Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22659

127 (2018) 97–103
September

Effects of eggshells for lead ions removal from aqueous solution

Hasan Koçyiğit*, Büşra Şahin

Department of Environmental Engineering, Aksaray University, 68100 Aksaray, Turkey, emails: kocyigithasan@hotmail.com (H. Koçyiğit), bussra.sahinn@hotmail.com (B. Şahin)

Received 14 February 2018; Accepted 22 June 2018

ABSTRACT

Characteristics and efficiency of untreated eggshells (UNES) were investigated as a low-cost adsorbent in removal of Pb^{2+} ions from aqueous solution. Initial findings showed UNES potential to be applied as an effective sorbent due to high concentrations of carbon and calcium and high porosity and availability of functional groups. Adsorption experiments were studied with varying pH, contact time, and UNES concentration. Maximum percentages of Pb^{2+} ions removal were recorded at optimum pH, contact time, and adsorbent concentration. At optimum conditions of the above-mentioned parameters, more than 92% yield was obtained within 10 min at UNES dose of 2.5 g/100 mL for the initial Pb^{2+} concentration of 100 mg/L. Evaluation of the isotherms and kinetics confirmed that UNES has high value of adsorption capacity. Adsorption capacity was calculated from the Langmuir as 3.0172 mg/g at 20°C. The system was best described by the pseudo-second-order kinetic, which its equation provided evidence in favor of the adsorption kinetic. This experiment demonstrated the ability of UNES as an effective, sustainable, and low-cost adsorbent for removal of the heavy metal ions in different wastewaters.

Keywords: Adsorption; Eggshells; Lead ions; Low cost

1. Introduction

Adsorption has been recognized as a promising technique due to its ease of operation, simplicity of design, high efficiency, and comparable low cost of application in decoloration process [1,2]. Adsorption of different heavy metals has been studied using low-cost adsorbents including agricultural wastes. Some of the advantages of using agricultural waste for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective of adsorption effluent, low cost, free availability, and easy regeneration [3–7]. Lead (Pb^{2+}) is classified as a priority hazardous substance by various agencies including the Agency for Toxic Substances and Disease Registry [8,9]. Since Pb^{2+} pollution in drinking water leads to important health problems for people, it is seen as significant environmental issue. Pb^{2+} is related to industrial activities. Lead is broadly used in the manufacture of batteries and accumulators, in the manufacture of pigments and paints, in the petrochemical sector as a stabilizer for plastics and as a detonator for explosives, among other applications [10,11]. Lead is considered a potential carcinogen in humans [11,12]. Activated carbon is usually used as the versatile material due to high surface area, microporous structure, and high adsorption capacity [13]. However, activated carbon is expensive and there is a need for its regeneration after each adsorption experiment. In order to decrease the cost of adsorption, low-cost forest wastes are presently considered promising adsorbents for adsorption [14–16]. Recently, our laboratories have developed untreated eggshells (UNES) as a potential adsorbent for the removal of Pb^{2+} from its aqueous solutions.

Eggshells (ES) are well-known waste materials, which are everyday generated on a large scale from household, restaurants, food industries, bakeries, etc. [17]. ES, a biodegradable natural material, is a widespread domestic by-product that is abundant and available at a very cheap [18]. Because of

* Corresponding author.

Presented at the 15th International Conference on Environmental Science and Technology (CEST-2017), 31 August–2 September 2017, Rhodes, Greece.

its unique natural spongy structures and loud ingredient of calcite, ES has been used in many applications including as an adsorbent for ecological remediation [19]. ES-based materials have shown powerful affiliations to different heavy metal ions and thus can be used as an inexpensive adsorbent for soil remediation and wastewater treatment [20,21]. The purpose of this study is to investigate the optimum conditions for the removal of Pb^{2+} from its aqueous solutions using UNES as a biosorbent. This paper includes results of the effects of pH, contact time, and UNES dosage on its removal along with adsorption isotherms.

2. Materials and methods

2.1. Aqueous solution

The Pb^{2+} simulated solutions were prepared from $Pb(NO_3)_2$ (Merck Chemicals GmbH, Germany). About 1.593 g of $Pb(NO_3)_2$ was weighed and a standard Pb^{2+} concentration of 1,000 mg/L was prepared, and further working solutions of 100 mg/L was prepared by serial dilution as and when required. All chemicals were analytical grade, as they were purchased from Merck. The initial pH of Pb^{2+} solution was adjusted to the desired pH by adding 1 mol/L HCl or NaOH solutions.

2.2. Preparation of UNES as an adsorbent

The UNES were collected and washed with distilled water several times to remove dirt particles and dried for 3 h in an oven at 150°C and then allowed to cool at room temperature, subsequently it was crushed and then finally sieved into particle size of 0.5 mm (see Fig. 1). The sieved adsorbent was stored in an air-tight container. No other chemical modification was taken place [22,23]. Ash content was determined at 650°C. Moisture content was determined at 105°C in accordance with Oyeleke method [24]. Fiber was also determined by means of Oyeleke method. Crude nitrogen was determined by means of Kjeldahl method and crude protein was obtained by multiplying the value of nitrogen with a protein conversion factor 6.25. Both lipid and fiber were determined according to the work of AOAC [25], while carbohydrate was estimated from: CHO = 100 – (%ash + %crude lipid + %crude protein + %fiber) [26].

2.3. Analytical methods

Before the start of the experiments, UNES were dried and placed in ball mill and obtained crumbs were sifted to acquire the size of smaller than 100 μm. The pH measurements were performed with LABQUEST2 digital meter. Adsorption experiments were performed in batch systems, using UNES amount, pH, and contact time as variables. The Pb^{2+} concentrations in the initial and effluent samples were analyzed using the Perkin Elmer Optima 2100 DV model inductively coupled plasma optical emission spectrometry (ICP-OES). The chemical characteristics of surface functional groups for UNES were determined by Fourier transform infrared (FTIR) spectroscopy at a wavelength range between 400 and 4,000 cm^{-1}. The surface morphologies for UNES were examined by scanning electron microscopy (SEM). The chemical composition of the UNES sample was determined by X-ray fluorescence machine [16]. The experiments were carried out by contacting precisely weighted samples of UNES with 100 mL of Pb^{2+} solutions in the sealed 250 mL Erlenmeyer flasks. The suspensions were conducted on a thermal shaker at a shaking speed of 250 rpm at 20°C in triplicate. After the specified time, suspensions were filtered through filter study 0.45 μm pore size membrane filters. After adsorption, the mixtures were filtered and the filtrates were analyzed for Pb^{2+} content using an ICP-OES at 261.42 nm.

2.4. Pb^{2+} adsorption capacity

The experiments were performed at different process variables for the ES, the concentration of Pb^{2+} deposited onto UNES surface utilizing the accompanying mathematical expression:

$$q_e\left(\frac{\text{mg}}{\text{g}}\right) = \frac{\left(C_0 - C_e\right)\times V}{1,000\times w} \quad (1)$$

where q_e is the amount of Pb^{2+} deposited on UNES (mg/g), C_e is the initial solute concentration in the solution before

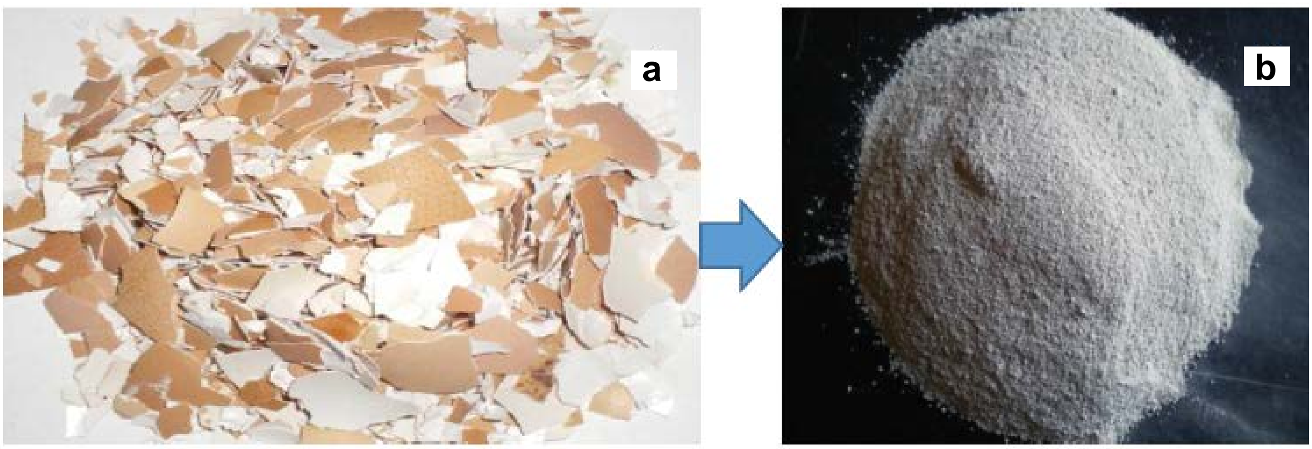

Fig. 1. (a) Natural eggshell and (b) UNES adsorbent [43].

adsorption (mg/L), C_0 is the final concentration of solute in the solution after adsorption (mg/L), V is the volume of the metal solution (L), and w is the weight of the UNES adsorbent. Adsorption system was quantified by calculating the adsorption percentage (E %) as defined by Eq. (2):

$$E\left(\text{adsorption}\right)\left(\%\right) = \frac{\left(C_0 - C_e\right)}{1{,}000 \times C_0} \tag{2}$$

Adsorption experiments were performed in triplicate and the mean values of instances were submitted. In addition, blank examples were used to compare the results through all adsorption system. Data submitted are the mean values from the adsorption tests, error bars are indicated in Figs. 2–4.

3. Results and discussion

3.1. Effect of contact time for Pb^{2+}

Contact time is an important parameter in the adsorption of heavy metals for the different wastewater treatments. The adsorption of Pb^{2+} has been investigated on UNES as a function of time in the range of 1–150 min. Based on the literature survey on the removal of heavy metals using natural adsorbents, it is decided to use these parameters [27]. The efficiency initially increased rapidly and the equilibrium

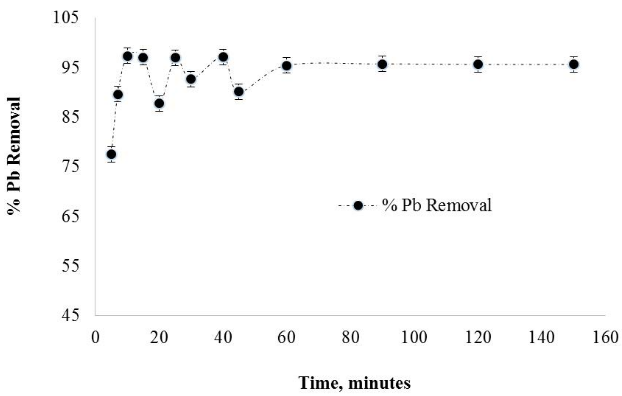

Fig. 2. Effect of % Pb^{2+} using UNES as an adsorbent.

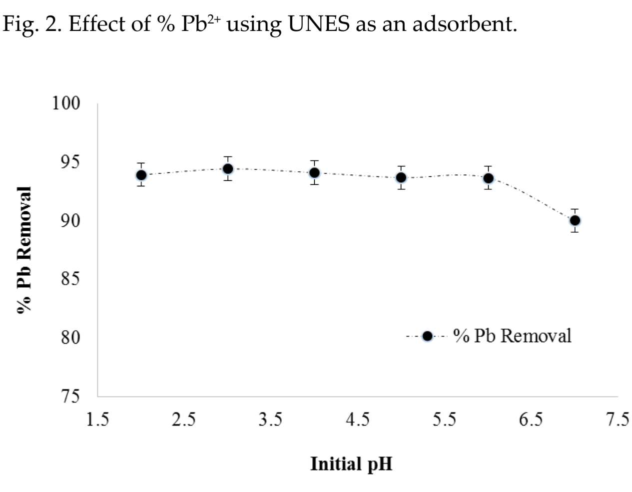

Fig. 3. Effect of pH on the yield of Pb^{2+} using UNES.

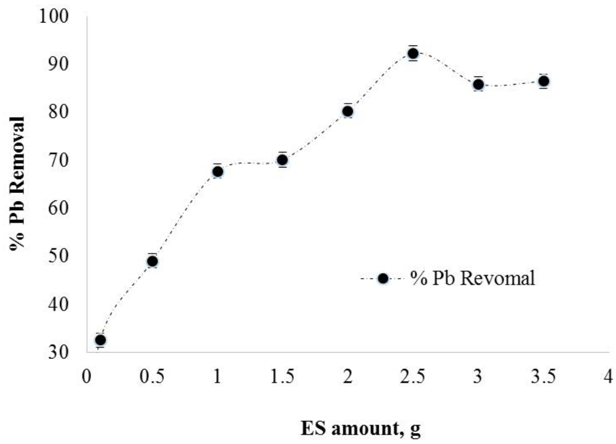

Fig. 4. Effect of UNES dose on adsorption of Pb^{2+}.

was attained in 15 min at efficiency of 97% (97 mg/g). The maximum Pb^{2+} yield which were found 97.35% (97.35 mg/g) at contact time of 10 min for UNES (Fig. 2).

There are many different studies in the literature providing findings for the optimum contact times [13,24]. Optimum contact time could vary according to the type of adsorbent used in the operation, the heavy metal scrap that is removed, and other operating conditions. After the effect of contact time on adsorption was investigated, the effects of other parameters could be obtained based on the optimum contact time [28]. Heraldy et al. [16] use tomato waste and apple juice residue as a natural adsorbent in the removal of Pb(II) ion. In this study, the effect of contact time is investigated between 0 and 90 min, 15 min are selected as the optimum contact time. Using *Anadara inaequivalvis* shells, Bozbaş and Boz [29], states that the optimum contact time for reaching the maximum removal efficiency for Pb(II) and Cu(II) are 7 and 10 min, respectively. In Boeykens et al. [11], 79%, 29%, 83%, 58%, 89%, and 65% Pb yields were observed for the adsorption of 60 mg/L Pb concentration in the aqueous solution after optimum contact time (60 min), in the different agro-industrial wastes (peanut shell, sugarcane bagasse, avocado peel, pecan nutshell, wheat bran, and banana peel), respectively.

3.2. Effect of pH on Pb^{2+}

pH plays a major role in heavy metals adsorption as it effects superficial load, metal ion speciation, complexation, and binding sites of the adsorbent [30,31]. In fact, pH is considered to be the most significant factor that controls the adsorption of heavy metal ions [32,33]. The Pb^{2+} removal efficiency of UNES at different pH values is shown in Fig. 3. Values of pH > 6 have not been studied, since it precipitated as $Pb(OH)_2$, being the process of entrapment actually a combination of adsorption and microprecipitation. It was found that Pb^{2+} uptake by UNES was a function of the initial solution pH. Fig. 3 shows that the maximum Pb^{2+} removal efficiencies that were found 94.43% (94.43 mg/g) at pH 3.0 at 100 mg/L of initial concentration for UNES. Refs. [18,34,35] also observed the same experimental results. The optimum initial pH value for Pb^{2+} adsorption by UNES was determined to be 3.0. Massimi et al. [36] provided evidence for an apparent increase in the different heavy metals removals by 12 food waste materials from 22% to 99% when the pH value increased from 2 to 5.5. Similarly, Han et al. [37] indicated that using of biochar (CM100, CM400, and BB600) was exactly associated with adsorption level for Pb^{2+} when pH was increased from 1.5 to 5.0.

3.3. Effect of UNES amount

The adsorbent amount in aqueous solution is a momentous parameter in the adsorption works because it makes the capacity of an adsorbent for a given initial concentration of the adsorbate [3]. Effect of UNES amounts on the elimination yields of Pb^{2+} are indicated in Fig. 4. It was observed that the Pb^{2+} removal yield of the UNES was a function of UNES amounts in the aquatic solution. The amount of Pb^{2+} adsorbed increase from about 32.56% to 92.28% (92.28 mg/g) with an increase in UNES amount from 0.1 to 2.5 g. The maximum adsorption efficiency of Pb^{2+} onto the UNES was found to be 92.28% (92.28 mg/g) at the dose of 2.5 g/L UNES. It can be explained as UNES amount increased, more and more surface area available metal ions will be exposed to more active sites for binding [38]. As compared with some low-cost adsorbents in the previous literature, the organic waste used in our study is of relatively higher adsorption capacity and ranges within the most efficient and best adsorbent for Pb^{2+}. Many investigators have tried out different adsorbents to remove heavy toxic metals from wastewater efficiently. Comparative study of removal of commonly occurring heavy metals in wastewater by using different adsorbents has been done. It has been concluded that Pb removal can be removed efficiently by using different adsorbents with between 29% and 99% removal efficiencies [39].

3.4. Proximate analysis and chemical composition of UNES

As presented in Table 1, the chemical composition of the UNES shows that calcium oxide was the most abundant component. Proximate analysis was conducted according to ASTM D 5832-95, ASTM D 3172-89, and ASTM D 2867-95 standards [40–44].

3.5. SEM and FTIR analysis

The surface structure of UNES (empty) is found as a porous structure using SEM. In the sample obtained after the adsorption process, the pores are covered with heavy metals and a flat surface structure was available (Figs. 5(a) and (b)).

Table 1
Proximate analysis and chemical composition of UNES adsorbent [40–42]

Proximate analysis	Wt.%	Chemical composition	Wt.%
Moisture	0.5	C	21.1286
Ash	43.5	Na_2O	0.1046
Crude fiber	3.0	MgO	0.9261
Protein	1.35	P_2O_5	0.4149
Carbohydrate	51.7	CaO	76.9922

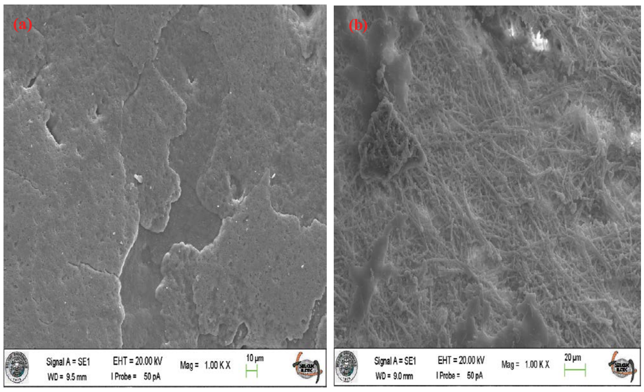

Fig. 5. SEM image of (a) UNES before adsorption and (b) UNES after adsorption (1,000×).

The presence of functional groups on the surface of UNES was confirmed using FTIR analysis. In addition, FTIR analysis provides information on possible mechanism(s) involved in metal ion adsorption. The FTIR spectra analysis of ES (before and after sorption) of heavy metal ions was conducted to investigate the vibration frequency changes of the functional groups in the adsorbent. The FTIR spectra represent a number of adsorption bonds that identifies the type of chemical bonds (functional groups), indicating the complex nature of the adsorbent as shown in Figs. 6(a) and (b).

3.6. Adsorption isotherm and kinetic models

Isotherm factors for the adsorption of Pb^{2+} upon UNES at 20°C are submitted in Table 2. The best suitable was provided by Langmuir model as compared with the other isotherms to detect the highest relation coefficient value of 0.99. Langmuir isotherm is proposing that the Pb^{2+} were sucked onto the UNES in a monolayer. The highest monolayer adsorption value was determined to be 3.02 mg/g for the UNES. The necessary characteristic of the Langmuir isotherm can be used to estimate the affinity between the adsorbent and adsorbate using isolation factor, "R_L." The R_L was specified as 0.04 for the concentration of 100 mg/L Pb^{2+}, which showed that the adsorption of Pb^{2+} by UNES was positive in the system. These results were in line with the results of former works [44–46]. Taşar et al. [47] investigated the equilibrium adsorption of Pb^{2+} onto peanut shell and the adsorption model was well described with Langmuir. Similarly, the adsorption of Pb^{2+} onto walnut wood active carbon was investigated and the isotherm data of Pb^{2+} were correlated by the Langmuir [48]. Moreover, some researchers used organic wastes including data-modified walnut shell [34], orange barks [49], banana shell [50], apple pulp [6], peanut shell [51], and the watermelon shell [63] for the removal of Pb^{2+}. The equilibrium data for all adsorbent were well described by Langmuir.

In this study, various kinetic models including, pseudo-first (Psefo) and second-order (Pseso) kinetics were applied to the experimental data in order to investigate the mechanisms of UNES adsorption. Comparing the kinetic values, it can be finalized that the Peso model supplied the

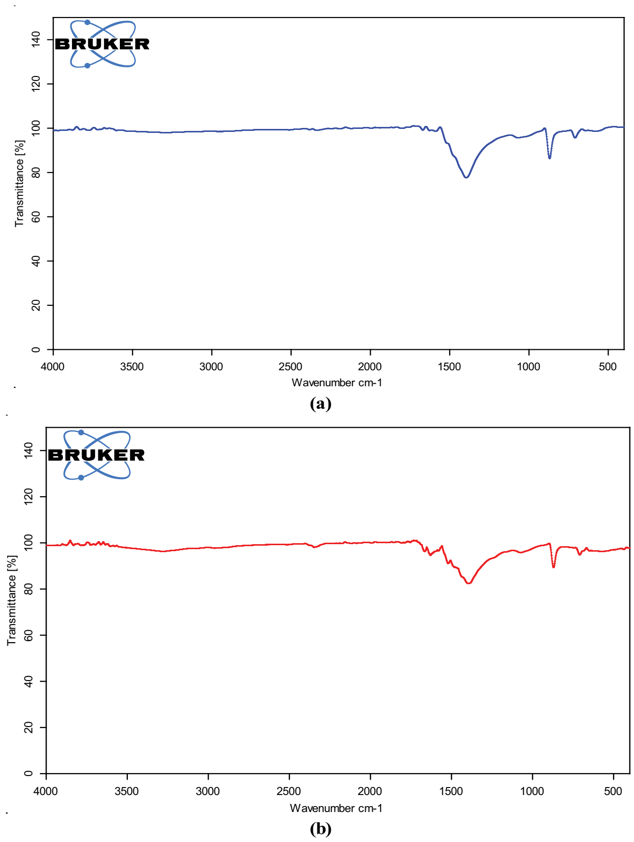

Fig. 6. The FTIR spectra of (a) UNES before adsorption and (b) UNES after adsorption.

best correlation parameter. The major correlation factors and the arrangement of calculating and experimental q_e both showed that the kinetics of Pb^{2+} over UNES monitored the Pseso (Table 2). For this reason, the speed-limiter stage may be chemical adsorption through participation or exchange of electrons between adsorbent and the adsorbate. Prior investigations of adsorption on Pb^{2+} with different natural wastes adsorbents remarked that lead ions removal followed Pseso [52–56]. The results of the present studies on Pb^{2+} are similar to past investigations.

3.7. Comparison of Pb^{2+} removal with different adsorbents reported in literature

Numerous literature reviews pertaining to the use of different adsorbents for wastewater heavy metals removal have been published over the last few decades. A list showing the adsorption removal of different adsorbents for the adsorption of lead from aqueous solutions is given in Table 3. As it can be seen, the observed removal efficiencies of acorn shell for Pb^{2+} are comparable with other low-cost adsorbents.

4. Conclusions

This paper examines the removal of Pb^{2+} from water solutions using UNES. Based on the experimental results obtained using UNES, which is a low-cost waste material, the optimum removal efficiencies in the metal input concentration of 100 mg/L are between pH 3.0 and pH 4.0. The adsorption of Pb^{2+} rapidly occurs in 15 min and remained stable at later times. The maximum adsorption efficiencies by the UNES is obtained between 92% and 98% for Pb^{2+} ions under the optimum conditions (Pb^{2+}_{initial} = 100 mg/L, UNES amount = 2.5 g/100 mL, contact time = 10 min, pH = 3.0, stirring speed = 250 rpm, T = 25°C). Experimental data are consistent with very high correlation coefficient for Langmuir isotherm. The speed of the adsorption processes is explained by the Pseso kinetic model, which is more compatible with the other kinetic models. The results show that UNES is an environment-friendly adsorbent in the removal of Pb+2 from the water environment.

Table 2
Best-fit parameters for kinetics and isotherm of Pb^{2+} adsorption onto the UNES

Models	Equations	Factor 1	Factor 2	Factor 3	R^2
Langmuir	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}, \quad R_L = \frac{1}{1+K_L C_e}$	$q_m = 3.02$	$K_L = 2.69$	$R_L = 0.04$	0.99
Freundlich	$q_e = K_F \sqrt[n]{C_e}$	$K_F = 4.47$	$n = 9.31$	–	0.91
D-R	$\ln q_e = \ln q_{\max} - \beta\varepsilon^2$	$\varepsilon^2 = 49.77$	–	–	0.58
Psefo	$\ln(q_e - q_t) = \ln q_e - k_1 \times t$	$k_1 = 0.05$	$q_e = 1.52$		0.42
Pseso	$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_w}$	$k_2 = 0.11$	$q_e = 1.66$	–	0.99

k_1 (min^{-1}) and k_2 (g/mg/min) are the pseudo-first-order and pseudo-second-order apparent adsorption rate constants; q_m indicates the monolayer adsorption capacity of adsorbate (mg/g); K_L is the Langmuir constant related to the energy of adsorption (L/mg); C_e is the equilibrium solution concentration (mg/L); K_F is the Freundlich constant related to the sorption capacity of adsorbent (L/mg); β is the desorption constant (mol^2/J^2); R_L (dimensionless) is the separation factor for Langmuir model; D-R: Dubinin–Radushkevich model. q_e depicts the amount of Cd^{+2} adsorbed per unit weight of adsorbed at equilibrium (mg/g); $q_{\max}$ is the maximum biosorption capacity of D-R (mg/g); q_w and q_t are amounts of adsorbed ions at equilibrium and at time t, respectively (mg/g) for pseudo-first-order adsorption; ε is the Polanyi potential for D-R; and n is the adsorption intensity for Freundlich isotherm.

Table 3
Comparison of adsorption removal of various adsorbents for Pb^{2+}

Adsorbent	Removal (%)	pH	Adsorbent amount (g)	Pb^{2+} (mg/L)	References
Almond shell	68	6–7	0.5	200	[57]
Antep pistachio	90	5.5	1.0	30	[58]
Groundnut shell	82.81	4.9	1.0	–	[59]
Hazelnut shell	90	6–7	0.5	200	[57]
Palm shell	–	3–5	–	10–700	[60]
Pecan shell	–	5.5	4	100	[61]
Pistachio shell	83	6–9	0.1	30	[62]
Walnut shell	95	4	10	100	[35]
Tomato waste	97	4.0	1.0	20	[16]
Walnut shell	92	4.0	8	20	[34]
Watermelon	98.8	4.21	0.5	100	[63]
Olive stone	88	5.0	10	150	[56]
Active carbon	80	4.0	0.1	50	[48]
Biochar	98	6.5	2	100	[64]
UNES	**95**	**3.0**	**2.5**	**100**	This study

References

[1] A.A. El-Bindary, M.A.A. El-Kawi, A.M. Hafez, I.G.A. Rashed, E.E. Aboelnaga, Removal of reactive blue 19 from aqueous solution using rice straw fly ash, J. Mater. Environ. Sci., 7 (2016) 1023–1036.

[2] S.A. Carmalin, C.E. Lima, Removal of emerging contaminants from the environment by adsorption, Ecotoxicol. Environ. Saf., 150 (2018) 1–17.

[3] S.W. Liao, C.I. Lin, L.H. Wang, Kinetic study on lead (II) ion removal by adsorption onto peanut hull ash, J. Taiwan Inst. Chem. Eng., 42 (2011) 166–172.

[4] L. Mouni, D. Merabet, A. Bouzaza, L. Belkhiri, Adsorption of Pb (II) from aqueous solutions using activated carbon developed from apricot stone, Desalination, 276 (2011) 148–153.

[5] T.S. Anirudhan, S.S. Sreekumari, Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons, J. Environ. Sci., 23 (2011) 1989–1998.

[6] T. Depci, A.R. Kul, Y. Onal, Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from van apple pulp: study in single- and multi-solute systems, Chem. Eng. J., 200–202 (2012) 224–236.

[7] C. Saka, BET, TG-DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with $ZnCl_2$, J. Anal. Appl. Pyrolysis, 95 (2012) 21–24.

[8] J.K. Bediako, S. Kim, W. Wei, Y.S. Yun, Adsorptive separation of Pb(II) and Cu(II) from aqueous solutions using as-prepared carboxymethylated waste Lyocell fiber, Int. J. Environ. Sci. Technol., 13 (2016) 875–886.

[9] H. Çelebi, O. Gök, Use of AQIS for adsorption of Pb^{2+} from aqueous solution, Sigma J. Eng. Nat. Sci., 35 (2017) 69–75.

[10] Agency for Toxic Substances and Disease Registry (ATSDR), Division of Toxicology and Human Health Science, Lead, 2007, Available at: https://www.atsdr.cdc.gov/, [Accessed 24-March-2018].

[11] S.P. Boeykens, A. Saralegui, N. Caracciolo, M.N. Piol, Agroindustrial waste for lead and chromium biosorption, J. Sustainable Dev. Energy, Water Environ. Syst., 6 (2018) 341–350.

[12] H. Ali, E. Khan, M.A. Sajad, Phytoremediation of heavy metals-concepts and applications, Chemosphere, 91 (2013) 869–881.

[13] K.L. Wasewar, P. Kumar, S. Chand, B.N. Padmini, T.T. Teng, Adsorption of cadmium ions from aqueous solution using granular activated carbon and activated clay, Clean-Soil Air Water, 38 (2010) 649–656.

[14] M.H.S. Ghazi, N. Modirshahla, M.A. Behnajady, B. Vahid, Adsorption of C.I. Acid Red 97 dye from aqueous solution onto walnut shell: kinetics, thermodynamics parameters, isotherms, Int. J. Environ. Sci. Technol., 12 (2015) 1401–1408.

[15] G.Z. Kyzas, Z. Terzopoulou, V. Nikolaidis, E. Alexopoulou, D.N. Bikiaris, Low-cost hemp biomaterials for nickel ions removal from aqueous solutions, J. Mol. Liq., 209 (2015) 209–218.

[16] E. Heraldy, W.W. Lestari, D. Permatasori, D.D. Arimurti, Biosorbent from tomato waste and apple juice residue for lead removal, J. Environ. Chem. Eng., 6 (2018) 1201–1208.

[17] H. Daraei, A. Mittal, M. Noorisepehr, F. Daraei, Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, Environ. Sci. Pollut. Res., 20 (2013) 4603–4611.

[18] H. Wang, B. Gao, J. Fang, Y.S. Ok, Y. Xue, K. Yang, X. Cao, Engineered biochar derived from eggshell-treated biomass for removal of aqueous lead, Ecol. Eng., (2017) ,Doi: https://doi.org/10.1016/j.ecoleng.2017.06.029.

[19] P.S. Guru, S. Dash, Sorption on eggshell waste-a review on ultrastructure: biomineralization and other applications, Adv. Colloid Interface Sci., 209 (2014) 49–67.

[20] M. Ahmad, Y. Hashimoto, D.H. Moon, S.S. Lee, Y.S. Ok, Immobilization of lead in a Korean military shooting range soil using eggshell waste: an integrated mechanistic approach, J. Hazard. Mater., 209–210 (2012) 392–401.

[21] Y.A. Almaroai, A.R.A. Usman, M. Ahmad, D.H. Moon, J.S. Cho, Y.K. Joo, C. Jeon, S.S. Lee, Y. Ok, Effects of biochar, cow bone, and eggshell on Pb availability to maize in contaminated soil irrigated with saline water, Environ. Earth Sci., 71 (2014) 1289–1296.

[22] A. Zahir Hussain, K.M. Mohamed Sheriff, Removal of heavy metals from wastewater using low cost adsorbents, Arch. Appl. Sci. Res., 6 (2014) 52–54.

[23] H. Çelebi, O. Gök, Evaluation of lead adsorption kinetics and isotherms from aqueous solution using natural walnut shell, Int. J. Environ. Res., 11 (2017) 83–90.

[24] O.A. Oyeleke, Outline of Food Analysis, ABU Press, Nigeria, 1984, p. 79.

[25] A.O.A.C., Official Methods of Analysis, 18th ed., Association of Analytical Chemists, Washington DC, 2005.

[26] N.Y. Al-Awwal, U.L. Ali, Proximate analyses of different samples of egg shells obtained from Sokoto Market in Nigeria, Int. J. Sci. Res., 4 (2015) 564–566.

[27] L.P. Ramteke, P.R. Gogate, Treatment of water containing heavy metals using a novel approach of immobilized modified sludge biomass based adsorbents, Sep. Purif. Technol., 163 (2016) 215–227.

[28] O. Gök, Ö. Çimen Mesutoğlu, Olive pomace as low-cost adsorbent for the removal heavy metals, J. Faculty Eng. Archit. Gazi Univ., 32 (2017) 507–516.

[29] S.K. Bozbaş, Y. Boz, Low-cost biosorbent: *Anadara inaequivalvis* shells for removal of Pb(II) and Cu(II) from aqueous solution, Process Saf., 103 (2016) 144–152.
[30] Ihsanullah, F.A. Al-Khaldi, B. Abu-Sharkh, A.M. Abulkibash, M.I. Qureshi, T. Laoui, M.A. Atieh, Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes, Desal. Wat. Treat., 3994 (2015) 1–13.
[31] D. Zhao, X. Gao, C. Wu, R. Xie, S. Feng, C. Chen, Facile preparation of amino functionalized graphene oxide decorated with Fe_3O_4 nanoparticles for the adsorption of Cr(VI), Appl. Surf. Sci., 384 (2016) 1–9.
[32] M. Ahmad, K. Manzoor, P. Venkatachalam, S. Ikram, Kinetic and thermodynamic evaluation of adsorption of Cu (II) by thiosemicarbazide chitosan, Int. J. Biol. Macromol., 92 (2016) 910–919.
[33] A.I.A. Sherlala, A.A.A. Raman, M.M. Bello, A. Asghar, A review of the applications of organo-functionalized magnetic graphene oxide nanocomposites for heavy metal adsorption, Chemosphere, 193 (2018) 1004–1017.
[34] A. Almasi, M. Omidi, M. Khodadadian, R. Khamutian, M.B. Gholivand, Lead (II) and cadmium (II) removal from aqueous solution using processed walnut shell: kinetic and equilibrium study, Toxicol. Environ. Chem., 94 (2012) 660–671.
[35] R. Wolfova, E. Pertile, P. Fecko, Removal of lead from aqueous solution by walnut shell, J. Environ. Chem. Ecotoxicol., 5 (2013) 159–167.
[36] L. Massimi, A. Giuliano, M.L. Astolfi, R. Congedo, A. Masotti, S. Canepari, Efficiency evaluation of food waste materials for the removal of metals and metalloids from complex multi-element solutions, Materials, 11 (2018) 1–15.
[37] L. Han, L. Qian, R. Liu, M. Chen, J. Yan, Q. Hu, Lead adsorption by biochar under the elevated competition of cadmium and aluminum, Sci. Rep., 7 (2017) 1–11.
[38] P.S. Kumar, S. Ramalingam, S.D. Kirupha, A. Murugesan, T. Vidhyadevi, S. Sivanesan, Adsorption behavior of nickel (II) onto cashew nut shell: equilibrium, thermodynamics, kinetics, mechanism and process design, Chem. Eng. J., 167 (2011) 122–131.
[39] A. Kaur, S. Sharma, Removal of heavy metals from waste water by using various adsorbents – a review, Indian J. Sci. Technol., 10 (2017) 1–14.
[40] S. Mopoung, P. Moonsri, W. Palas, S. Khumpai, Characterization and properties of activated carbon prepared from tamarind seeds by KOH activation for Fe(III) adsorption from aqueous solution, Sci. World J., 2015 (2015) 1–9.
[41] M.N. Freire, J.N.F. Holanda, Characterization of avian eggshell waste aiming its use in a ceramic wall tile paste, Cerâmica, 52 (2006) 240–244.
[42] A.S.M. Bashir, Y. Manusamy, Characterization of raw eggshell powder (ESP) as a good bio-filler, J. Eng. Res. Technol., 2 (2015) 56–60.
[43] S.C. Onwubu, Using Eggshell for the Development of a Quality Alternative Material to Pumice in Reducing the Surface Roughness of Heat-Cured Acrylic Resins, MSc Thesis, 2016, pp. 23–24.
[44] G. Kashi, On the analysis of phenol removal from drinking water by batch reactor using powdered eggshell, Biosci. Biotechnol. Res. Comm., 10 (2017) 287–296.
[45] C.O. Ijagbemi, M.H. Baek, D.S. Kim, Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, J. Hazard. Mater., 166 (2009) 538–546.
[46] E. Pehlivan, T. Altun, S. Cetin, M. Iqbal Bhanger, Pb (II) sorption by waste biomass of hazelnut and almond shell, J. Hazard. Mater., 167 (2009) 1203–1208.
[47] S. Taşar, F. Kaya, A. Ozer, Biosorption of lead (II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies, J. Environ. Chem. Eng., 2 (2014) 1018–1026.
[48] M. Ghaedi, H. Mazaheri, S. Khodadoust, S. Hajati, M.K. Purkait, Application of central composite design for simultaneous removal of methylene blue and Pb^{2+} ions by walnut wood activated carbon, Spectrochim. Acta, Part A, 135 (2015) 479–490.
[49] N. Azouaou, M. Belmedani, H. Mokaddem, Z. Sadaoui, Adsorption of Pb from aqueous solution onto untreated orange barks, Chem. Eng. Trans., 32 (2013) 55–60.
[50] Z. Abbasi, M. Alikarami, E.R. Nezhad, F. Moradi, V. Moradi, Adsorptive removal of Co^{2+} and Ni^{2+} by peels of banana from aqueous solution, Univers. J. Chem., 1 (2013) 90–95.
[51] N.S.M. Tahiruddin, S.Z.A. Rahman, Adsorption of lead in aqueous solution by a mixture of activated charcoal and peanut shell, World J. Sci. Technol. Res., 1 (2013) 102–109.
[52] M. Najafi, Y. Yousefi, A.A. Rafati, Synthesis, characterization and adsorption studies of several heavy metal ions on amino-functionalized silica nano hollow sphere and silica gel, Sep. Purif. Technol., 85 (2011) 193–205.
[53] M. Momcilovic, M. Purenovic, A. Bojic, A. Zarubica, M. Randelovic, Removal of lead (II) ions from aqueous solutions by adsorption onto pinecone activated carbon, Desalination, 276 (2011) 53–59.
[54] G. Vazquez, O. Mosquera, M.S. Freire, G. Antorrena, J. Gonzalez-Alvarez, Alkaline pre-treatment of waste chestnut shell from a food industry to enhance cadmium, copper, lead and zinc ions removal, Chem. Eng. J., 184 (2012) 147–155.
[55] A.P.A. Salvado, L.B. Campanholi, J.M. Fonseca, C.R.T. Tarley, J. Caetano, D.C. Dragunski, Lead (II) adsorption by peach palm waste, Desal. Wat. Treat., 48 (2012) 335–343.
[56] G. Blazquez, M. Calero, A. Ronda, G. Tenorio, M.A. Martın-Lara, Study of kinetics in the biosorption of lead onto native and chemically treated olive stone, J. Ind. Eng. Chem., 20 (2014) 2754–2760.
[57] K. Yetilmezsoy, S. Demirel, Artificial neural network approach for modeling of Pb (II) adsorption from aqueous solution by Antep pistachio (*Pistacia vera* L.) shells, J. Hazard. Mater., 153 (2008) 1288–1300.
[58] S.R. Shukla, S.P. Roshan, Removal of Pb(II) from solution using cellulose-containing materials, J. Chem. Technol. Biotechnol., 80 (2005) 176–183.
[59] G. Issabayeva, M.K. Aroua, N.M. Sulaiman, Continuous adsorption of Pb(II) ions in a column packed with palm shell activated carbon, J. Hazard. Mater., 155 (2008) 109–113.
[60] J.C.P. Vaghetti, E.C. Lima, B. Royer, B.M. da Cunha, N.F. Cardoso, Pecan nutshell as biosorbent to remove Cu(II), Mn(II) and Pb(II) from aqueous solutions, J. Hazard. Mater., 162 (2009) 270–280.
[61] M. Kazemipour, M. Ansari, S. Tajrobehkar, M. Majdzadeh, H.R. Kerman, Removal of Pb(II), cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone, J. Hazard. Mater., 150 (2008) 322–327.
[62] S. Janyasuthiwong, S.M. Phiri, P. Kijjanapanich, E.R. Rene, G. Esposito, P.N.L. Lens, Copper, lead and zinc removal from metal contaminated wastewater by adsorption onto agricultural wastes, Environ. Technol., 36 (2015) 3071–3083.
[63] J.M. Barbosa, C. Lopez-Velandia, A. del Pilar Maldonado, L. Giraldo, J.C. Moreno-Pirajan, Removal of lead (II) and zinc (II) ions from aqueous solutions by adsorption onto activated carbon synthesized from watermelon shell and walnut shell, Adsorption, 19 (2013) 675–685.
[64] A.K. Karunanayake, O.A. Todd, M. Crowley, L. Ricchetti, C.U. Pittman Jr, R. Anderson, D. Mohan, T. Mlsna, Lead and cadmium remediation using magnetized and nonmagnetized biochar from Douglas fir, Chem. Eng. J., 331 (2018) 480–491.