

Metal removal using chemically modified eggshells: preparation, characterization, and statistical analysis

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Received 24 February 2019; Accepted 9 July 2019

ABSTRACT

In this study, a novel adsorbent was prepared from eggshells using inexpensive single-step modification method. Chemical surface modification of eggshell samples that were collected from local homes was investigated using three modifying agents, namely, NaOH, HNO₃ and KMnO₄ at different concentrations and contact times. The produced adsorbents were investigated for lead removal from aqueous solution. The obtained results on removal efficiencies were statistically analyzed with the response surface method. The obtained results revealed that samples modified with KMnO₄ showed high affinities for lead ions, when compared with those modified with NaOH and HNO₃. The statistical analysis demonstrated that the modifying agent has a significant role in the modification process. Poor statistical models were developed for samples modified with NaOH and HNO₃. However, a reliable model was developed for samples modified with KMnO₄, which was adequately used to predict the responses. Modified and unmodified eggshell samples were characterized using standard methods that included X-ray diffraction, Fourier transform infrared, scanning electron microscope/energy dispersive spectrometer. The characterization outcome indicated that manganese oxides were successfully loaded on the eggshell surfaces. Moreover, the porous structure of the modified eggshell was noticeably enhanced and the BET surface area of the modified eggshell at the best conditions was found to be 90 m²/g. The obtained results showed that eggshell waste could be used efficiently as a promising low-cost adsorbent for metal removal using simple direct modification process. Effects of operational parameters showed that lead removal efficiency increased with pH and adsorbent dosage, while it was decreased with increasing the initial concentration. The experimental data at the equilibrium was best fitted to Langmuir isotherm with a maximum adsorption capacity of 700 mg/g and removal efficiency of 98%. Kinetic studies indicated that the pseudo-second-order model best fitted the experimental data. The thermodynamic study revealed that the free energy, ΔG , was found to be negative, which indicates that the adsorption was spontaneous and favorable. Furthermore, the positive value of enthalpy, ΔH , (55 kJ/mole) indicated that the adsorption was endothermic. Chemisorption mechanism of lead removal using K-ES was confirmed since the activation energy, E_a , which was found to be more than 40 kJ/mole.

Keywords: Adsorption; Low-cost adsorbent; Surface modification; RSM modeling; Kinetics; Thermodynamics

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1. Introduction

Due to increasing and rapid urbanization and anthropogenic activities in recent decades, significant environmental pollutants have emerged. Various contaminants have been introduced to the water environment that included heavy metals, particularly lead (Pb(II)). Lead is discharged daily to the environment from different industrial practices such as car manufacturing, electrical, electroplating, mining, pesticides and batteries. The presence of lead in natural waters has severe negative impacts on human health and the ecological system, including flora and fauna. In addition to the severe damage of lead on the environment, it is nonbiodegradable and can be accumulated in the food chain [1,2]. Therefore, controlling its concentrations in wastewater is an utmost priority to satisfy the limits of standard and regulations and preclude related problems. Among several techniques used for removal of heavy metals from aqueous solutions, adsorption is considered as one of the best widely used technique in wastewater treatment due to its efficiency for the removal of many pollutants and simplicity in design and operation [3,4]. Accordingly, many researchers have conducted studies to develop highly efficient as well as low-cost adsorbents to be used in the adsorption process for wastewater treatment. In the last decades, many studies have been conducted to develop eco-friendly adsorbents with no hazardous by-products and have a low cost. In this regard, a large number of natural waste materials, which have attractive properties such as less sludge generation, possible regeneration and availability of these materials in abundance, have been studied for the development of low-cost and highly efficient adsorbents for water and wastewater treatment [5]. The most common techniques of adsorbents development from low-cost waste materials are activated carbon production and surface modification. Waste-based activated carbon is a versatile adsorbent because they have high removal efficiency for a wide range of pollutants due to their high porous structure and surface area. However, the production process of activated carbon is complicated because it is usually conducted at high temperatures, needs expensive chemicals to be used as activating agents and not easily regenerated on commercial scales [4]. In this perspective, the development of low-cost adsorbent through surface modification could be a promising alternative. There are many chemicals used for surface modifications such as oxidizing agents (hydrogen peroxide), organic acids and compounds (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycolic acid, ethylenediamine, formaldehyde, epichlorohydrin, methanol) and bases (sodium hydroxide, calcium hydroxide, sodium carbonate) [4,6,7]. The purpose of surface modification process is not only to increase the adsorption efficiency but also to prevent coloration of aqueous solution and remove soluble organic compounds [5]. According to Hokkanen et al. [4], there are two categories of modification methods; monomer grafting and direct modification. Monomer grafting method allows a wide range of specific functional groups to attach to the adsorbent backbone, whereas indirect modification method, chemical modifying agent enables the functional groups to attach to the hydroxyl groups of the adsorbent. Adsorbent

preparation using direct chemical modification can be achieved through halogenations, esterification, oxidation, etherification, and acid and alkali treatment [4]. Alkali treatments with bases such as NaOH are commonly used to enhance the adsorption capacity of adsorbents by attaching hydroxyl anions, which are negatively charged to adsorbent surface that results in more attraction of cationic species such as heavy metals. Adsorbent surface modifications with acids such as HCl and HNO₃ are used to enhance the proportion of active surfaces by reducing the positively charged surfaces with hydrogen ions, which increases negatively charged surfaces. Surface modification with oxidizing agents such as KMnO₄ and H₂O₂ leads to the oxidation of OH groups on the adsorbent to the aldehyde or carboxyl groups [4]. The direct method was successfully employed to enhance removal efficiencies of heavy metals for many waste materials such as rice husk [8], sawdust [9,10], carrot residues [11], peanut husk [12], sugarcane bagasse [13,14] and Juniper fiber [15].

Hen eggshell is a biological sorbent produced daily as waste in considerable amounts from different sources, including household, restaurants and hotels. Annually, consumption of eggs is expanding due to the dramatical population increase, which in turn results in the generation of considerable amounts of eggshell. Recently, modified eggshells have been investigated for removal of various pollutants from wastewater such as basic yellow 28 dye [16], reactive red 198 dye [17], Cr(VI) [18–20], oxalic acid [21], humic acid [22], Cu (II) [23], arsenate [6], Hg (II) [24] and lead Pb(II) [25]. Considering the reviewed literature, chemically modified eggshells have been recently investigated for the removal of various heavy metals. However, less attention has been paid to the removal of lead. Moreover, the reported studies of developing low-cost adsorbents from eggshells for lead removal focused on the use of hydroxyapatite derived from eggshells, for example, Meski et al. [26] have investigated the synthesis of carbonate hydroxyapatite (CHAP) from eggshells for lead removal from aqueous solution. Eggshells were crushed, dried and mixed with nitric acid for 1 h. Consequently, phosphate solution was slowly added to the mixture at ebullition temperature for 1 h. The resulting material was then filtered, dried and ground. Adsorption results revealed that maximum adsorption capacity was 500 mg/g, where more than 99% of lead was removed at pH 3, initial concentration of 200 mg/L and dosage of 1 g/L. Furthermore, Liao Dexiang et al. [27] extracted carbonate hydroxyapatite from eggshells for Pb(II) removal. Eggshells were washed and dried, then mixed with nitric acid at a temperature between 30°C and 40°C and pH of 1–3 for 2–3 h. Subsequently, the slurry was mixed with Ca(OH)₂ solution for 24 h at temperatures between 50°C and 60°C and pH of 9–12, followed by drying and grinding. The results revealed that the maximum adsorption capacity of 101 mg/g at an initial pH of 6.0 was reported.

From the above discussion, it is clear that the use of eggshell as a low-cost adsorbent for lead removal has been reported with and without chemical modifications. However, the published literature showed that relatively complex methods have been used to modify eggshells. Consequently, finding simple and cheap preparation methods is an attractive option. To the best of our knowledge, the production of efficient adsorbent from eggshells for lead removal using

single-step modification with KMnO_4 , HNO_3 and NaOH has not been investigated. Therefore, the primary objective of this study is to investigate the chemical modification of eggshells using different agents, namely, NaOH , HNO_3 and KMnO_4 for lead removal. The production process was statistically analyzed. Response surface methodology (RSM) (central composite design CCD) was employed for experimental design.

2. Materials and methods

2.1. Chemicals

Analytical grade chemical reagents were used and purchased from (BDH laboratories supplies, Poole, UK). All solutions were prepared with ultrapure deionized water (Milli-Q unit).

2.2. Raw materials

Raw materials (eggshells waste) were collected from different local houses and dried in an air oven at 80°C for 24 h. The dried eggshells were crushed, sieved to a particle size between 40 and $100\ \mu\text{m}$ and kept in air-tight containers for characterization of different physiochemical characteristics and chemical surface modification.

2.3. Eggshells chemical surface modification

The eggshell powder was chemically modified using the direct method. Eggshell samples were immersed in the modifying solutions as follows; 2.5 g of eggshell were soaked in 50 mL of different concentrations of the modifying solutions, 0.01, 0.505 or 1 M for HNO_3 and NaOH and 0.1, 0.25 and 0.4 for KMnO_4 . The mixture was stirred for 6, 27 and 48 h at room temperature. Then, the treated eggshell samples were extensively washed with distilled water to remove residual chemicals. Subsequently, eggshell samples were dried overnight in an oven at 80°C . Eggshell samples treated with NaOH , HNO_3 and KMnO_4 were designated as Na-ES, HN-ES and K-ES, respectively.

2.4. Design of experiments

RSM using the central composite design (CCD) was employed for experimental design and analysis of the surface modification process. Three modifying agents were investigated, namely, NaOH , HNO_3 and KMnO_4 . Two independent

factors namely concentration and contact time were studied, where three levels of each factor were adopted. The removal efficiency of lead in percentage was used as a response to evaluate the relative significance of each factor. The levels of each factor were coded as high (+1), low (-1) and 0 (central). Table 1 summarizes factors and levels investigated for eggshell modification.

To identify the most significant factors with a minimum number of experiments, RSM technique was employed. RSM technique, statistical analysis and mathematical model were adopted to develop the relationship between independent factors (concentration and time) and dependent factor (removal efficiency), which can be estimated using low-degree polynomial model. In RSM, first-order and quadratic or second order models are usually used [28]. The quadratic model polynomial form is presented in the following formula:

$$Y = \beta_0 + \sum_{i=1}^K \beta_i X_i + \sum_{i=1}^K \beta_{ii} X_i^2 + \sum_{i=1}^{K-1} \sum_{j=i+1}^K \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is the predicted response, β_0 is a constant term coefficient, β_i is a linear term, β_{ii} is a quadratic term, β_{ij} is an interaction term, ε is an error term, X_i , X_j are the coded values of independent factors and K is the number of independent factors. Analysis of variance (ANOVA) and determination coefficient (R^2) were used to investigate the goodness of obtained models. p -value was used to investigate the relative significance of each factor. Design-Expert software was used to develop the experimental design and statistical analysis of the eggshell modification process. With one center per block and one replicate, a total number of nine experiments were investigated. The design matrix of each modifying agent in coded values was generated using Design-Expert software that is presented in Table 2.

2.5. Material characterization

Surface functional groups of the eggshell before and after modification were determined using Fourier transform infrared (FTIR) spectroscopy technique (Thermo Electron Corporation, (Waltham, Massachusetts, U.S.), Nicolet Nexus 670 FT-IR Spectrometer). The FTIR spectra of raw and modified materials were recorded between 500 and $4,000\ \text{cm}^{-1}$, where KBr was used for recording the transmission spectra. In this regard, a very small amount of the sample 1%–2% was mixed

Table 1
Factors and levels investigated for eggshells modification

Modifying agent	Factor	Symbol	Coded factors		
			-1	0	+1
NaOH	Concentration, M	A	0.01	0.505	1
	Time, h	B	6	27	48
HNO_3	Concentration, M	A	0.01	0.505	1
	Time, h	B	6	27	48
KMnO_4	Concentration, M	A	0.1	0.25	0.4
	Time, h	B	6	27	48

Table 2
Design matrix of each modifying agent

Run	Coded factors	
	Factor 1	Factor 2
	A	B
1	-1	-1
2	1	-1
3	-1	1
4	1	1
5	-1	0
6	1	0
7	0	-1
8	0	1
9	0	0

and ground with dry KBr pellets in mortar. Then, the mixture was placed under hydraulic pressure to form a homogeneous and transparent pellet, which was placed in the IR sample holder and analyzed. Scanning electron microscope (SEM) (JEOL 5800 LV, USA) was employed to investigate the morphology of the sample surface, which visualizes sizes and shapes of pores on the sample surface of raw and modified samples. Energy dispersive spectrometer (EDS) was used to study the chemical composition of raw and surface-modified materials. X-ray diffraction (XRD) technique was applied to examine crystalline structures of the raw and modified materials and to quantify and identify mineral phases, XRD spectra were recorded at an angle ranging between 10 and 80 degrees, with a step size of 0.02°/s using Ultima IV X-ray diffractometer. Standard multi-point Brunauer–Emmett–Teller (BET) method [29] was employed to study porous characteristics of raw and modified adsorbent samples, including pore size, pore volume and specific surface area. Nitrogen adsorption isotherms at -196°C were plotted for the modified samples using (Micromeritics, ASAP 2020 V3.05 H, Georgia, USA) an automatic adsorption unit.

2.6. Adsorption of lead from synthetic solutions

Adsorption performance of eggshell samples before and after surface modifications at different conditions was evaluated, where lead ions were used as the adsorbate. A stock solution of 1,000 mg/L of Pb(II) was prepared from nitrate salts by dissolving 1.6 g Pb ((NO₃)₂) in 1 L of deionized water. The stock solution was acidified by adding HNO₃ until a pH value of less than 2, before making up to 1,000 mL. The desired concentration of Pb(II) was prepared using proper dilutions.

A 50 mL volume of 150 mg/L of the lead solution was placed in contact with 10 mg of raw and modified eggshell samples in 125 mL Erlenmeyer flask and pH values were adjusted using 0.1 N of NaOH and 0.1 N of HNO₃. Flasks were kept under stirring conditions at room temperature for 1 h and, subsequently, samples were filtered using Whatman grade 42 filter paper and analyzed using atomic absorption spectroscopy (PerkinElmer, Analyst 700, Waltham, Massachusetts, U.S.).

Adsorption kinetics of lead removal using K-ES was conducted by adding 0.1 g of K-ES to 500 mL of 100 mg/L of the lead solution and pH value of 5 under stirring conditions, after which, 10-mL samples were collected using syringe at different contact times. The effect of pH on lead removal by K-ES was investigated at pH values between 2 and 9, where 10 mg of K-ES was added to 50 mL of 100 ppm of lead solution and placed on a shaker at a shaking speed of 200 rpm for 1 h at room temperature, where pH values were adjusted using diluted NaOH or HCl. Effects of initial concentrations on removal efficiency of lead using K-ES were investigated at three dosages, namely, 2.5, 5 and 10 mg that were added under stirring conditions to 50 mL solution of lead at various initial concentrations and initial pH value of 5 for 1 h. Adsorption equilibrium experiments were performed by varying the initial concentration from 25 to 175 mg/L at a dosage of 0.1 g/L, and a pH value of 5 at room temperature. The thermodynamic study was conducted by adding 10 mg of K-ES to 50 mL of 100 mg/L at temperatures of 25°C, 40°C and 60°C and the mixture was kept under stirring conditions for 1 h.

3. Results and discussions

3.1. Statistical analysis and modeling

Lead removal efficiencies of raw and modified eggshells under different conditions are presented in Table 3. The table shows that removal efficiencies were enhanced due to modification. Statistical analysis for lead removal by the modified eggshell was performed according to RSM (CCD) design, where significant factors of the modification process together with their interactions on lead removal with a confidence level of more than 95% were identified.

Analysis of variance (ANOVA) was performed using the Design-Expert software, where data transformation was conducted for responses that were not normally distributed to satisfy the ANOVA assumption. Moreover, to remove bias from the model, some model terms were refined. Tables 4–6 show the ANOVA outcome of Na-ES, HN-ES and K-ES, respectively. The obtained results indicate that, for Na-ES and HN-ES, *p*-values of all terms, including the model, is higher than 0.05, which indicates that they are statistically insignificant. On the other hand, *p*-values of all terms except *A*² for K-ES, including the model, are less than 0.05, which indicated that they have a significant effect on lead removal. In this case, *A*, *B*, *AB*, *B*² and the model itself are statistically significant, while *A*² is insignificant. Moreover, the coefficient of determination (*R*²) was used to investigate the goodness of the obtained models. High values of *R*² imply that the model has high reliability. Moreover, the difference between *R*²-adjusted and *R*²-predicted is an indication of model adequacy. For an adequate model, this difference should not exceed 0.2. Essential model characteristics of the eggshell modified with different agents are summarized in Table 7. As shown in the table, for Na-ES and HN-ES poor coefficients of determination, *R*² (0.2 and 0.55) were obtained. Furthermore, negative values of *R*²-adjusted for both modifying agents imply that the overall mean is a better predictor of the response than the derived model. Good *R*² value (0.98) was obtained for K-ES.

Table 3
Lead removal by raw and modified eggshell under different conditions

Modifying agent	Un-coded factors		Coded factors		Response (Lead removal) (%)
	Factor 1	Factor 2	Factor 1	Factor 2	
NaOH	A Concentration (M)	B Contact time (h)	A	B	
	0.01	6	−1	−1	60.9507
	1	6	1	−1	20.4025
	0.01	48	−1	1	22.3351
	1	48	1	1	31.7765
	0.01	27	−1	0	75.7460
	1	27	1	0	61.6586
	0.505	6	0	−1	16.4651
	0.505	48	0	1	96.4053
	0.505	27	0	0	12.1110
HNO ₃	0.01	6	−1	−1	10.0145
	1	6	1	−1	1.7094
	0.01	48	−1	1	7.8374
	1	48	1	1	6.3600
	0.01	27	−1	0	69.3616
	1	27	1	0	24.4969
	0.505	6	0	−1	50.9507
	0.505	48	0	1	25.8848
	0.505	27	0	0	30.5344
	KMnO ₄	0.1	6	−1	−1
0.4		6	1	−1	51.2630
0.1		48	−1	1	97.3213
0.4		48	1	1	96.7654
0.1		27	−1	0	69.2575
0.4		27	1	0	97.1811
0.25		6	0	−1	48.8133
0.25		48	0	1	96.8244
0.25		27	0	0	88.7578
–		Raw eggshell	–	–	26.64816

Table 4
ANOVA for response surface reduced cubic model of Na-ES

Source	Sum of squares	Df	Mean square	F-value	p-value
Model	1,599.95	5	319.99	0.17	0.9580
A–A	340.42	1	340.42	0.18	0.7007
B–B	462.86	1	462.86	0.24	0.6556
AB	624.74	1	624.74	0.33	0.6066
A ²	29.15	1	29.15	0.015	0.9093
B ²	142.78	1	142.78	0.075	0.8018

Also, R^2 -adjusted and R^2 -predicted are in good agreement, and the difference was found to be 0.15, which confirms the model adequacy. As part of model adequacy, the value of adequate precision, which measures the signal to noise ratio should be greater than 4. Low values of adequate precision were observed for Na-ES and HN-ES. A ratio of 2.57 and 1.62 indicate inadequate signal and this model should

not be used to navigate the design space. For K-ES, adequate precision of the obtained model was found to be 17.31, which indicates an adequate signal and confirms that the model can be used adequately to navigate the design space. The predictive efficiency of the obtained statistical models is indicated by the value of the average absolute deviation (AAD), where low AAD values indicate a highly reliable model. For Na-ES

Table 5
ANOVA for response surface reduced cubic model of HN-ES

Source	Sum of squares	Df	Mean square	F-value	p-value
Model	2,280.10	5	456.02	0.76	0.6334
A–A	497.72	1	497.72	0.83	0.4297
B–B	85.07	1	85.07	0.14	0.7317
AB	11.65	1	11.65	0.019	0.8980
A ²	500.97	1	500.97	0.83	0.4284
B ²	1,184.69	1	1,184.69	1.97	0.2548

Table 6
ANOVA for response surface reduced cubic model of K-ES

Source	Sum of squares	Df	Mean square	F-value	p-value
Model	25.83	5	5.17	37.37	0.0066
A–A	2.55	1	2.55	18.44	0.0232
B–B	18.87	1	18.87	136.45	0.0013
AB	1.48	1	1.48	10.69	0.0468
A ²	0.40	1	0.40	2.92	0.1859
B ²	2.54	1	2.54	18.35	0.0234

Table 7
Essential model characteristics

Modifying agent	Transformation	R ²	Adj. R ²	Pred. R ²	Adeq. precision	AAD %
NaOH	None	0.2191	–1.0825	–6.7084	1.258	0.22
HNO ₃	None	0.5586	–0.1770	–3.1719	2.566	0.114
KMnO ₄	Square root	0.98	0.96	0.81	17.31	0.03

and HN-ES, AAD values were found to be 0.22 and 0.114, respectively. Average absolute deviation value of 0.03% was obtained for K-ES, which implies that the derived model possesses reliable predictive capability. The obtained empirical models for K-ES, based on the coded and actual values, are presented in Eqs. (2) and (3), respectively, whereas for Na-ES and HN-ES are presented in Eqs. (4)–(7), respectively.

$$\sqrt{R(\%)} = 9.5 + 0.65A + 1.77B - 0.6AB - 0.45A^2 - 1.13B^2 \quad (2)$$

$$\sqrt{R(\%)} = 1.72 + 19.55A + 0.271B - 0.193AB - 19.98A^2 - 2.554B - 0.03B^2 \quad (3)$$

$$R(\%) = 47.29 - 7.53A + 8.78B + 12.5AB + 3.82A^2 - 8.45B^2 \quad (4)$$

$$R(\%) = 50.804 - 63.41A + 0.846B + 1.20AB + 15.58A^2 - 0.0192B^2 \quad (5)$$

$$R(\%) = 52.02 - 9.11A - 3.77B + 1.71AB - 15.83A^2 - 24.34B^2 \quad (6)$$

$$R(\%) = 11.68244 + 42.4A + 2.72B + 0.164AB - 64.59A^2 - 0.0552B^2 \quad (7)$$

where R is lead removal, A is concentration of modifying agent and B is the contact time.

Comparison between actual and predicted responses is shown in Table 8 and plotted in Fig. 1. The obtained results revealed that for K-ES the actual and predicted removal efficiencies are in great agreement, while for Na-ES and HN-ES pronounced differences between the actual and predicted responses were observed.

3.2. Response surface plots

Response surface contour plots and the three-dimensional (3-D) graphs of lead removal for Na-ES, HN-ES and K-ES are depicted in Fig. 2. For Na-ES, effects of NaOH concentration and contact time and their interactions are depicted in Fig. 2a. At low values of contact time, the concentration seems to be the dominating factor, where lead removal was decreased with increasing concentrations. However, as contact time increases, both concentration and the interactions have an insignificant impact on lead removal. For HN-ES as depicted in Fig. 2b, all factors, including interactions, have the same trend, where lead removal increases with increasing values of independent factors until it reaches maximum values. After which, the removal efficiency decreases with further increasing values of independent factor. The effect of KMnO₄ concentration, contact time and their interactions on

Table 8
Comparison between actual and predicted responses for Na-ES, HN-ES and K-ES

Modifying agent	Un-coded factors		Lead removal (%)		
	Factor 1	Factor 2	Actual	Predicted	
	<i>A</i> concentration (M)	<i>B</i> contact time (h)			
NaOH	0.01	6	60.9507	53.90851	
	1	6	20.4025	14.11897	
	0.01	48	22.3351	46.48108	
	1	48	31.7765	56.68109	
	0.01	27	75.7460	58.64392	
	1	27	61.6586	43.84915	
	0.505	6	16.4651	30.12981	
	0.505	48	96.4053	47.69717	
	0.505	27	12.1110	47.36261	
	HNO ₃	0.01	6	10.0145	26.43074
		1	6	1.7094	4.801224
		0.01	48	7.8374	15.48269
1		48	6.3600	0.681024	
0.01		27	69.3616	45.29551	
1		27	24.4969	27.07991	
0.505		6	50.9507	31.44264	
0.505		48	25.8848	23.90851	
0.505		27	30.5344	52.01437	
KMnO ₄		0.1	6	22.6232	23.92545
		0.4	6	51.263	54.92151
		0.1	48	97.3213	93.1938
	0.4	48	96.7654	94.89798	
	0.1	27	69.2575	70.54005	
	0.4	27	97.1811	94.1388	
	0.25	6	48.8133	43.56837	
	0.25	48	96.8244	102.9642	
	0.25	27	88.7578	90.2531	

lead removal is presented in Fig. 2c. The contact time seems to have a greater influence on lead removal than the concentration. The increase in contact time from 6 to 48 h showed a noticeable enhancement in removal efficiency up to 97%.

Moreover, the obtained graph shows that by increasing the contact time, removal efficiency increases until a specific value, where insignificant removal was noticed by a further increase in contact time. This might be attributed to the fact that by increasing the contact time, more manganese oxides are loaded on the eggshell surface. At a particular time, the surface becomes saturated and further increment leads to an insignificant increase in the removal efficiency. Interaction effects of the concentration–contact time were found to have positive impacts on the removal efficiency, as depicted in Fig. 2c. As depicted in the figure, the obtained results indicate that the removal efficiency was noticeably enhanced with the increase in both concentration and contact time. The increase in both concentration and contact time might allow more manganese oxides to be attached to the eggshell surface until saturation takes place, where insignificant removal occurs by a further increase in both factors.

Based on the obtained results, eggshell samples modified with KMnO₄ showed higher removal efficiencies than that modified with HNO₃ and NaOH. The BET surface area of samples modified with various modifying agents that showed the highest removal efficiencies are depicted in Table 9. It was observed that samples modified with NaOH and HNO₃ have lower surface area than that modified with KMnO₄, which is in good agreement with the trend of removal efficiencies.

Moreover, the statistical analysis revealed that poor models were obtained for Na-ES and HN-ES, which cannot be used adequately for response prediction, whereas good one was obtained for K-ES. Among K-ES samples, the highest removal efficiency was achieved for samples modified at the following conditions; concentration of 0.25 M and contact time of 48 h. Further characterizations were conducted for K-ES produced at these conditions. Table 10 shows comparative removal efficiencies and adsorption capacities of lead using hydroxyapatite-based adsorbents. The results indicated that K-ES has an efficient, competitive capability for lead removal from aqueous solutions.

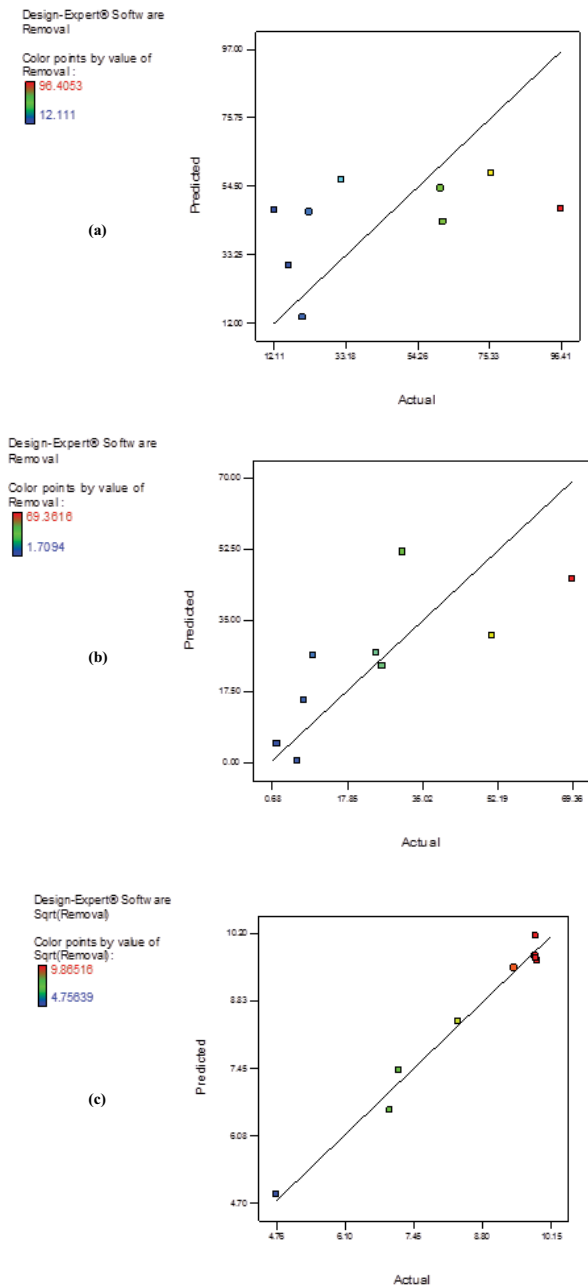


Fig. 1. Actual vs. predicted responses plot of (a) Na-ES, (b) HN-ES and (c) K-ES.

3.3. Material characterization

The surface morphology of raw and modified eggshell samples using SEM is depicted in Fig. 3. The micrographs of eggshells depicted in Fig. 3a clearly show a complicated network of fibers, which could be attributed to protein fibers that present in the membrane of the eggshell. The obtained results are in consistency with the results documented by Tsai et al. [32], who characterized eggshells and eggshell membrane in details. The protein fiber network disappeared in the micrograph of K-ES as depicted in Fig. 3b, and small

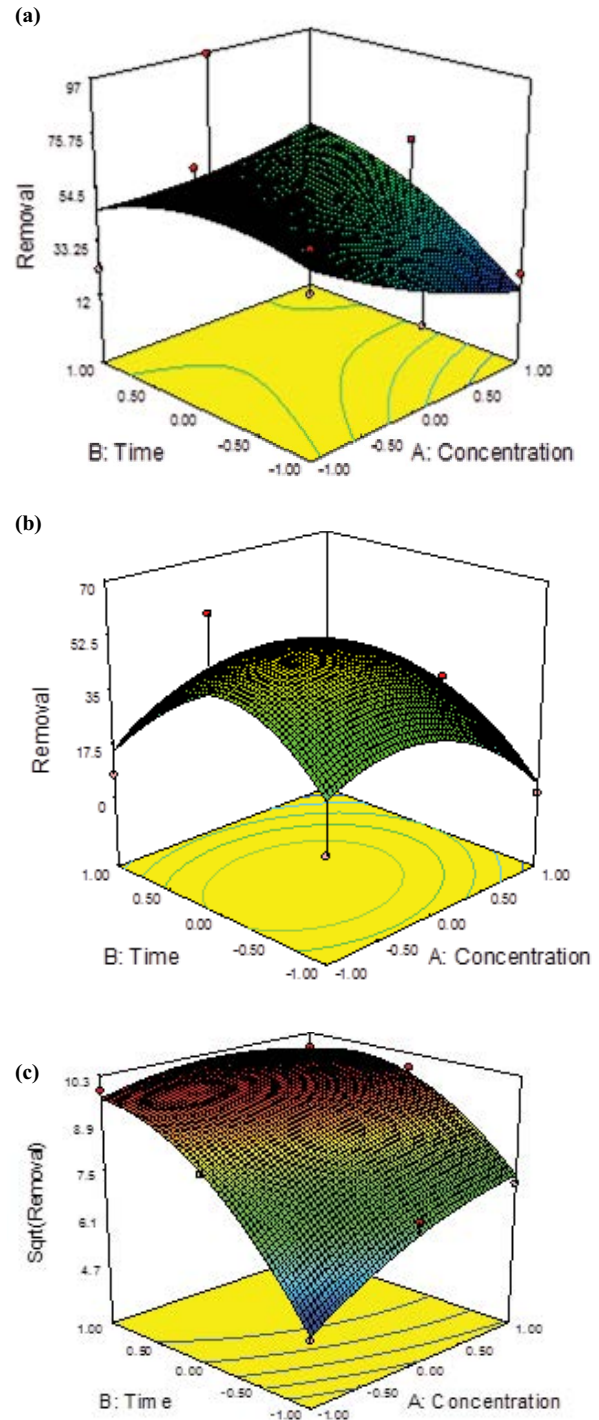


Fig. 2. 3-D surface plot for lead removal of (a) Na-ES, (b) HN-ES and (c) K-ES.

particles were observed, which might be attributed to manganese oxide particles formed during the modification with $KMnO_4$. Similar micrographs were reported by Girma et al. [33], who synthesized mixed hydrous oxides, including manganese oxides for fluoride removal from aqueous solutions. The small particles in K-ES were confirmed in the XRD

spectra with smaller crystal size compared with the unmodified eggshell. Tables 11 and 12 show the elemental compositions of the surface of raw and K-ES. In each sample, the elemental analysis of two local spots was investigated, and average values were considered as presented in the tables. The major compositions of both raw and K-ES are calcium, carbon and oxygen. Moreover, K and Mn were observed in the modified sample. As shown in Table 13, major components of K-ES are C and O, indicating that the oxygen functional groups are present on the surface.

The SEM/EDS was also conducted for K-ES after adsorption. The SEM results depicted in Fig. 4 and EDS presented in Table 13 confirm the presence of lead ions on the surface of K-ES.

The patterns of XRD of raw eggshells and K-ES are shown in Figs. 5a and b, respectively. In XRD spectra of the raw eggshells, the presence of main diffraction peaks at 2θ values of 23.362° , 29.66° , 31.789° , 36.274° , 39.747° , 43.466° , 47.420° , 48.802° , 57.7° , 58.452° , 60.995° , 61.748° , 63.387° , 66.002° , 69.509° and 73.187° might be ascribed to calcium carbonate in the phase of calcite. The obtained pattern was matched with XRD stored in the database of the International Center for Diffraction Data, where the obtained peaks were noticeably matched the calcite crystalline phase. A similar pattern was observed by Ahmad et al. [34] who used magnesiothermally modified eggshells for phosphorus removal. Similar peaks were observed for K-ES shown in Fig. 5b, which indicates that insignificant change on the main crystal structure due to the modification process and the modification occurred on the surface. However, there is a sharp decrease in the intensities of K-ES compared with raw eggshells, which might be ascribed to the decrease of crystal size due to the modification. Similar findings were reported by Markovski et al. [35]

who investigated calcite modified by α - MnO_2 for arsenate removal.

The nitrogen adsorption/desorption isotherms at -196°C revealed that eggshells modified with KMnO_4 have a porous structure. Table 14 shows the textural characteristics of unmodified eggshells, K-ES and Pb-loaded K-ES, including BET surface area, external surface area (S_{ext}), micropore surface area (S_{mic}), pore volume (V_p) and pore diameter (D_p). Unmodified eggshell has a poor porous structure, where the BET surface area was found to be $2.5769 \text{ m}^2/\text{g}$ and pore volume $0.004674 \text{ cm}^3/\text{g}$. The obtained results are in good agreement with the surface area of raw eggshells reported in the literature, which were found to be between 0.07 and $1.03 \text{ m}^2/\text{g}$, while pore volume varied from 0.00022 to $0.0065 \text{ cm}^3/\text{g}$ [27,31]. Porous characteristics of eggshells were noticeably enhanced after modification, where the BET surface area and pore volume increased from 2.58 to $90.3980 \text{ m}^2/\text{g}$ and from 0.0047 to $0.35 \text{ cm}^3/\text{g}$, respectively. The enhancement in the surface area might be ascribed to the high reduction in crystal size as confirmed in the XRD spectra and due to the formation of amorphous manganese oxides. The nitrogen adsorption/desorption isotherm plot of K-ES is depicted in Fig. 6. The plot indicates that the K-ES isotherm is type IV, which indicates that the structure is mesoporous. Insignificant change was observed on the porous structure of K-ES after adsorption of lead, which might be ascribed to the adsorption of lead ions as a monolayer on the K-ES surface without affecting the porous structure.

The eggshells and K-ES FTIR spectra were recorded within 500 – $4,000 \text{ cm}^{-1}$, as shown in Fig. 7. The spectra of eggshell show a prominent and broadband at around $3,440 \text{ cm}^{-1}$ that might be ascribed to OH-stretching group, while the band at around $1,665 \text{ cm}^{-1}$ might be ascribed to C–N stretching group. The presence of N could be attributed to the membrane eggshell protein fibers, which contain amides and amines as confirmed by the stretching group of C–N at around $1,037 \text{ cm}^{-1}$. The results are in agreement with EDS analysis, where N was observed on the surface of eggshell samples. The sharp peak at around $1,418 \text{ cm}^{-1}$ might be assigned to the characteristic peak of C–O stretching bond in carbonate. Moreover, sharp peaks observed at 709 and 874 cm^{-1} might be ascribed to deformation form of the carbonate, in-plane and out-plane, respectively [36]. These results are in consistency with those reported by Elkady et al. [17], who investigated eggshell bio-composite beads for reactive red dye removal. Similar functional groups were also observed in the spectra of K-ES as depicted in Fig. 7b. Moreover, a new band was observed in the spectra of K-ES

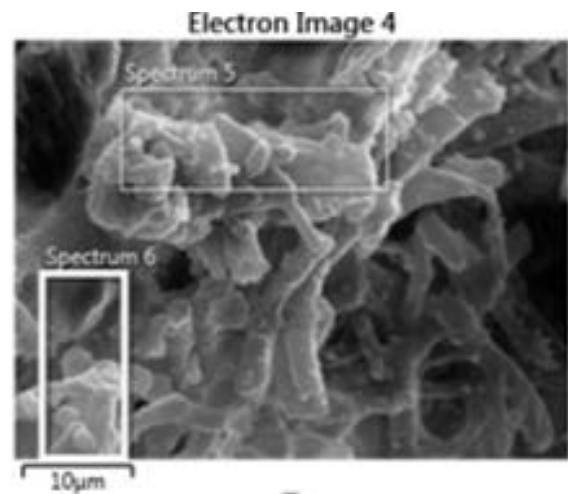
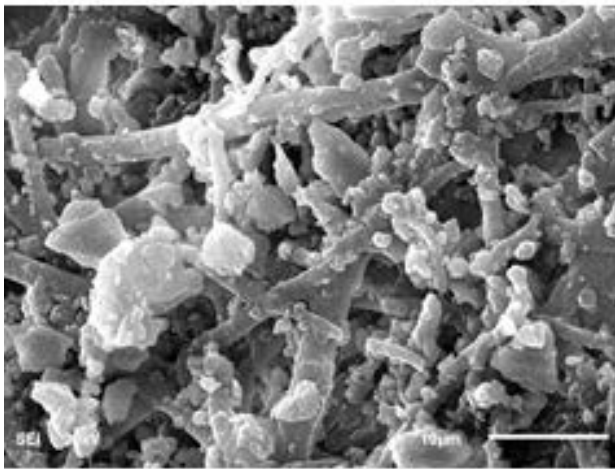
Table 9
BET surface area of samples that showed the highest lead removal efficiencies

Modifying agent	Factor	BET (m^2/g)
NaOH	Concentration (M)	0.505
	Time (h)	48
HNO_3	Concentration (M)	0.01
	Time (h)	27
KMnO_4	Concentration (M)	0.25
	Time (h)	48

Table 10
Comparison of adsorption capabilities of lead using different modified adsorbents

Adsorbent	Removal efficiency (%)	Adsorption capacity (mg/g)	Reference
Hydroxyapatite extracted from eggshell	99	500	Meski et al. [26]
Hydroxyapatite extracted from eggshell	–	101	Liao Dexiang et al. [27]
Synthesized calcium hydroxyapatite	–	85	Yasukawa et al. [30]
Hydroxyapatite/polyurethane composite foams	99.9	150	Jang et al. [31]
Eggshell modified with KMnO_4	97	690	This study

(a)



(b)

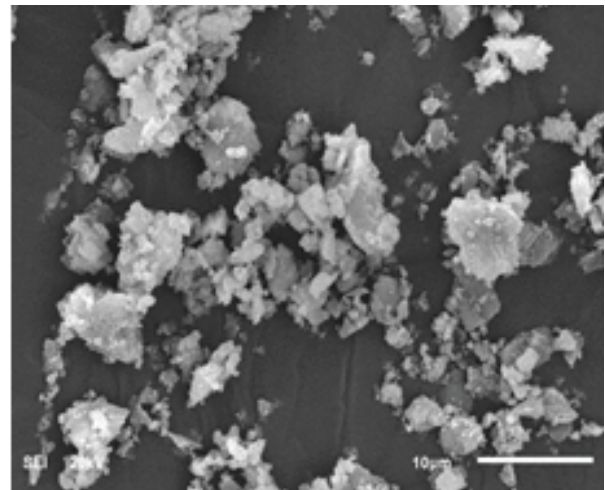
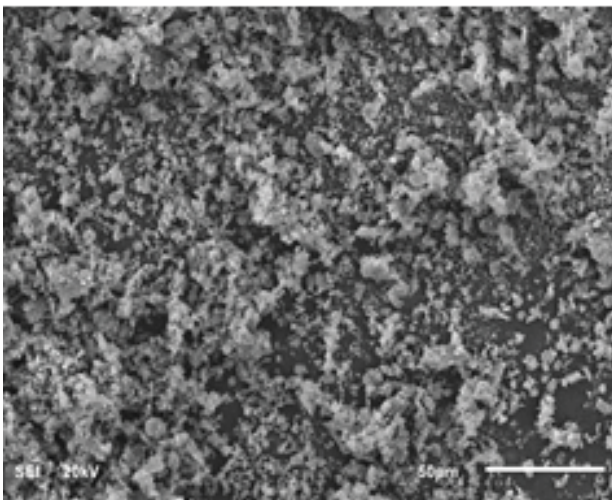


Fig. 3. SEM micrographs of (a) unmodified eggshells and (b) K-ES.

Table 11
Localized spot elemental analysis of raw eggshells

Local spot	Ca (%)	C (%)	O (%)	N	S	Cu
Spot1	7.24	35.45	35.94	18.14	2.30	0.92
Spot2	6.52	36.86	36.42	16.79	2.23	1.18
Average	6.88	36.155	36.18	17.465	2.265	1.05

compared with raw eggshell at around 539 cm^{-1} . This might be ascribed to the characteristics band of Mn–O vibrations, indicating that manganese oxides are present onto K-ES. Similar peaks were also documented by Markovski et al. [35]. The FTIR spectra of Pb-loaded K-ES are depicted in Fig. 7c. The shift of C–O peak from $1,408$ to $1,394\text{ cm}^{-1}$ and from 873 to 875 cm^{-1} and the presence of a peak at 837.5 cm^{-1} in the Pb-loaded K-ES spectra might be ascribed to the interaction between Pb(II) ions and carbonate group on K-ES surface. In

addition, Mn–O peak was shifted from 539 cm^{-1} in the spectra of K-ES to 543 cm^{-1} in the spectra of Pb-loaded K-ES, which might be attributed to the interaction between Pb(II) and manganese oxide on the surface of K-ES.

3.4. Effects of adsorption operational factors on lead removal

Fig. 8a shows the effect of pH on lead removal by K-ES, where the results clearly indicate that there is an increase in

Table 12
Localized spot elemental analysis of K-ES

Local spot	Ca (%)	C (%)	O (%)	Mn (%)	K (%)	Cu
Spot1	20.07	30.55	41.62	3.13	0.08	4.55
Spot2	24.54	23.03	46.43	0.33	0.13	5
Average	22.305	26.79	44.025	1.73	0.105	4.775

Table 13
Localized spot elemental analysis of K-ES after lead adsorption

Local spot	Ca (%)	C (%)	O (%)	Mn (%)	Pb (%)	Cu
Spot1	10.89	13.46	29.93	2.50	34.52	8.69
Spot2	10.41	13.75	30.63	2.72	35.16	7.33
Average	10.65	13.605	30.28	2.61	34.84	8.01

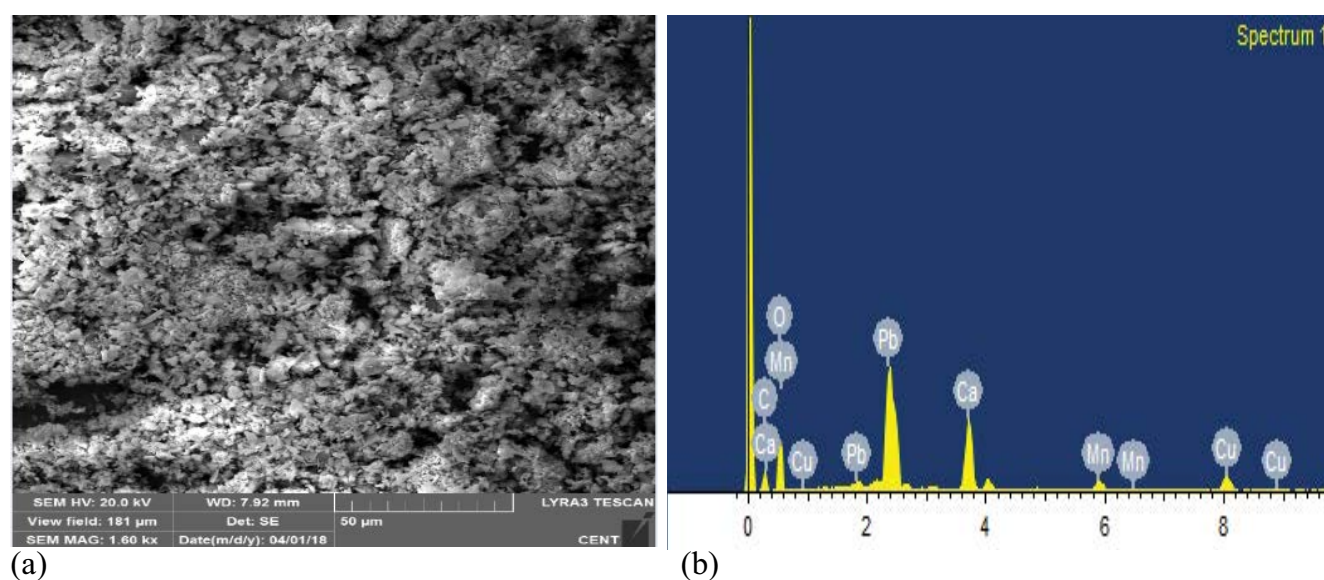


Fig. 4. (a) SEM and (b) EDS for K-ES after lead removal.

the removal efficiency with the increase in pH values. When pH was increased from 2 to 9, the removal efficiency was found to increase from 5% to 98%. At lower pH values, where an excess of hydrogen ions is present, there is competition for active surface sites of K-ES between lead ions and hydrogen ions; therefore, low removal efficiencies were obtained. However, as pH was increased, H^+ ions decreased, so the competition decreased and, therefore, higher removal efficiencies were observed. Moreover, as pH was increased, the surface charge of adsorbent becomes more negative, which reduce the repulsion between lead ions and the adsorbent surface that resulted in enhancing the removal efficiency [37]. Similar findings were reported in the literature [38].

The influence of initial lead concentration on the removal efficiency is illustrated in Fig. 8b. The results indicated that an insignificant change of lead removal was observed at 10 mg dosage, when the initial concentration was increased from 25 to 200 mg/L. This might be ascribed to the availability of enough active sites on the adsorbent surface that

uptake Pb(II) ions up to a concentration of 200 mg/L. At higher concentrations, those sites were saturated; hence, the removal efficiency decreased as noticed at a concentration of 400 mg/L. This is in agreement with the trend observed at lower dosages, where active sites are limited. Removal efficiencies were found to decrease with increasing initial concentrations from 25 to 400 mg/L at dosages of 2.5 and 5 mg. High removal efficiency was observed at concentrations of 25 mg/L due to the availability of active sites on the adsorbent surface. Once those sites are saturated at higher concentrations, lower removal efficiencies were obtained.

3.5. Kinetic study

Lead removal kinetics is depicted in Fig. 9, where the obtained results showed a dramatical increase in removal efficiency from 5 to 30 min; then, a slight increase was obtained at 45 min. After 45 min, the equilibrium of lead removal was reached. The fast removal during the first 30 min is ascribed

to the presence of active sites on the adsorbent site. Once those sites are occupied, removal becomes slow till equilibrium is reached where adsorbed ions equal to desorbed ones.

The obtained experimental results were fitted to pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model was fitted to the obtained results using Eq. (8).

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{K_1}{2.303} \times t \quad (8)$$

where q_t (mg/g) adsorption capacity at time t (min), q_e (mg/g) is equilibrium adsorption capacity, and K_1 (1/min) is the pseudo-first-order constant rate. Values of $\log(q_e - q_t)$ were plotted against t (min), q_e and K_1 were computed from the slope and y-axis intercept of the graph. The pseudo-second-order kinetic model was also fitted to the experimental data using Eq. (9).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (9)$$

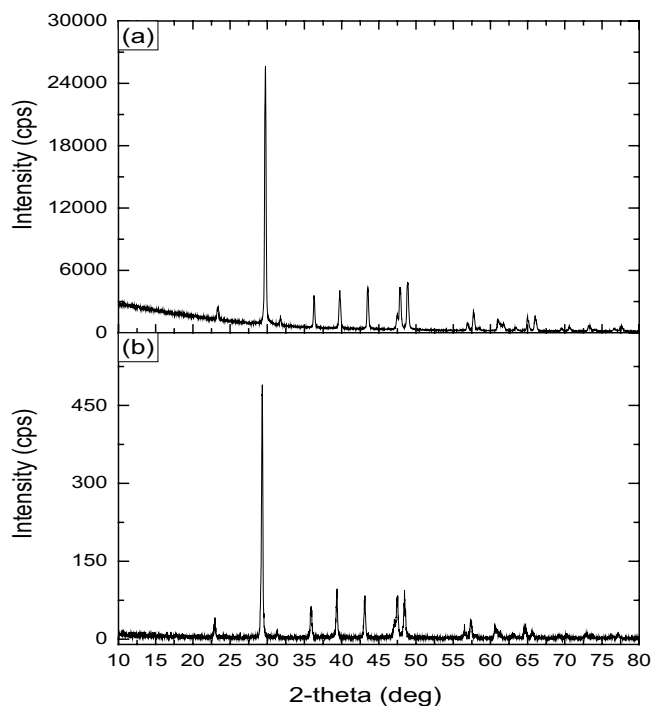


Fig. 5. XRD patterns of (a) eggshells and (b) K-ES.

Table 14
Textural parameters of unmodified eggshells, K-ES and Pb-loaded K-ES

Sample	BET (m ² /g)	S _{ext} (m ² /g)	S _{mic} (m ² /g)	V _p (cm ³ /g)	D _p (Å)
Unmodified eggshells	2.5769	0.8788	1.6981	0.004674	54.0085
K-ES	90.398	82.8792	7.5189	0.352784	117.3326
Pb-loaded K-ES	89.98	82.8792	7.5189	0.352784	117.3326

where K_2 (g/mg min) is the pseudo-second-order constant rate, time was plotted vs. t/q . Parameters of the model, q_e and K_2 , were computed from the y-axis intercept and the slope of the graph. The pseudo-first and second order plots of the experimental data are presented in Figs. 10 and 11, respectively. The parameters of each model were summarized in Table 15. The obtained results of kinetic models revealed that the experimental data were best fitted to the pseudo-second-order model due to high R^2 value and the good agreement between calculated and experimental values of q_e , as shown in Table 15.

3.6. Thermodynamic studies

The effect of temperature on lead removal by K-ES is illustrated in Fig. 12. The obtained results indicated that the removal efficiency was found to increase by increasing the temperature. Similar findings were reported by Naushad et al. [38], who investigated lead removal using synthesized composite cation exchanger.

The adsorption nature of lead on K-ES was investigated by determining the thermodynamic parameters including enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) which were calculated using Eqs. (10)–(12).

$$\Delta G = -RT \ln K_c \quad (10)$$

R is the universal constant (8.314 J/mol.K), K is the thermodynamic temperature in Kelvin (K), while K_c is constant at the equilibrium, which was calculated using Eq. (11).

$$K_c = \frac{C_{Ae}}{C_e} \quad (11)$$

where C_{Ae} (mg/L) is the concentration of lead on the K-ES at the equilibrium and C_e (mg/L) is the concentration of lead in the solution at the equilibrium. Enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) were calculated using K_c values as expressed in Eq. (12).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$\ln K_c$ was plotted vs. $1/T$ as depicted in Fig. 13 and the slope and the y-axis intercept were used to calculate (ΔH) and (ΔS) as shown in Table 16. The adsorption degree of spontaneity and favorability is indicated by free energy (ΔG). The results revealed that as the temperature was increased, negative values of (ΔG) were found to

increase, which indicate that the adsorption is energetic and more favorable. The positive value of (ΔH) indicates that adsorption nature is endothermic. Also, the positive value of (ΔS) implies an increase of randomness during the adsorption of Pb(II). The activation energy E_a , which indicates the type of adsorption, was computed using Eq. (13). The activation energy value between 5 and 40 kJ/mole indicates physical adsorption, while E_a values between 40 and 800 kJ/mole imply chemisorption [28]. The activation energies obtained in this study were found to be higher than 40 kJ/mole, as shown in Table 16. Therefore, adsorption of lead using K-ES is chemisorption process.

$$E_a = \Delta H^\circ + RT \tag{13}$$

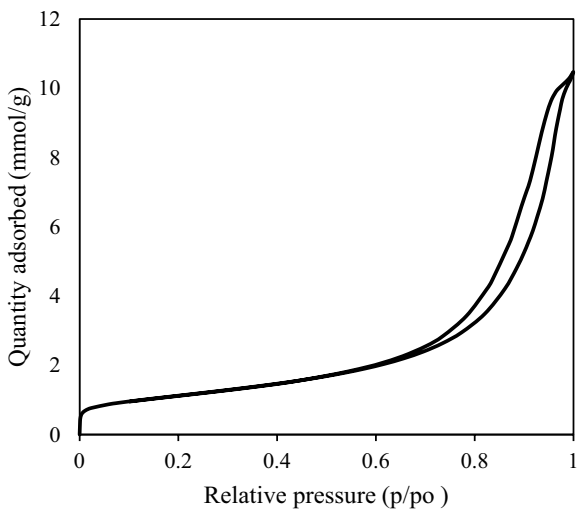


Fig. 6. BET N₂ adsorption/desorption isotherms plot of K-ES adsorbent.

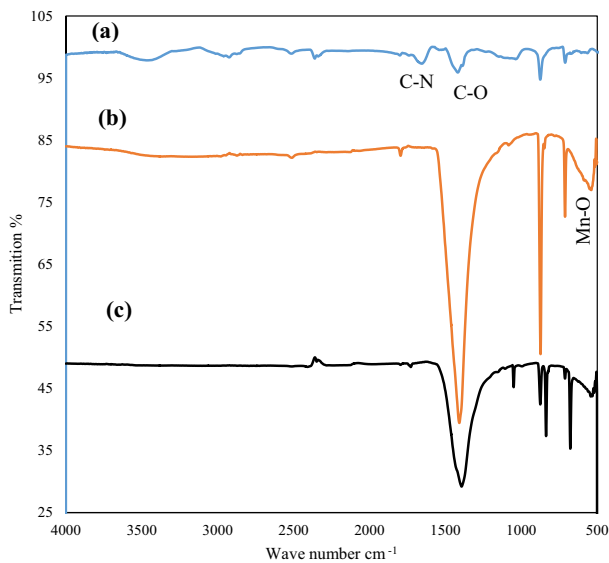


Fig. 7. FTIR spectra of (a) eggshell, (b) K-ES and (c) K-ES after adsorption.

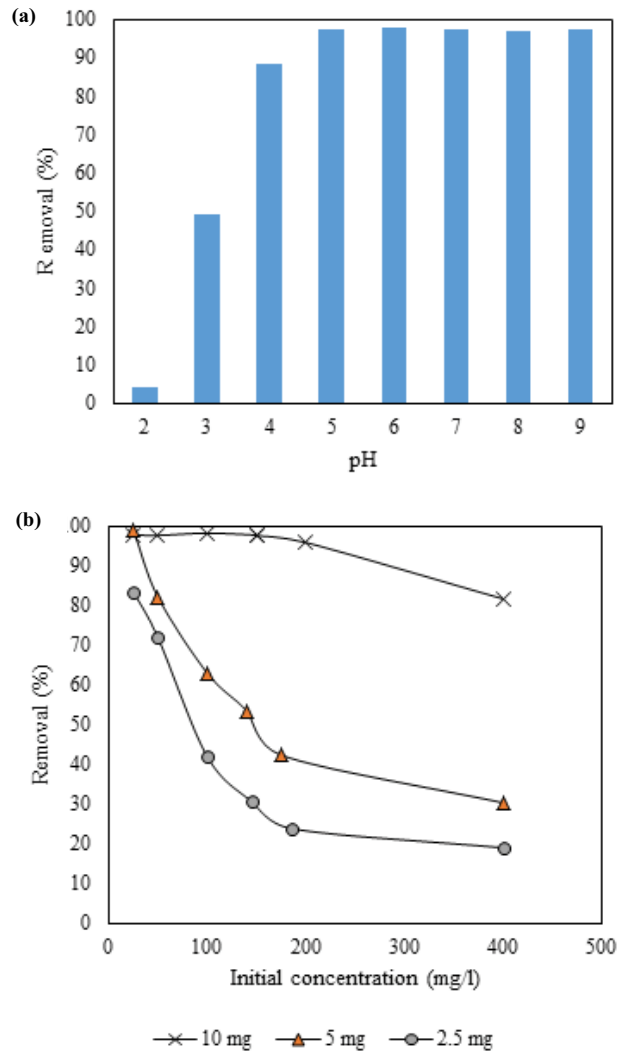


Fig. 8. Effect of operational factors on Pb(II) removal by K-ES (a) pH and (b) initial concentration.

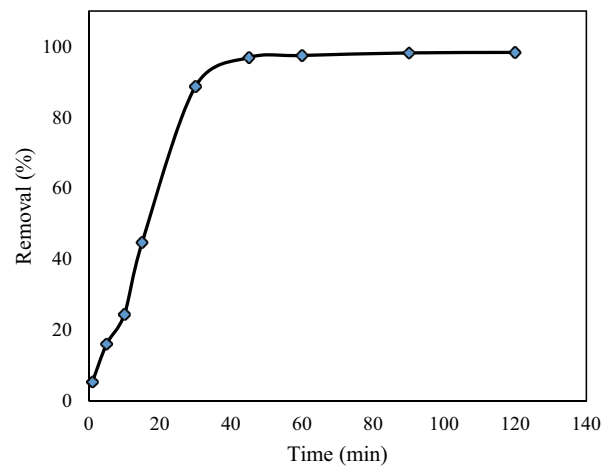


Fig. 9. Experimental kinetics of lead removal by K-ES.

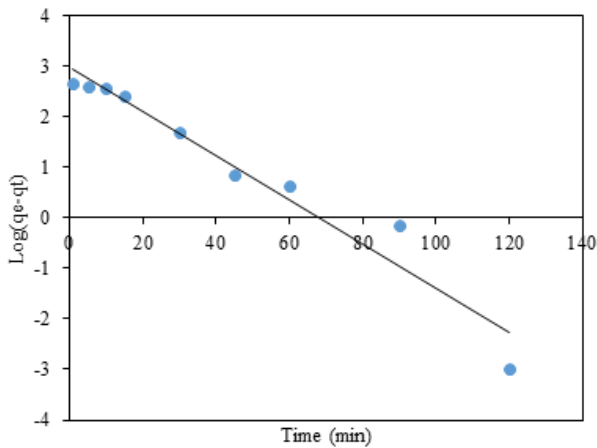


Fig. 10. Pseudo-first-order plot for Pb(II) removal on K-ES.

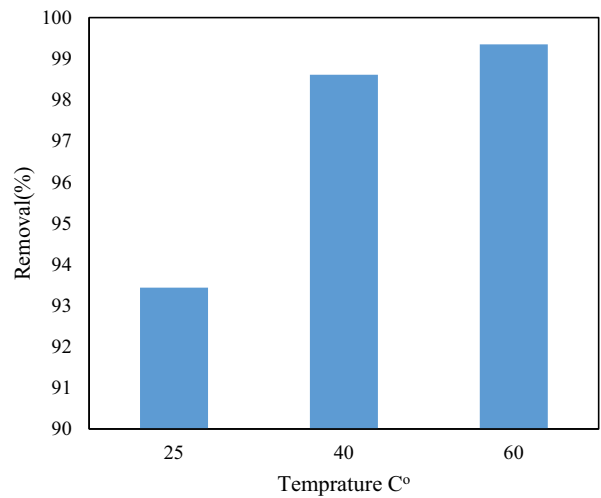


Fig. 12. Effect of temperatures on lead removal by K-ES.

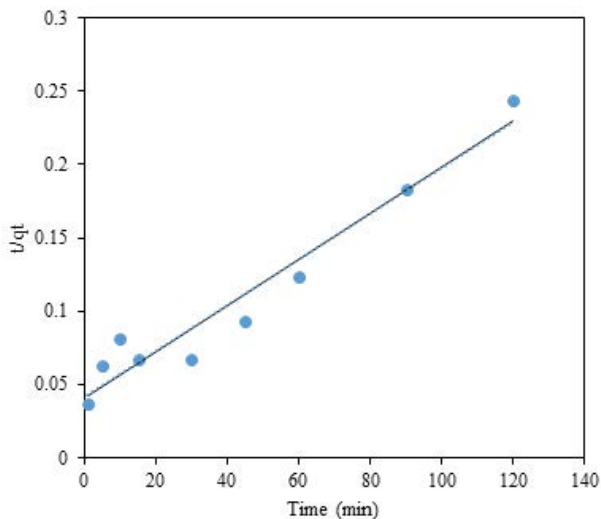


Fig. 11. Pseudo-second-order plot for Pb(II) removal on K-ES.

Table 15
Pseudo-first and second order parameters for Pb(II) removal on K-ES

Model parameter	Pseudo-first-order	Pseudo-second-order
R^2	0.95	0.99
K	0.0789	0.0002
Theoretical q_e (mg/g)	945	495.7
Experimental q_e (mg/g)	491.68	491.68

3.7. Equilibrium isotherms

The experimental data at the equilibrium of Pb(II) removal by K-ES at different initial concentrations were fitted to various isotherm models, including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich. The linear

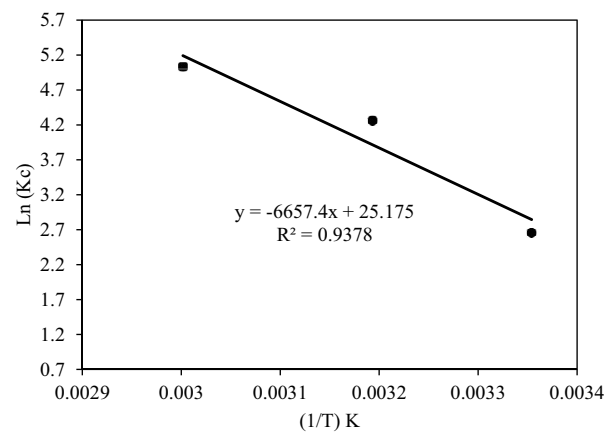


Fig. 13. $\ln K_c$ vs. $1/T$ graph employed in the evaluation of thermodynamic parameters.

form of Langmuir model (Eq. (14)) was used to fit the experimental data, where q_e is the equilibrium concentration in the solid phase, C_e is the equilibrium concentration in the liquid phase at different adsorbent dosages and q_m (mg/g) is thermal monolayer concentration in the solid phase and b is model constant. The slope and the intercept of the graph of C_e/q_e vs. C_e were used to calculate the model parameters as depicted in Fig. 14a and presented in Table 17. Linear Freundlich isotherm form shown in Eq. (15) was fitted to the experimental data, where K_f and n are the Freundlich constant and the heterogeneity factor, respectively. The model parameters were determined from the slope and the intercept of the plot of $\ln q_e$ against $\ln C_e$, as shown in Fig. 14b. The obtained results were also fitted to Temkin isotherm using Eq. (16), where A_T (L/mg) is binding energy constant at equilibrium, T is absolute temperature (K), R is the universal gas constant and b is Temkin isotherm constant. The slope and the intercept of q_e vs. $\ln C_e$ were employed to compute the model parameters as presented in Fig. 14c. The experimental data were also fitted to Dubinin–Radushkevich

Table 16
Thermodynamic parameters of Pb(II) adsorption on K-ES

Temperature °C	ΔG (kJ/mole)	E_a (kJ/mole)	ΔH (kJ/mole)	ΔS (J/mole)
25°C	-6.583	57.828	55.350	209.302
40°C	-11.102	57.953	55.350	209.302
60°C	-13.939	58.119	55.350	209.302

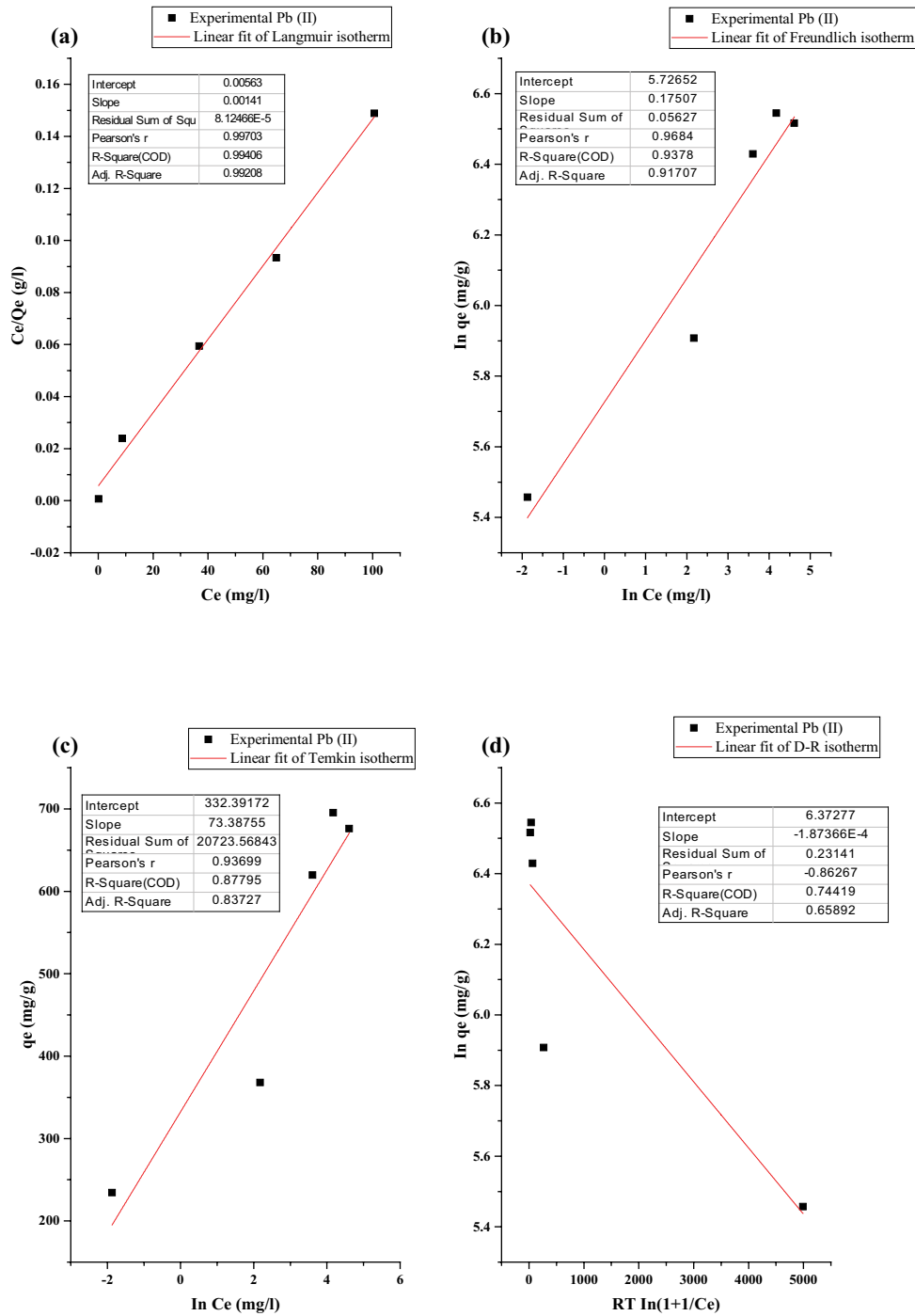


Fig. 14. Equilibrium isotherms of lead removal using K-ES; (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubinin–Radushkevich.

Table 17
Parameters of equilibrium isotherm models of Pb(II) removal by K-ES

Model parameter	Value
Langmuir	
R^2	0.99
q_m (mg/g)	709.133
b (L/g)	0.25
Freundlich	
R^2	0.94
K_f	306.9
n	5.712
Temkin	
R^2	0.88
B_T (J/mol)	73.388
A_T (L/g)	92.691
Dubinin–Radushkevich	
R^2	0.744
B_D (mole ² /J ²)	9.3683E-05
q_D (mg/g)	585.680
E (J/mole)	73.06

(D-R) isotherm model using Eq. (17), where q_D is theoretical adsorption capacity at saturation, B_D (mole²/J²) is D-R isotherm constant, T is absolute temperature (K) and R is the universal gas constant. The D-R isotherm mean energy E (J/mole), which indicates adsorption type, was computed using Eq. (18), where $\ln q_e$ was plotted against $RT \ln(1 + 1/C_e)$ and the slope and the intercept of the graph were used to calculate the model parameters, as depicted in Fig. 14d. The parameters of the investigated isotherms were summarized in Table 17.

$$\left(\frac{C_e}{q_e}\right) = \frac{C_e}{q_m} + \frac{1}{b \times q_m} \quad (14)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (15)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (16)$$

$$\ln q_e = \ln q_D - 2B_D RT \ln \left(1 + \frac{1}{C_e}\right) \quad (17)$$

$$E = \frac{1}{\sqrt[2]{2B_D}} \quad (18)$$

The obtained equilibrium isotherm results revealed that among various fitted isotherm models, Langmuir isotherm was best fitted to the experimental data. It showed the highest R^2 value (0.99), the best agreement between R^2 and R^2_{adj} , and the best agreement between the experimental and

modeled maximum adsorption capacity, as shown in Table 17. Accordingly, lead removal using K-ES can be well described by Langmuir isotherm, where lead ions are adsorbed as a monolayer on the homogeneous surface of K-ES with a maximum adsorption capacity of 700 mg/g.

3.8. Removal mechanism

Several mechanisms might be involved in lead removal by K-ES, including ion exchange, metal complexation, electrostatic attraction, precipitation and biosorption. Although the initial pH was adjusted at a value of 5, the final pH after adsorption was found to increase, where Pb(II) might be precipitated. However, the equilibrium of lead removal using K-ES was attained in a few minutes, as shown in the kinetic study, while metal coprecipitations usually occur at long contact times as reported by Meski et al. [26] and Sposito [39]. Moreover, the adsorption of lead by K-ES was described with Langmuir isotherm, which assumes monolayer adsorption until saturation is obtained. This is in contrary to the precipitation mechanism that is generally indicated by the absence of saturation. Similar findings were reported by Meski et al. [26], who investigated lead removal using hydroxyapatite derived from the eggshell.

Moreover, lead removal might also be ascribed to the ion exchange between Ca ions of the K-ES and Pb ions, which were confirmed by FTIR after adsorption [40]. Metal complexation and electrostatic interactions between negatively charged MnO oxides and positively charged lead ions could also be dominant. Besides, adsorption of Pb with the porous structures of K-ES might be involved where the BET surface area of K-ES was found to be 90 m²/g, due to the presence of amorphous manganese oxides.

The thermodynamic study suggested that chemisorption is the dominant process for lead removal using K-ES. The increase in removal due to increase in temperature implies that the chemisorption plays a significant role in enhancing the removal at higher temperatures. Moreover, the enthalpy (ΔH) and the activation energies (E_a) obtained in this study were found to be more than 40 kJ/mole, which confirms the chemisorption process [41].

Moreover, the chemisorption process was confirmed by equilibrium isotherm study, where Langmuir isotherm was best fitted the experimental data, which suggests that lead ions are adsorbed as a monolayer on K-ES surface. These results are in agreement with those of the BET surface area of Pb-loaded K-ES, where insignificant change on the porous structure was observed.

4. Conclusions

A novel low-cost adsorbent for lead removal was synthesized from eggshells waste using single-step chemical modification. The modification process was investigated using three modifying agents, namely, NaOH, HNO₃ and KMnO₄, under different conditions and the effect of modifying agent concentration and contact time on lead removal efficiency was investigated. RSM and CCD were employed for statistical analysis. The obtained results indicated that the modifying agent has a crucial role in the modification process, where the highest removal

efficiencies were obtained for eggshell samples modified with potassium permanganate. Statistical analysis revealed that for Na-ES and HN-ES, insignificant effects of the process parameters, including concentration and contact time were observed. Moreover, poorly developed models were obtained, and therefore, cannot be used to predict the response. For K-ES, the statistical analysis showed that the effect of process parameters, including concentration, contact time and their interactions are statistically significant. In addition, the obtained model was found to be significant, reliable and adequate. Therefore, it was adequately used to predict the responses. The produced adsorbent at the best conditions was characterized by XRD, FTIR, SEM/EDS and BET. The characterization results revealed that the considerable enhancement in removal efficiencies was ascribed to the formation of manganese oxides on eggshells surface. Moreover, the surface area of the modified eggshells was noticeably enhanced from 2.57 to 90 m²/g, when compared with unmodified eggshells. The effects of different operational factors such as pH, initial concentration, temperature and adsorbent dosage on the removal efficiency of K-ES for lead were investigated. Lead removal efficiencies were found to increase with increasing pH, adsorbent dosage and temperature, while decrease with increasing the initial concentration. The kinetic study showed that the experimental data were well described with the pseudo-second-order model. The obtained experimental data at the equilibrium were fitted to various adsorption isotherm models including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich, where Langmuir isotherm was found to be best fitted with a maximum adsorption capacity of 700 mg/g and removal efficiency of 98%. The thermodynamic study showed that the Gibbs free energy ΔG was found to vary between -6.583 and -13.939 kJ/mole, which indicates that the adsorption of lead using K-ES is favorable and energetic. Moreover, the enthalpy ΔH was found to be $+55$ kJ/mole and the activation energies E_a were found to vary between 57 and 58 kJ/mole, which implies that the adsorption is endothermic and chemisorption process is the dominant mechanism. Therefore, eggshells waste could be used efficiently as a promising low-cost adsorbent for lead removal using single-step modification process.

Acknowledgments

The authors would like to express their gratitude to King Fahd University of Petroleum and Minerals (Dhahran, Saudi Arabia) for the technical and financial support provided throughout the investigation.

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