CO_3^{2-}). Based on that, the values of the ion activity product for cerussite ($\{\text{Pb}\}\{\text{CO}_3\}$, where $\{ \}$ refers to ion activity = activity coefficient \times molar concentration) range from 3.3×10^{-9} to 9.7×10^{-8} . These values are higher than the K_{sp} of cerussite (7.9×10^{-14}), indicating favorable conditions for the formation of this solid. Analogous calculations of the ion activity product for hydrocerussite ($\{\text{Pb}\}^3\{\text{CO}_3\}^2\{\text{OH}\}^2$) resulted in values that range from 4.4×10^{-39} to 2.6×10^{-28} , which are higher than its K_{sp} (3.16×10^{-46}), and hence the conditions also favor the formation of hydrocerussite.

The above analysis indicates that the precipitate formed in the Pb-eggshell system of this study could be cerussite or/and hydrocerussite. There is no agreement in the literature about the relative stability of cerussite and hydrocerussite. For aqueous Pb^{2+} in contact with CaCO_3 in open systems, Bilinski and Schindler [56] concluded that hydrocerussite is the most stable solid phase, whereas Taylor and Lopata [53] indicated that cerussite is thermodynamically more stable than hydrocerussite at all pH values. On the other hand, for a closed aqueous system (i.e., with no exchange of atmospheric CO_2), hydrocerussite becomes more stable at $\text{pH} > 7$ [51].

Stoichiometric analysis was carried out to investigate the extent to which the experimental data of Pb^{2+} precipitation with eggshells are aligned with the formation of cerussite and hydrocerussite. Figure 10 plots the concentration of reacted Pb^{2+} (expressed as the difference between the initial and final Pb^{2+} concentration in solution) versus the drop in the carbonate level estimated from the alkalinity measurement of the control solution (with eggshells but without Pb^{2+}) and of the Pb^{2+} solution for two s/w ratios. The dotted line in Figure 10 represents the stoichiometry of the cerussite formation. This line has a slope of 1.0 since 1 mol of Pb^{2+} reacts with 1 mol carbonate to form cerussite. The solid

line represents the stoichiometry for hydrocerussite formation and has a slope of 1.5 (3 mol of Pb^{2+} reacts with 2 mol of carbonate to form hydrocerussite). Most of the experimental data lie within the two lines, which is consistent with the notion that the removal of Pb^{2+} from the eggshell solution is due to the formation of lead carbonate. As shown in Figure 10, some of the experimental data are above the lines of cerussite and hydrocerussite formation. This is expected and could be attributed to two reasons: (1) not all Pb^{2+} precipitated but some was sorbed on the eggshells which resulted in a higher reacted Pb^{2+} than what could be predicted by stoichiometry, and (2) the eggshells could release additional carbonate during the reaction to reach a new equilibrium state and this could result in an apparent lower CO_3^{2-} change than that estimated based on the reaction stoichiometry. Nonetheless, the observed drop in Pb^{2+} versus the drop in alkalinity is justified based on the stoichiometry for the formation of lead carbonate.

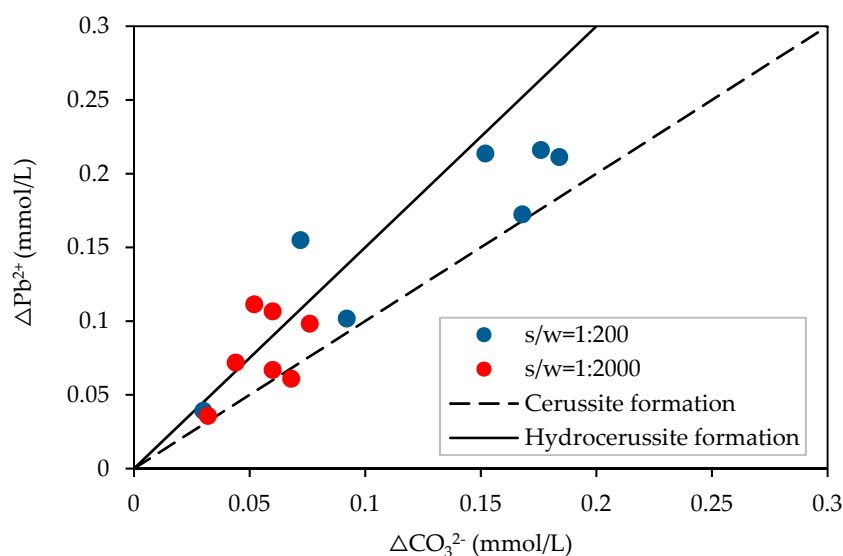


Figure 10. Alignment of experimental results of eggshells (size 150–500 μm) with the stoichiometry for the formation of cerussite and hydrocerussite. ΔPb^{2+} refers to the difference in the initial and final Pb^{2+} concentration in solution, while ΔCO_3^{2-} refers to the drop in the carbonate level estimated as the difference in the alkalinity of the control solution and of the Pb^{2+} solution for each bottle.

3.6. FTIR Analysis

The change in functional groups of eggshells before and after Pb^{2+} removal was examined using FTIR spectroscopy. Figure 11 shows the typical FTIR spectrum of raw and used eggshells with 40 mg/L Pb^{2+} solution. The infrared bands at 712 and 872 cm^{-1} are associated with the respective in-plane and out-of-plane bending vibrations of calcium carbonate (CaCO_3) in its polymorph form of calcite [35,57]. A broad band in the range of 1300–1500 cm^{-1} , centered at 1422 cm^{-1} , is recognized as a C–O stretching mode vibration of CaCO_3 [57]. Such bands have also been identified as ν_4 , ν_2 , and ν_3 vibration modes of carbonate ion, respectively [58]. These bands are observed in both samples, providing evidence to the stability and inertness of calcite when exposed to the Pb^{2+} solution. Furthermore, raw eggshells were characterized by a major absorption peak at 2350 cm^{-1} , corresponding to a C=O stretching vibration [59]. However, such a peak was not detected in the used eggshells sample, indicating that this carbonate polymorph was less stable and was released into the Pb^{2+} solution to cause removal by precipitation.

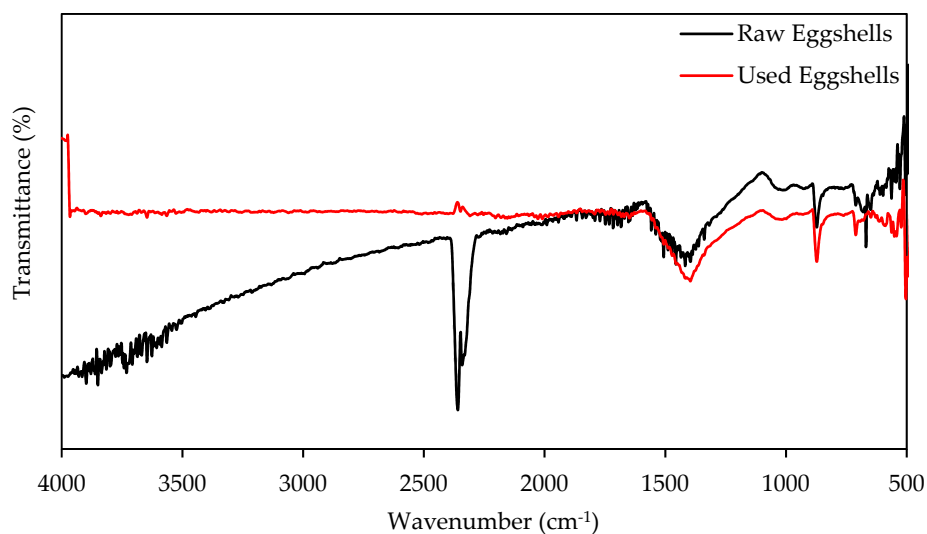


Figure 11. FTIR analysis of eggshells before and after Pb^{2+} removal (40 mg/L Pb^{2+} , s/w ratio 1:200, and particle size 150–500 μm).

3.7. SEM Analysis

SEM micrographs of Figures 12–14 illustrate the eggshells with a particle size of 150–500 μm before and after Pb^{2+} removal. Figure 12 of raw eggshells (processed based on the procedure in Section 2.2) shows the agglomeration of small particles, with the absence of connecting channels. This supports the BET results, suggesting eggshells to be a non-porous material. This conclusion is further supported by the N_2 isotherm type II curve (Figure 4), corresponding to non-porous materials. Similar findings have been reported for raw eggshells in other work [29,35]. In addition, the micrographs show that the surface texture of raw eggshells is rough and uneven.

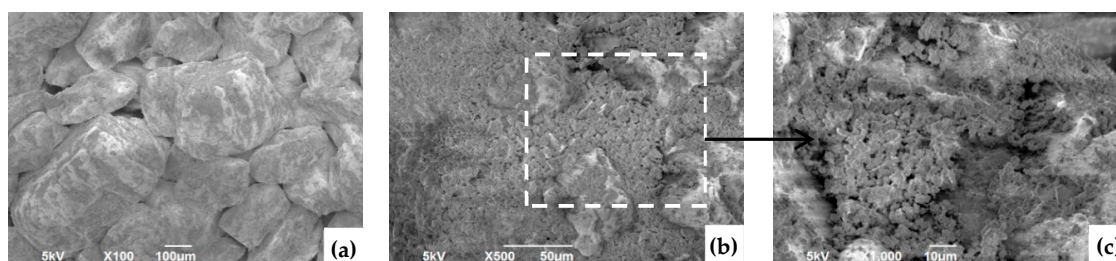


Figure 12. Raw eggshells, particle size 150–500 μm at magnification (a) $\times 100$, (b) $\times 500$, and (c) $\times 1000$.

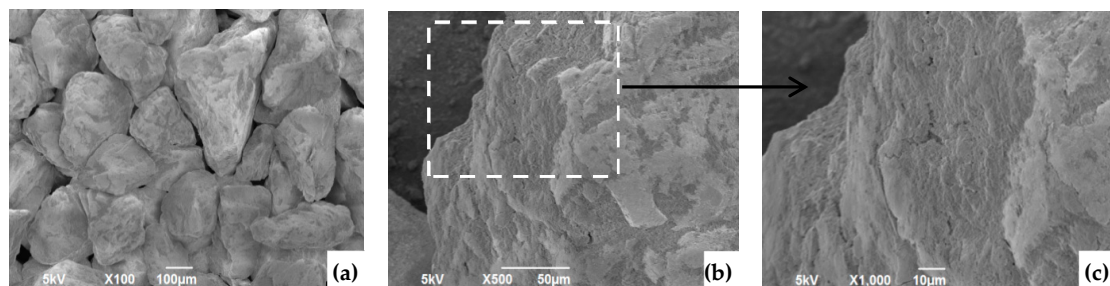


Figure 13. Eggshells, particle size 150–500 μm , after Pb^{2+} removal process with s/w ratio of 1:200 and 20 mg/L Pb^{2+} solution at magnification (a) $\times 100$, (b) $\times 500$, and (c) $\times 1000$.

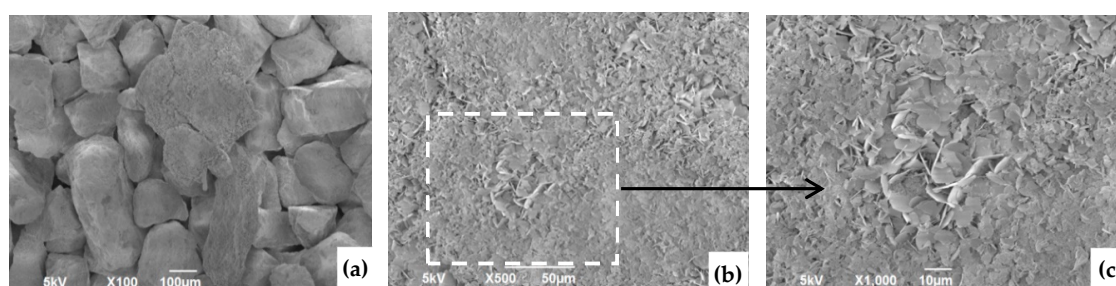


Figure 14. Eggshells, particle size 150–500 μm , after Pb^{2+} removal process with s/w ratio of 1:2000 and 20 mg/L Pb^{2+} solution at magnification (a) $\times 100$, (b) $\times 500$, and (c) $\times 1000$.

The removal process induced changes to the morphology of the eggshells. Figure 13 presents the microstructure of eggshells post-exposure to Pb^{2+} with an s/w ratio of 1:200. It is clear that the surface of the eggshells is different from that of the raw eggshells. In fact, the surface is denser and less porous, owing to the deposition of Pb^{2+} and formation of lead carbonate (PbCO_3). At a lower s/w ratio of 1:2000 (Figure 14), more Pb^{2+} has been deposited on the eggshells surface, leading to the growth of needle-like PbCO_3 crystals. The morphology of PbCO_3 illustrated herein is consistent with that reported in previous studies [60,61]. This is also consistent with the trend of a higher removal capacity of eggshells (m) at lower s/w ratios (Figure 6). Nevertheless, SEM micrographs presented herein cannot be used to differentiate the mechanism of Pb^{2+} deposition onto the eggshells, i.e., microprecipitation or sorption.

4. Conclusions

Eggshells are a common biowaste that could be recycled for the removal of Pb^{2+} from wastewater, thus promoting the use of nature-based sustainable solutions for both waste management and wastewater treatment. In this study, the influence of the particle size of ground eggshells and s/w ratio on removal of Pb^{2+} from aqueous solutions was investigated. Results show that the percent Pb^{2+} removal was not significantly different for particle sizes 150–500 μm and $<150 \mu\text{m}$ despite the large difference in the surface area of the two eggshell sizes. A high percentage removal (up to 99%) of Pb^{2+} by eggshells was achieved for low initial Pb^{2+} concentrations ($<30 \text{ mg/L}$) across all s/w ratios studied. SEM images confirmed that the surface of eggshells used for Pb^{2+} removal became denser and less porous due to Pb^{2+} deposition and lead carbonate formation. Needle-like PbCO_3 crystals were observed in samples with a lower s/w ratio, which coincides with the trend where eggshells exhibited higher removal capacity at lower s/w ratios. A developed predictive relationship suggests that the removal capacity of eggshells normalized to the initial Pb^{2+} concentration is almost inversely proportional to the s/w ratio. The relationship explains differences in the Pb^{2+} removal capacities of eggshells reported by others. The developed relationship could be utilized to design batch reactors for Pb^{2+} removal by eggshells subject to economic and environmental constraints.

The study also attempted to quantify the role of different removal mechanisms in the total removal of Pb^{2+} . Results confirmed that precipitation played a major role in the removal of Pb^{2+} by eggshells. However, this role was reduced as the s/w ratio and initial concentration of Pb^{2+} became higher. The difference between the extent of Pb^{2+} removal by eggshells and eggshell water suggested that sorption also played a role in Pb^{2+} removal. This was confirmed by the direct quantification of the concentration of Pb^{2+} sorbed on the eggshells and by the results from FTIR spectroscopy. Indeed, FTIR spectroscopy of eggshells highlighted the presence of high- and low-stability calcium carbonate polymorphs that existed in raw eggshells. While the former polymorph was detected in the used eggshells sample, the latter was not, signifying its release into the Pb^{2+} solution to cause removal by precipitation. It was also observed that the contribution of both sorption and precipitation dropped at the high concentration. It was speculated that such decline was due to a decrease in the available carbonates needed for precipitation coupled with a decrease in the solution pH.

Author Contributions: Conceptualization, M.A.H., M.A.M. and H.E.-H.; data curation, M.A.H., H.S. and M.A.M.; formal analysis, M.A.H., H.S. and M.A.M.; funding acquisition, M.A.H. and H.E.-H.; investigation, H.S.; methodology, M.A.H., M.A.M. and H.E.-H.; project administration, M.A.H. and H.E.-H.; resources, H.E.-H.; supervision, M.A.H., M.A.M. and H.E.-H.; validation, M.A.H. and M.A.M.; visualization, M.A.H., M.A.M. and H.E.-H.; writing—original draft, H.S.; writing—review and editing, M.A.H., M.A.M. and H.E.-H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by UAE University, grant number 31N322; the National Water Center at UAE University grant number 31R150; and The APC was funded by the National Water Center at UAE University grant number 31R150.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Anantha, R.K.; Kota, S. Removal of lead by adsorption with the renewable biopolymer composite of feather (*Dromaius novaehollandiae*) and chitosan (*Agaricus bisporus*). *Environ. Technol. Innov.* **2016**, *6*, 11–26. [\[CrossRef\]](#)
2. Gupta, V.K.; Agarwal, S.; Saleh, T.A. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *J. Hazard. Mater.* **2011**, *185*, 17–23. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Ritchey, A.K.; O'Brien, S.H.; Keller, F.G. Chapter 152—Hematologic manifestations of childhood illness. In *Hematology*, 7th ed.; Hoffman, R., Benz, E.J., Silberstein, L.E., Heslop, H.E., Weitz, J.I., Anastasi, J., Salama, M.E., Abutalib, S.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 2215–2237.e9, ISBN 978-0-323-35762-3.
4. Burke, D.M.; Morris, M.A.; Holmes, J.D. Chemical oxidation of mesoporous carbon foams for lead ion adsorption. *Sep. Purif. Technol.* **2013**, *104*, 150–159. [\[CrossRef\]](#)
5. Canfield, R.L.; Henderson, C.R.; Cory-Slechta, D.A.; Cox, C.; Jusko, T.A.; Lanphear, B.P. Intellectual impairment in children with blood lead concentrations below 10 µg per deciliter. *N. Engl. J. Med.* **2003**, *348*, 1517–1526. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Lanphear, B.P.; Matte, T.D.; Rogers, J.; Clickner, R.P.; Dietz, B.; Bornschein, R.L.; Succop, P.; Mahaffey, K.R.; Dixon, S.; Galke, W.; et al. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels: A pooled analysis of 12 epidemiologic studies. *Environ. Res.* **1998**, *79*, 51–68. [\[CrossRef\]](#)
7. Cooper, W.C.; Wong, O.; Kheifets, L. Mortality among employees of lead battery plants and lead-producing plants, 1947–1980. *Scand. J. Work Environ. Health* **1985**, *11*, 331–345. [\[CrossRef\]](#)
8. Lancranjan, I.; Popescu, H.I.; GAvănescu, O.; Klepsch, I.; Serbănescu, M. Reproductive ability of workmen occupationally exposed to lead. *Arch. Environ. Health* **1975**, *30*, 396–401. [\[CrossRef\]](#)
9. Lanphear, B.P.; Roghmann, K.J. Pathways of lead exposure in urban children. *Environ. Res.* **1997**, *74*, 67–73. [\[CrossRef\]](#)
10. Mahmoud, M.T.; Hamouda, M.A.; Al Kendi, R.R.; Mohamed, M.M. Health risk assessment of household drinking water in a district in the UAE. *Water* **2018**, *10*, 1726. [\[CrossRef\]](#)
11. Health Canada. *Guidelines for Canadian Drinking Water Quality—Summary Table*; Water and Air Quality Bureau; Healthy Environments and Consumer Safety Branch, Health Canada: Ottawa, ON, Canada, 2019.
12. US EPA. *National Primary Drinking Water Regulations*; EPA 816-F-09-004; Office of Water United States Environmental Protection Agency: Washington, DC, USA, 2009.
13. Arunlertaree, C.; Kaewsomboon, W.; Kumsopa, A.; Pokethitiyook, P.; Panyawathanakit, P. Removal of lead from battery manufacturing wastewater by egg shell. *Songklanakarin J. Sci. Technol.* **2007**, *29*, 13.
14. Dermentzis, K.; Valsamidou, E.; Marmanis, D. Simultaneous removal of acidity and lead from acid lead battery wastewater by aluminum and iron electrocoagulation. *J. Eng. Sci. Technol. Rev.* **2012**, *5*, 1–5. [\[CrossRef\]](#)
15. Khaoya, S.; Pancharoen, U. Removal of lead (II) from battery industry wastewater by HFSLM. *Int. J. Chem. Eng. Appl.* **2012**, 98–103. [\[CrossRef\]](#)
16. Macchi, G.; Pagano, M.; Santori, M.; Tiravanti, G. Battery industry wastewater: Pb removal and produced sludge. *Water Res.* **1993**, *27*, 1511–1518. [\[CrossRef\]](#)
17. WHO. *A Compendium of Standards for Wastewater Reuse in the Eastern Mediterranean Region*; World Health Organization, Regional Office for the Eastern Mediterranean: Cairo, Egypt, 2006.
18. Babel, S.; Kurniawan, T.A. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.* **2003**, *97*, 219–243. [\[CrossRef\]](#)

19. Sweidan, H.; Hamouda, M.; El-Hassan, H.; Maraqa, M. A framework for the investigation of biowaste materials as potential adsorbents for water treatment. In Proceedings of the 4th World Congress on Civil, Structural, and Environmental Engineering, Rome, Italy, 7–9 April 2019.
20. Podstawczyk, D.; Witek-Krowiak, A.; Chojnacka, K.; Sadowski, Z. Biosorption of malachite green by eggshells: Mechanism identification and process optimization. *Bioresour. Technol.* **2014**, *160*, 161–165. [\[CrossRef\]](#)
21. Eba, F.; Biboutou, R.K.; Nlo, J.N.; Bibalou, Y.G.; Oyo, M. Lead removal in aqueous solution by activated carbons prepared from *Cola edulis* shell (Alocacée), *Pentaclethra macrophylla* husk (Mimosaceae) and *Aucoumea klaineana* sawdust (Burseraceae). *Afr. J. Environ. Sci. Technol.* **2011**, *5*, 197–204. [\[CrossRef\]](#)
22. El-Naas, M.H.; Al-Rub, F.A.; Ashour, I.; Al Marzouqi, M. Effect of competitive interference on the biosorption of lead(II) by *Chlorella vulgaris*. *Chem. Eng. Process. Process Intensif.* **2007**, *46*, 1391–1399. [\[CrossRef\]](#)
23. Rashed, M.N. Fruit stones from industrial waste for the removal of lead ions from polluted water. *Environ. Monit. Assess.* **2006**, *119*, 31–41. [\[CrossRef\]](#)
24. Sekar, M.; Sakthi, V.; Rengaraj, S. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J. Colloid Interface Sci.* **2004**, *279*, 307–313. [\[CrossRef\]](#)
25. Yan, T.; Luo, X.; Lin, X.; Yang, J. Preparation, characterization and adsorption properties for lead (II) of alkali-activated porous leather particles. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *512*, 7–16. [\[CrossRef\]](#)
26. Ritchie, H.; Roser, M. Meat and Dairy Production. Available online: <https://ourworldindata.org/meat-production> (accessed on 7 September 2020).
27. Stadelman, W.J. EGGS[Structure and Composition. In *Encyclopedia of Food Sciences and Nutrition*, 2nd ed.; Caballero, B., Ed.; Academic Press: Oxford, UK, 2003; pp. 2005–2009. ISBN 978-0-12-227055-0.
28. Ahmad, M.; Usman, A.R.A.; Lee, S.S.; Kim, S.-C.; Joo, J.-H.; Yang, J.E.; Ok, Y.S. Eggshell and coral wastes as low cost sorbents for the removal of Pb²⁺, Cd²⁺ and Cu²⁺ from aqueous solutions. *J. Ind. Eng. Chem.* **2012**, *18*, 198–204. [\[CrossRef\]](#)
29. Park, H.J.; Jeong, S.W.; Yang, J.K.; Kim, B.G.; Lee, S.M. Removal of heavy metals using waste eggshell. *J. Environ. Sci.* **2007**, *19*, 1436–1441. [\[CrossRef\]](#)
30. Soares, M.; Marto, S.; Quina, M.; Gando-Ferreira, L.; Quinta-Ferreira, R. Evaluation of eggshell-rich compost as biosorbent for removal of Pb(II) from aqueous solutions. *Water Air Soil Pollut.* **2016**, *227*, 1–16. [\[CrossRef\]](#)
31. Vijayaraghavan, K.; Jegan, J.; Palanivelu, K.; Velan, M. Removal and recovery of copper from aqueous solution by eggshell in a packed column. *Miner. Eng.* **2005**, *18*, 545–547. [\[CrossRef\]](#)
32. Yeddou, N.; Bensmaili, A. Equilibrium and kinetic modelling of iron adsorption by eggshells in a batch system: Effect of temperature. *Desalination* **2007**, *206*, 127–134. [\[CrossRef\]](#)
33. Zhang, T.; Tu, Z.; Lu, G.; Duan, X.; Yi, X.; Guo, C.; Dang, Z. Removal of heavy metals from acid mine drainage using chicken eggshells in column mode. *J. Environ. Manag.* **2017**, *188*, 1–8. [\[CrossRef\]](#)
34. Pramanpol, N.; Nitayapat, N. Adsorption of reactive dye by eggshell and its membrane. *Agric. Nat. Resour.* **2006**, *40*, 192–197.
35. Tsai, W.T.; Yang, J.M.; Lai, C.W.; Cheng, Y.H.; Lin, C.C.; Yeh, C.W. Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresour. Technol.* **2006**, *97*, 488–493. [\[CrossRef\]](#)
36. Witek-Krowiak, A.; Chojnacka, K.; Podstawczyk, D.; Dawiec, A.; Pokomeda, K. Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. *Bioresour. Technol.* **2014**, *160*, 150–160. [\[CrossRef\]](#)
37. Andersson, M.P.; Sakuma, H.; Stipp, S.L.S. Strontium, nickel, cadmium, and lead substitution into calcite, studied by density functional theory. *Langmuir* **2014**, *30*, 6129–6133. [\[CrossRef\]](#)
38. Davis, A.D.; Webb, C.J.; Sorensen, J.L.; Dixon, D.J.; Hudson, R. Geochemical thermodynamics of cadmium removal from water with limestone. *Environ. Earth Sci.* **2018**, *77*, 37. [\[CrossRef\]](#)
39. Lee, Y.-C.; Kim, E.J.; Yang, J.-W.; Shin, H.-J. Removal of malachite green by adsorption and precipitation using aminopropyl functionalized magnesium phyllosilicate. *J. Hazard. Mater.* **2011**, *192*, 62–70. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Xie, Y.; Giammar, D.E. Effects of flow and water chemistry on lead release rates from pipe scales. *Water Res.* **2011**, *45*, 6525–6534. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Xie, L.; Giammar, D.E. Chapter 13 Influence of phosphate on adsorption and surface precipitation of lead on iron oxide surfaces. In *Developments in Earth and Environmental Sciences*; Barnett, M.O., Kent, D.B., Eds.; Adsorption of Metals by Geomedia II: Variables, Mechanisms, and Model Applications; Elsevier: Amsterdam, The Netherlands, 2007; Volume 7, pp. 349–373.

42. Vijayaraghavan, K.; Joshi, U.M. Chicken eggshells remove Pb(II) ions from synthetic wastewater. *Environ. Eng. Sci.* **2013**, *30*, 67–73. [\[CrossRef\]](#)
43. APHA; AWWA; WEF. *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; Rice, E.W., Baird, R.B., Eaton, A.D., Eds.; American Public Health Association: Washington, DC, USA, 2017.
44. U.S. EPA. *Method 3050B: Acid Digestion of Sediments, Sludges, and Soils, Revision 2*; U.S. EPA: Washington, DC, USA, 1996.
45. Spagnoli, A.A.; Giannakoudakis, D.A.; Bashkova, S. Adsorption of methylene blue on cashew nut shell based carbons activated with zinc chloride: The role of surface and structural parameters. *J. Mol. Liq.* **2017**, *229*, 465–471. [\[CrossRef\]](#)
46. Martín-Lara, M.A.; Blázquez, G.; Ronda, A.; Pérez, A.; Calero, M. Development and characterization of biosorbents to remove heavy metals from aqueous solutions by chemical treatment of olive stone. *Ind. Eng. Chem. Res.* **2013**, *52*, 10809–10819. [\[CrossRef\]](#)
47. García-Mendieta, A.; Olguín, M.T.; Solache-Ríos, M. Biosorption properties of green tomato husk (*Physalis philadelphica* Lam) for iron, manganese and iron–manganese from aqueous systems. *Desalination* **2012**, *284*, 167–174. [\[CrossRef\]](#)
48. Queirós, M.V.A.; Bezerra, M.N.; Feitosa, J.P.A. Composite superabsorbent hydrogel of acrylic copolymer and eggshell: Effect of biofiller addition. *J. Braz. Chem. Soc.* **2017**, *28*, 2004–2012. [\[CrossRef\]](#)
49. da Silva Castro, L.; Barañano, A.G.; Pinheiro, C.J.G.; Menini, L.; Pinheiro, P.F. Biodiesel production from cotton oil using heterogeneous CaO catalysts from eggshells prepared at different calcination temperatures. *Green Process. Synth.* **2019**, *8*, 235–244. [\[CrossRef\]](#)
50. Habte, L.; Shiferaw, N.; Mulatu, D.; Thenepalli, T.; Chilakala, R.; Ahn, J.W. Synthesis of nano-calcium oxide from waste eggshell by sol-gel method. *Sustainability* **2019**, *11*, 3196. [\[CrossRef\]](#)
51. Godelitsas, A.; Astilleros, J.M.; Hallam, K.; Harissopoulos, S.; Putnis, A. Interaction of calcium carbonates with lead in aqueous solutions. *Environ. Sci. Technol.* **2003**, *37*, 3351–3360. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Macchi, G.; Marani, D.; Pagano, M.; Bagnuolo, G. A bench study on lead removal from battery manufacturing wastewater by carbonate precipitation. *Water Res.* **1996**, *30*, 3032–3036. [\[CrossRef\]](#)
53. Taylor, P.; Lopata, V.J. Stability and solubility relationships between some solids in the system PbO–CO₂–H₂O. *Can. J. Chem.* **1984**, *62*, 395–402. [\[CrossRef\]](#)
54. Powell, K.J.; Brown, P.L.; Byrne, R.H.; Gajda, T.; Hefter, G.; Leuz, A.-K.; Sjöberg, S.; Wanner, H. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb²⁺ + OH[−], Cl[−], CO₃^{2−}, SO₄^{2−}, and PO₄^{3−} systems (IUPAC Technical Report). *Pure Appl. Chem.* **2009**, *81*, 2425–2476. [\[CrossRef\]](#)
55. Snoeyink, V.L.; Jenkins, D. *Water Chemistry*; Wiley: New York, NY, USA, 1980; ISBN 978-0-471-05196-1.
56. Bilinski, H.; Schindler, P. Solubility and equilibrium constants of lead in carbonate solutions (25 °C, *I* = 0.3 mol dm^{−3}). *Geochim. Cosmochim. Acta* **1982**, *46*, 921–928. [\[CrossRef\]](#)
57. Li, Z.; Yang, D.-P.; Chen, Y.; Du, Z.; Guo, Y.; Huang, J.; Li, Q. Waste eggshells to valuable Co₃O₄/CaCO₃ materials as efficient catalysts for VOCs oxidation. *Mol. Catal.* **2020**, *483*, 110766. [\[CrossRef\]](#)
58. Abeywardena, M.R.; Elkaduwe, R.K.W.H.M.K.; Karunarathne, D.G.G.P.; Pitawala, H.M.T.G.A.; Rajapakse, R.M.G.; Manipura, A.; Mantilaka, M.M.M.G.P.G. Surfactant assisted synthesis of precipitated calcium carbonate nanoparticles using dolomite: Effect of pH on morphology and particle size. *Adv. Powder Technol.* **2020**, *31*, 269–278. [\[CrossRef\]](#)
59. Ismail, S.; Ahmed, A.S.; Anr, R.; Hamdan, S. Biodiesel production from castor oil by using calcium oxide derived from mud clam shell. *J. Renew. Energy* **2016**, *2016*, 8. [\[CrossRef\]](#)
60. Seignez, N.; Gauthier, A.; Bulteel, D.; Buatier, M.; Recourt, P.; Damidot, D.; Potdevin, J.L. Effect of Pb-rich and Fe-rich entities during alteration of a partially vitrified metallurgical waste. *J. Hazard. Mater.* **2007**, *149*, 418–431. [\[CrossRef\]](#)
61. Ng, D.-Q.; Lin, Y.-P. Effects of pH value, chloride and sulfate concentrations on galvanic corrosion between lead and copper in drinking water. *Environ. Chem.* **2015**, *13*, 602–610. [\[CrossRef\]](#)

