

Modeling and Optimizing Lead Ions Adsorption by Walnut Shell modified by Sepiolite from Aqueous Solution by Response Surface Methodology

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ABSTRACT: Activated carbon from the walnut shell modified by sepiolite (AC/SEP) composite was synthesized and applied for the adsorption of toxic lead (Pb(II)) ions from industrial effluents. AC/SEP composite was characterized by Fourier Transform InfraRed (FT-IR) spectrometer, Field Emission Scanning Electron Microscopy (FESEM), Brunauer–Emmett–Teller (BET), and X-Ray Diffraction (XRD) analyses. Effects of pH, amount of adsorbent, Lead initial concentration, and contact time on removal percentage were studied by Central Composite Design (CCD). The optimal condition for maximum Lead removal by AC/SEP adsorbent (99.07%) was as follows: pH= 5.00, adsorbent amount: 0.05 g, initial concentration 20.00 mg/L, and contact time: 25.00 min in 10 mL of pollutant volume. Also, the adsorption kinetics, thermodynamics, and isotherms were determined. Adsorption isotherms (q_{max} : 269.67 mg/g) and kinetics showed that the sorption process was better modeled by the Langmuir and pseudo-second-order equation.

KEYWORDS: Lead, Sepiolite, Walnut shell, Adsorption, Activated carbon, Central Composite Design.

INTRODUCTION

Water contamination with pollutants like heavy metal ions and dyes is one of the main environmental problems of the present age that needs effective and immediate solutions to eliminate the pollutants [1, 2]. Harmful effects of these pollutants on living organisms occur when they selectively interact with and bind to biomolecules such as homocysteine and cysteine glutathione, disrupting the activity of enzymes, protein synthesis, and the metabolism

of living cells [3]. Heavy metals including copper, lead, cadmium, nickel, aluminum, mercury, and arsenic are dangerous toxins that are found in drinking water, building materials, breathing air, kitchen utensils, and even clothing. One of the main disadvantage of heavy metals is not metabolizing in the body. Some metals in small amounts are needed for the normally body function, but too much of them will cause poisoning [4].

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Lead can enter to the food chain in a variety of ways (water, air, and soil) and enter the body of living organisms. More than 200 million people in the world use drinking water with excessive levels of lead [3, 5]. The Environmental Protection Agency has a drinking water standard of 0.05 mg/L for lead ions. Depending on the concentration and duration of continuous uptake, lead ions can pose health risks. Lead is absorbed faster in soft tissues than in bones and other parts of the body [3]. It can have harmful effects on various organs of the body, such as the kidneys, liver, gastrointestinal tract, nerves, genitals, immunity, cardiovascular system, etc. Gastrointestinal lesions such as constipation, vomiting, weight loss, abdominal discomfort, paleness, fatigue, drowsiness, behavioral changes, and irritability are other symptoms. Due to special neurological and metabolic conditions, the effect of lead is greater in children and causes their mental retardation [6, 7].

Various methods for the remediation of heavy metal ions from water and wastewater like chemical precipitation, physical adsorption, membrane separation, biological decomposition, and ion-exchange adsorptions have been studied [8-10]. It is important that the conventional methods have some disadvantages and advantages. For example, chemical precipitation is cheap, but it creates a huge amount of sludge and causes other pollution problems [11]. Scientists illustrated that biological decomposition has high proficiency, but, it is not cheap. On the other side, membrane separation has high efficiency, but it is expensive [12]. On the contrary, adsorption is fast, efficient, cheap, easy-to-use, and more environmentally friendly. However, it is necessary to have an ideal adsorbent for the removal of pollutants from contaminated water and wastewater [13]. Activated carbon (AC), because of cheap biosources like pistachio shell [14], peanut shell [15], sunflower piths [16], rice husk ash [17], coconut shell [18], waste rice straw [19], coir pith [20], and hazelnut husks [21], besides its huge surface area [16, 22] is one of the ideal adsorbents used in the water and wastewater purification. But, because of the low mechanical strength of AC and its hydrophobic properties, the synthesis of composite with mineral materials to compensate for these deficiencies has been much studied [14, 18, 23].

Sepiolite is a silicate clay mineral and due to its structural properties, has unique properties such as high surface activity [24]. Like other silicate minerals, sepiolite is composed of two-dimensional continuous plates, but

lacks continuous octagonal plates [25]. Replacing the problem of silicon with aluminum ions in the quadrilateral layers of this mineral, by creating a negative charge, produce suitable places for the adsorption of cations and has a high adsorption capacity for heavy metals. Also, due to the discontinuity of the outer silicate plates, a significant number of silanol (Si-OH) functional groups are seen on the surface of this mineral. Sepiolite has a high ability to adsorb metal ions, inorganic and organic molecules [25]. The mineral sepiolite is structurally needle-shaped and the microscopic pores which are located parallel to the fibers, lead to the formation of a porous solid with large external surfaces [25-27]. This special structure has caused the penetration of organic and mineral materials to the mineral surface and has made sepiolite one of the suitable adsorbents [26]. In recent studies, natural sepiolite has been used as an adsorbent for the removal of heavy metal ions and various organic pollutants [28]. In this study, to be immobilized sepiolite onto activated carbon derived from walnut shell structure and usage of this composite for remediation of lead were studied.

To increase the sensitivity, reduce the disturbances (improve the selectivity), increase the accuracy, and also increase the signal-to-noise ratio in the analysis method, it is necessary to determine the best value for the factors involved in the measurement systems [29, 30]. In fact, optimization is determination of the appropriate values of the effective variables in the experiment. Response Surface Methodology (RSM) was applied for modeling the lead adsorption process by investigating the independent factors including pH, adsorbent dosage, initial concentration, and contact time on the lead removal percentage using Central Composite Design (CCD) [3, 31].

No studies on the adsorption of lead by the composite of activated carbon from walnut shell modified by sepiolite (AC/SEP) can be found. In this study, first, activated carbon was prepared from the walnut shell, then, AC/SEP composite was prepared by simple mixing of activated carbon and sepiolite in a simple way and it was applied for removal of lead ions from industrial effluents.

EXPERIMENTAL SECTION

Materials and Instruments

Walnut shells were gathered from the walnut fields of Chaharmahal Bakhtiari province (Iran) and sepiolite was sent from Nain (Iran). HCl (37%), NaOH, HNO₃ (65%),

and $\text{Pb}(\text{NO}_3)_2$ were prepared from Merck company (Germany). FT-IR spectrometer (Jasco 680-plus, Tokyo, Japan) was applied for FT-IR analysis in the range of 400–4000 cm^{-1} . The surface morphology was characterized by field emission scanning electron microscopy (FESEM) (MiRA3-TESCAN, Czech Republic). The samples were coated with gold film and the acceleration voltage of the apparatus was 15.0 kV. Nitrogen adsorption-desorption isotherms were obtained by applying a BEL: PHS 1020 sorptometer (China) by using N_2 gas at 77 K after degassing the sample in a vacuum for 12 h at room temperature. Powder XRD analyses were analyzed using a diffractometer (Panalytical X'PertPro, Almelo, The Netherlands), with a Cu anode. All analyses were run at 40 kV and 30 mA, and samples were scanned from 10° to 80° at 3°/min. Also, AASpect 203 Flame atomic Absorption Spectrometer (FAAS) was used for lead sample analysis.

Adsorbent preparation

Preparation of walnut shells-based activated carbon

Step 1) The prepared walnut shells were boiled in water for one hour to be cleaned of any impurities. It was then rinsed with deionized water to completely remove other organic impurities and other adhesives. The washed walnut shells were then dried for 24 hours at 105 °C to reach a constant weight. They were then crushed and ground and passed through a 65 micron sieve to equalize the particle size. The sliced walnut shells were kept in a desiccator to prepare for the next step.

Step 2) First, 15 mL of sodium hydroxide (1.25 M) was mixed with 10 mL of epichlorohydrin on a stirrer at room temperature. Then, 1 g of walnut shells prepared from the previous stage was floated in this solution at 40 °C for 30 min, and the temperature was regularly monitored by a thermometer. The mixture was then washed several times with water at neutral pH and the resulting material was dried at 65 °C to reach a constant weight. In the next step, the washed powder is placed in an oven at 400 °C for 4 h for getting pure activated carbon, the resulting powder is ground with a mortar for smoothing the adsorbent and kept in a clean and closed container for the adsorption process [32].

Preparation of AC/SEP composite

Amount of 0.5 g of walnut shell was poured in 6.32 mL of ethanol and stirred in a mixer. The container was closed completely for preventing the evaporation of ethanol.

Table 1: Preparation of Buffer Solutions.

pH	Solution 1 (mL)	Solution 2 (mL)
2	92.0	8.0
3	83.0	17.0
4	72.0	28.0
5	63.0	37.0
6	54.5	45.5

Solution 1: Dissolve 12.37 g of anhydrous boric acid, H_3BO_3 and 10.51 g of citric acid monohydrate in distilled water, and dilute to 1 L in a volumetric flask.

Solution 2: Dissolve 38.01 g of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in distilled water, and dilute to 1 L in a volumetric flask.

After 30 min, 0.5 g of sepiolite was added slowly to the container and leave it for 24 h until the resulting mixture stirred in the mixer. After that, the container placed in an oven at 40 °C until the ethanol evaporates, and finally the remaining solid powder is thoroughly ground in a mortar and kept for the removal of lead ions.

Batch adsorption experiments

The AC/SEP composite was added to 10 mL of the lead ions solution. Next, solution pH was adjusted by buffer solutions (Table 1) and placed on the stirrer and after the determined contact time, the lead solution was analyzed by atomic absorption spectrometer.

The adsorption capacity (q_e , mg/g) and the removal percentage of lead ions were defined by Eqs. (1) and (2):

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

Where C_0 is initial concentration (mg/L), C_e is equilibrium concentration (mg/L), V is the volume of lead (L) and m is the adsorbent mass (g).

And the lead removal percentage was expressed as the following equation:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 is the initial concentration (mg/L) and C_e is the concentration of the lead solution after adsorption process (mg/L) [29, 30].

Design of experiment

The target of applying the experimental design is including the interaction between parameters and decreasing the number of experiments, instead of excess experiments that waste time without invaluable information.

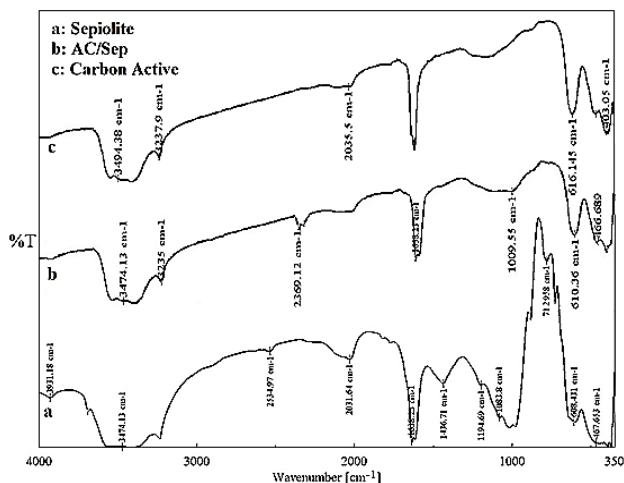


Fig. 1: FT-IR spectra of a) SEP, b) AC/SEP, and c) AC.

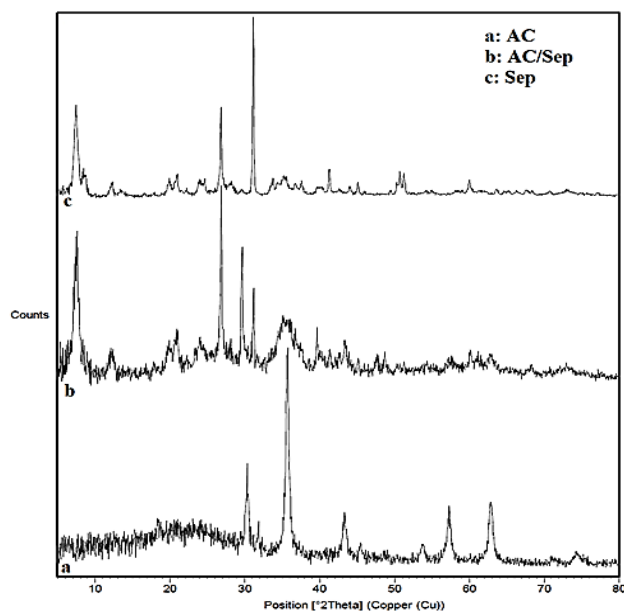


Fig. 2: XRD patterns of a) AC, b) AC/SEP, and c) SEP.

Central Composite Design (CCD) is the common method of experimental design for fitting a second order model and optimization [33]. The independent parameters were coded in two levels: high (+1) and low (-1), plus the axial points that coded as +2 and -2. A five-level-three-factor central composite design was applied to fit a second order response surface model that needed 30 experiments of the lead ions removal percentage. The mathematical relationship between the four independent parameters was determined by the second-order polynomial model as follows [34]:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \sum_{j=1}^n \beta_{ij} x_i x_j + \sum_{i=1}^n \beta_{ii} x_i^2 + \varepsilon \quad (3)$$

Where Y is the predicted response (R%), x_i and x_j are the coded values for the independent variables (initial concentration, pH, adsorbent dosage, and contact time), n is the number of parameters, β_0 is the model constant, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the cross-product coefficient, and ε is the residual term. Design-Expert 13 software was used for the fitting and analysis.

RESULTS AND DISCUSSION

Characterization studies

FT-IR analysis

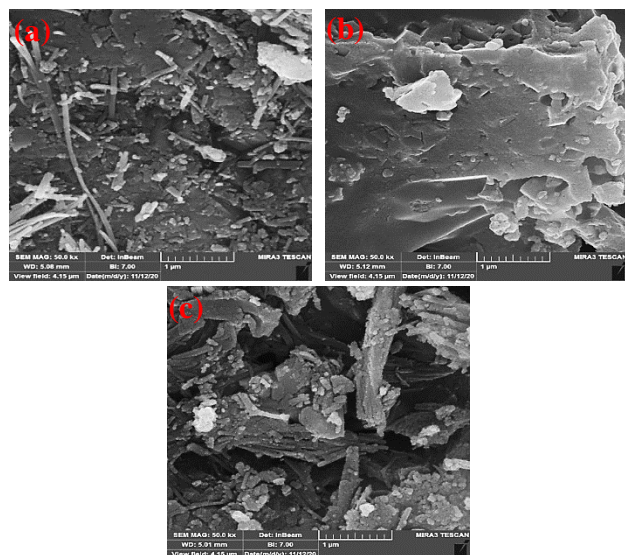
FT-IR spectra of SEP, AC-walnut shell, and AC/SEP composite in the range 400–4000 cm^{-1} are illustrated in Fig. 1. In the spectrum of SEP (Fig. 1a), the peaks in the range of 3240 to 3690 cm^{-1} is related to the hydroxyl groups, hydroxyl-silicon groups, hydroxyl structures of octagonal structure, water, and hydrated zeolite. In general, the absorption bands seen in the range of 400 to 1300 cm^{-1} are related to special bands of silicate minerals, which are mostly related to the bond between oxygen and silicon groups in the tetrahedral layer as well as fluctuations of oxygen-magnesium groups in octahedral plates. Therefore, the absorption bands seen in the range of 1000 to 1320 cm^{-1} of the FT-IR spectrum are related to the stretch bands of the oxygen-silicon bonds and the absorption bands in the range of 425 to 540 cm^{-1} which are the result of the bending of oxygen-silicon-oxygen groups in the structure of sepiolite [27]. Also, in Fig. 1c, a large number of functional groups are observed. The peak in the region of 3494 cm^{-1} is related to stretch -OH, the peak of 3237 cm^{-1} is related to the stretching vibration C-H bonds, the peak in 1597 cm^{-1} is related to the aromatic stretching vibrations C=C bonds, and the peak in the region of 1207 cm^{-1} correspond to the stretching vibration of the C-N bond [35]. As can be seen in Fig. 1b, in the spectrum of AC/SEP composite, all peaks of SEP and AC-walnut shell are clearly found.

XRD Analysis

As can be seen from Fig.2a, AC has diffraction peaks at $2\theta = 30.12, 36.32, 44.51, 53.17, 57.08,$ and 63.01° . Also, in the X-ray pattern of SEP (Fig. 2c), the peaks observed in $2\theta = 7.30, 20.50, 27.90,$ and 34.70° , which indicates the structure of the pure SEP [36, 37]. From Fig. 2b, can be seen that the index diffraction peaks of SEP and AC were observed in the X-ray pattern of AC/SEP composite.

Table 2: Textural properties of SEP, AC-walnut shell, and AC/SEP composite samples.

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
AC	142.5	1.84	0.11
SEP	194.7	0.48	1.95
AC/SEP	210.3	2.25	1.43

**Fig. 3: FESEM images of a) SEP, b) AC, and c) AC/SEP.**

FESEM Analysis

In Fig. 3, the FESEM images of SEP, AC-walnut shell, and AC/SEP composite show that the average particle size of all of the materials is less than 1 μm , and successful formation of AC/SEP composite was demonstrated, clearly.

BET analysis

Nitrogen adsorption-desorption isotherm and the pore size distribution of the SEP, AC-walnut shell, and AC/SEP composite from BJH method are characterized and the specific surface area, pore volume, and pore size are presented in Table 2. As can be seen from the results, the specific surface area of AC/SEP composite is more than the AC and SEP components, and it affects significantly on the removal percentage of lead ions.

Adsorption studies

Experimental design approach for the optimization of lead ions adsorption by AC/SEP adsorbent

In experimental design and optimization the adsorption process part, four factors include pH (X_1), adsorbent dosage (X_2), lead initial concentration (X_3), and contact time (X_4)

Table 3. Experimental parameters and considered range in the central composite design.

Factors	Unit	Symbol	Levels	
			Low (-1)	High (+1)
pH		X_1	2.00	6.00
Adsorbent dosage	g	X_2	0.025	0.125
Concentration	mg/L	X_3	5.00	25.0
Contact time	min	X_4	2.50	32.5

Table 4: Central composite design matrix for the removal percentage of lead by AC/SEP adsorbent.

Run	Factors				Response
	X_1	X_2	X_3	X_4	%R
1	3.00	0.10	10.00	10.00	87.00
2	4.00	0.08	15.00	17.50	86.00
3	3.00	0.10	20.00	25.00	87.00
4	3.00	0.05	20.00	10.00	66.00
5	5.00	0.05	20.00	25.00	99.90
6	5.00	0.05	10.00	10.00	79.70
7	5.00	0.10	20.00	10.00	89.00
8	5.00	0.10	10.00	25.00	75.00
9	3.00	0.05	10.00	25.00	90.00
10	4.00	0.08	15.00	17.50	86.00
11	3.00	0.05	20.00	25.00	82.00
12	5.00	0.05	10.00	25.00	99.80
13	4.00	0.08	15.00	17.50	90.00
14	3.00	0.10	10.00	25.00	91.00
15	5.00	0.10	20.00	25.00	93.00
16	5.00	0.05	20.00	10.00	88.00
17	3.00	0.10	20.00	10.00	92.00
18	3.00	0.05	10.00	10.00	81.00
19	5.00	0.10	10.00	10.00	77.00
20	4.00	0.08	15.00	17.50	89.00
21	4.00	0.08	15.00	2.50	78.00
22	4.00	0.02	15.00	17.50	75.00
23	4.00	0.08	15.00	17.50	82.00
24	2.00	0.08	15.00	17.50	68.00
25	4.00	0.08	5.00	17.50	84.00
26	6.00	0.08	15.00	17.50	74.00
27	4.00	0.08	15.00	32.50	92.00
28	4.00	0.08	25.00	17.50	89.00
29	4.00	0.08	15.00	17.50	81.00
30	4.00	0.13	15.00	17.50	77.00

were intended and 30 experiments using the Central Composite Design (CCD) were designed. Four independent parameters with levels and the designed matrix for the experiments were shown in Tables 3 and 4, respectively.

Table 5: ANOVA of the second-order polynomial equation for the removal percentage of lead by the AC/SEP adsorbent.

Source	SS _a	Df _b	MS _c	F Value	P Value
Model	1620.31	14	115.74	454.74	< 0.0001
X ₁	58.28	1	58.28	228.99	0.0041
X ₂	3.08	1	3.08	12.11	< 0.0001
X ₃	29.04	1	29.04	114.10	< 0.0001
X ₄	308.17	1	308.17	1210.81	< 0.0001
X ₁ X ₂	318.62	1	318.62	1251.89	< 0.0001
X ₁ X ₃	228.01	1	228.01	895.87	0.0003
X ₁ X ₄	6.25	1	6.25	24.56	< 0.0001
X ₂ X ₃	129.96	1	129.96	510.62	< 0.0001
X ₂ X ₄	196.00	1	196.00	770.10	0.0577
X ₃ X ₄	1.10	1	1.10	4.33	< 0.0001
X ₁ ²	183.93	1	183.93	722.69	< 0.0001
X ₂ ²	49.22	1	49.22	193.39	< 0.0001
X ₃ ²	45.32	1	45.32	178.07	< 0.0001
X ₄ ²	22.73	1	22.73	89.33	< 0.0001
Residual	3.31	13	0.25		
Lack of Fit	2.31	10	0.23	0.69	0.7122
Pure Error	1.00	3	0.33		
Cor Total	1967.59	29			

R²= 0.9945, Adj R²= 0.9847, Pred R²= 0.9785.

*Sum of square, ^bDegree of freedom, ^cMean square.

Regression analysis and analysis of variance

The lead removal percentage is the dependent factor (response) in CCD method and the second-order coded equation presenting the relation between response and independent factors affecting the adsorption process.

Y (%R)

$$\begin{aligned}
 &= +82.67 + 1.56X_1 - 0.36X_2 + 1.10X_3 + 3.58X_4 \\
 &- 4.46X_1X_2 + 3.78X_2X_3 + 0.63X_1X_4 + 2.85X_2X_3 \\
 &- 3.50X_2X_4 - 0.26X_3X_4 \\
 &- 2.59X_1^2 - 1.34X_2^2 + 1.29X_3^2 + 0.91X_4^2 \quad (4)
 \end{aligned}$$

The results of analysis of variance (ANOVA) for the removal percentage of lead by the AC/SEP adsorbent is shown in Table 5. The significance of factors is determined by the values of P. For removal percentage of lead, all four factors in this model are significant due to their P values less than 0.05 [38]. Lack of Fit (LOF) presents the residual sum of squares fraction happens because of the incompleteness of the model. A model is reliable if the P value of LOF is less than 0.05 [38]. The P value of LOF for the removal percentage of lead is 0.7122 that illustrates

the quadratic equations are valid. Also, the high correlation coefficient for the model (0.9945) confirms that the predicted model ideally fitted with the experimental data. The value of R²_{Adj} (0.9847) and R²_{Pred} (0.9785) presents the accuracy of the model for lead. Also, the predicted model for lead has a good PRESS value (96.55) presenting the power of the model [38].

Interaction of variables

Fig. 4a shows the 3D and contour plots of pH and adsorbent dosage in the lead removal process by the AC/SEP composite. As can be seen, when the pH increases and the amount of adsorbent decrease, the percentage of lead removal increases. Regarding the effect of the amount of adsorbent, this issue is confirmed due to the negative coefficient of the amount of adsorbent in the mentioned equation. Also at higher pHs, because lead has a positive charge and with increasing of pH, the adsorbent surface has a negative charge and the possibility of electrostatic bond formation is higher. The contour plot of these factors also confirms the 3D plot and the highest percentage of lead removal is done at pH 5.00 and the amount of adsorbent is 0.05 g.

Fig. 4b shows the 3D and contour plots of the simultaneous effect of pH and concentration, and the other two factors, the amount of adsorbent and the contact time are kept constant at their midpoint. As can be seen, when the pH increases, the percentage of lead removal increases, and also when the concentration increases, the percentage of lead removal increases. The unoccupied sites of adsorbent become fewer at higher concentration of lead ions and mass transfer is dependent on the lead ion initial concentration. Indeed, increment in lead concentration decreases resistance to the adsorption of solute from lead solution and accelerates the diffusion of lead ions from the solution onto the adsorbent owing to the growth of driving force (concentration gradients) [30]. Due to the positiveness of these coefficients, it is confirmed and the contour plot of these factors confirms the 3D plot. The highest percentage of lead removal is done at a concentration of 20.00 mg/L.

In Fig. 4c, when the contact time increases and the adsorbent dose decreases, the percentage of lead removal increases, and the maximum lead removal occurs during the contact time of 25.00 min, that it can be derived that the process equilibrium time probably occurs at the end of the considered range of time [39].

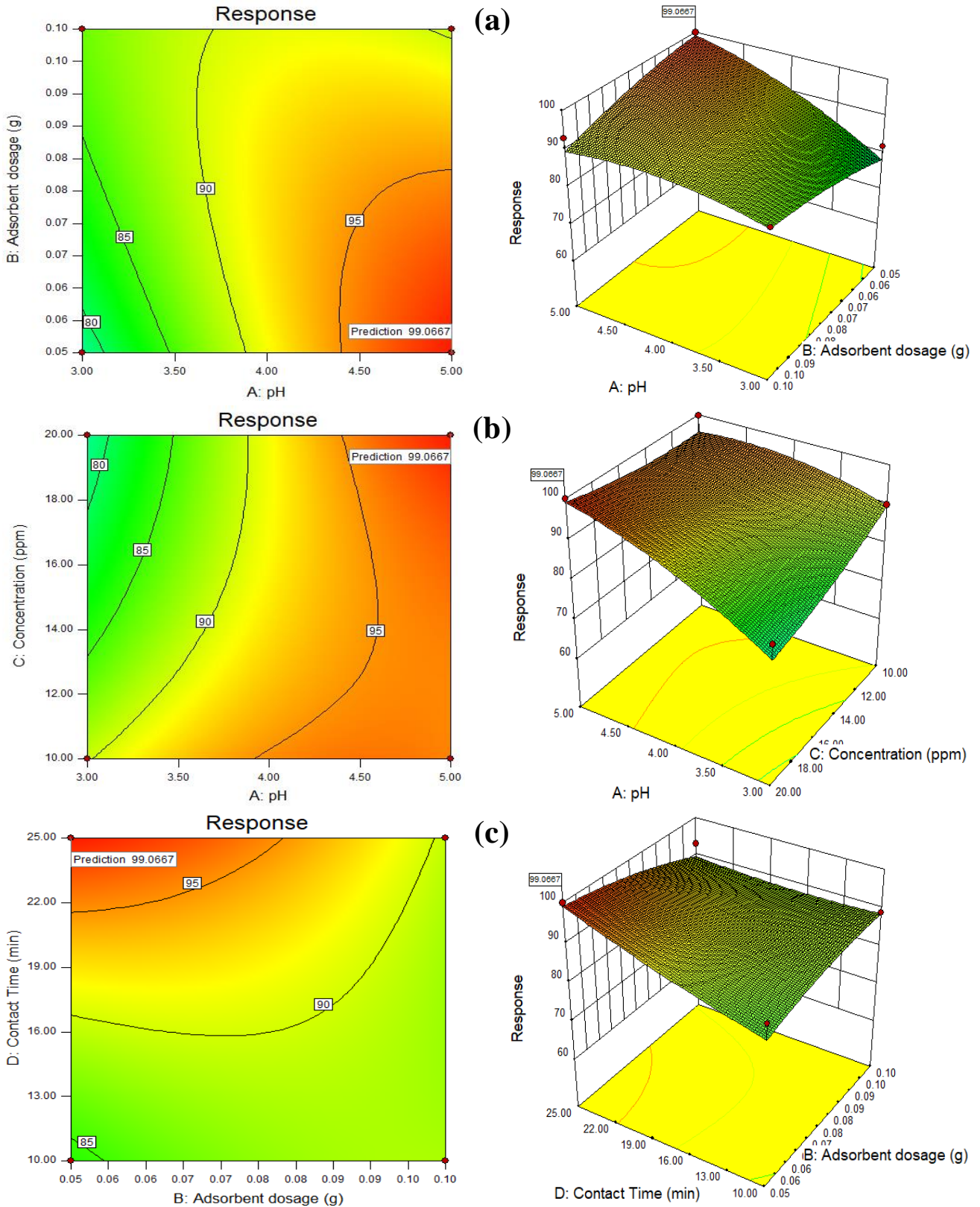


Fig. 4: The 3D response surface and contour plots for interactive effects of a) pH and Adsorbent dosage, b) pH and concentration, and c) Adsorbent dosage and contact time for the removal percentage of lead by the AC/SEP adsorbent.

Table 6: The optimal conditions for the maximum removal percentage of lead by the AC/SEP adsorbent.

	pH	Adsorbent dosage (g)	Contact time (min)	Concentration (ppm)	%Removal
Lead	5.00	0.05	25.00	20.00	99.07

Table 7: Isotherm parameters for the adsorption of lead by AC/SEP adsorbent.

Model	Equation	Parameters	Value
			Lead
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$ [22]	q_m (mg/g)	269.67
		K_L (L/mg)	6.1674
		R^2	0.9912
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$ [22]	n^{-1}	0.1934
		K_f (mg/g)(L/mg) ^{1/n}	5.3845
		R^2	0.9134

q_m : Maximum adsorption capacity shows a complete monolayer (mg/g), K_L : Langmuir constant or adsorption equilibrium constant (L/mg), n^{-1} : Isotherm constant presents the empirical parameter, K_f : Isotherm constant shows the capacity parameter (mg/g)(L/mg)^{1/n}.

Optimization

The optimal conditions for obtaining the maximum removal percentage of lead were extracted using the CCD. The maximum percentage of toxic lead removal (99.07%) at pH= 5.00 using AC/SEP adsorbent amount of 0.05 g was obtained with desirability 1.0 at the contact time of 25.00 min at the initial concentration of 20.00 mg/L (Table 6).

For validation of the model, the lead pollutant removal percentage was done at least four times by AC/SEP adsorbent and an experimental value of 99.00% for removal of lead presents the validity of the model.

Adsorption isotherm

Adsorption isotherms are necessary for the explanation of how lead concentration will interact with AC/SEP surface and are helpful to optimize the usage of the adsorbent for the removal of lead from aqueous solutions [40]. The constant parameters of the Langmuir and Freundlich isotherm equations were obtained using a plot of C_e/q_e vs. C_e that presents a straight line of slope $1/q_m$, the intercept $1/K_L q_m$, and a plot of $\ln q_e$ vs. $\ln C_e$ presents a straight line of slope $1/n$, the intercept $\ln K_f$ and the correlation coefficient (R^2) for isotherms are given in Table 7.

The q_m values and the equilibrium adsorption constants by Langmuir model were 269.67 mg/g and 6.1674 L/mg for lead that presenting the adsorption of lead metal ions onto by AC/SEP adsorbent is ideal. Results (R^2 values) of isotherm models showed that Langmuir adsorption

Table 8: Kinetic parameters for the adsorption of lead by AC/SEP adsorbent.

Model	Equation	Parameters	Value
			Lead
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$ [41]	k_1 (1/min)	0.1980
		q_e (calc)(mg/g)	19.741
		R^2	0.6874
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t$ [41]	k_2 (g/mg min)	0.1099
		q_e (calc) (mg/g)	199.33
		R^2	0.9896

k_1 : Rate constant of pseudo-first order sorption (1/min), k_2 : pseudo second-order rate constant of sorption (g/mg min).

Table 9: Thermodynamics parameters of lead by AC/SEP adsorbent.

T (K)	$\ln K_e$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	R^2
283.15	8.38	-18.79	-86.92	0.0694	0.9965
293.15	8.53	-19.14			
303.15	8.59	-19.89			
313.15	8.68	-20.65			
323.15	8.78	-21.48			
333.15	8.86	-22.26			

isotherm with $R^2 = 0.9912$ is more favorable lead metal ions adsorption process [1, 18].

Adsorption kinetics and thermodynamic studies

Kinetic parameters for the adsorption of lead ions by AC/SEP adsorbent are listed in Table 8. In the pseudo-first-order model, k_1 and q_e can be obtained from the intercept and slope of the plots of $\log(q_e - q_t)$ versus t .

Based on Table 8, because the correlation coefficient for the pseudo-second-order model for lead is close to 1, the kinetics of the adsorption process for lead metal ions are a kind of pseudo-second-order model and show that the adsorption rate belongs to the concentration of the metal ions on the AC/SEP surface [41].

Thermodynamics results (Table 9) present that the negativity of ΔG° values for lead metal ions shows that the adsorption process is spontaneous. The negative enthalpy change indicates that the lead metal ions adsorption process is exothermic. As well as the entropy change for adsorption of lead by AC/SEP adsorbent is representation of more disarray at the solid-soluble surface within adsorption process.

Application of AC/SEP adsorbent on real sample

Table 10 shows the results of lead ions adsorption applying the AC/SEP composite on the industrial sample.

Table 10: Removal percentages of lead by the AC/SEP composite from industrial wastewaters (N = 4).

Sample	Lead (mg/L)	% Removal
Industrial wastewater	10	99.12 ± 2.14
	20	96.88 ± 2.18
	30	92.49 ± 2.21

The sorption process was done using industrial wastewater spiked with lead ions in various amounts (10, 20, and 30 mg/L). Next, the spiked real sample was treated under relevant conditions of the method. According to Table 9, the ideal removal percentage of lead confirms a good performance of AC/SEP adsorbent on industrial real samples.

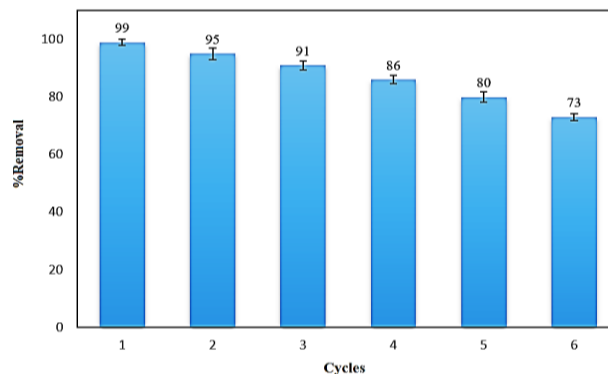
Based on the result of Table 6, the optimized concentration for the AC/SEP adsorbent is 20.00 mg/L. As can be seen in Table 10, the removal percentage at the optimal concentration is slightly different in real sample due to the presence of other substances. Also, with a large increase in the concentration of lead ions, the AC/SEP adsorbent surface is quickly saturated and the removal percentage is reduced.

Recyclability of the AC/SEP adsorbent

The adsorbent recovery process, which is a key economic factor in improving costs, is performed to reuse the adsorbent in subsequent cycles [43,44]. The adsorbent used in the adsorption process must have a high specific surface area, high porosity, suitable functional groups as the adsorption center, and high mechanical and chemical strength. It can also be easily restored and reused. In order to study the desorption of lead metal ions adsorbed by the adsorbent, the optimized amount of adsorbent to remove metal ions in the desorption process was used. In optimized conditions, nitric acid (1 M) solvent was selected to desorb lead ions. After five cycles, the adsorbents have an acceptable removal ability and the AC/SEP adsorbent can be used efficiently and cost-effectively for the removal of lead ions (Fig. 5). The decrease in the recovery stages after the sixth time of the adsorbent may be due to the inactivity of some adsorbent sites.

Comparison of different adsorbents for removal of lead ions

A comparison between adsorption capacities for lead ions removal of different adsorbents is demonstrated in Table 11. It should be emphasized that the adsorption

**Fig. 5: Regenerate of AC/SEP adsorbent by nitric acid (1 M) solvent for the removal of lead ions.**

capacity for AC/SEP is higher or similar in comparison with other materials. Based on the results, the performance of AC/SEP is good compared to other adsorbents.

CONCLUSIONS

Activated carbon from walnut shell modified by sepiolite composite (AC/SEP) was synthesized, characterized by FT-IR, BET, FESEM, and XRD techniques, and applied for remediation of toxic lead (Pb(II) ions) pollutant from industrial effluents. The results demonstrated that the lead adsorption process depends on the adsorbent dosage, pH, Lead initial concentration, and contact time. The adsorption kinetic follows the pseudo-second-order model and the isotherm follows the Langmuir model. AC/SEP is superior to AC and SEP, with a higher capacity for the remediation of toxic lead. AC/SEP adsorbent is more biodegradable and cost-effective than other adsorbents of mentioned pollutant and is not harmful to the environment. Also, the adsorbent was tested on a real sample of the industrial effluent, and the high removal percentage indicates the high ability and performance of the adsorbent on real sample. As a result, this type of adsorbent can be used effectively to remove the lead contaminants. Adsorbent recovery was studied in five rounds and the results showed that this adsorbent has a very good recovery ability and can be easily recovered and used several times.

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Table 11: Performance of some different adsorbents for removal of lead ions.

Adsorbent	Initial Concentration (mg/L)	pH	Adsorbent dosage (g)	Contact time (min)	q _m (mg/g)	Ref.
Apricot Stone Activated Carbon	-	8.00	-	20.0	80.63	[42]
Modified softwood sawdust	-	5.47	5.00	120	25.05	[43]
Corn silk modified by sepiolite	20.0	4.50	0.05	12.2	254.71	[44]
Corn Silk	400	4.90	0.15	30.0	2.046	[45]
Ponkan peel	15.0	5.00	-	60.0	112.1	[46]
Modified oil palm industry solid waste	15.0	5.00	5.00	15.0	92.24	[47]
Iranian domestic clinoptilolite	10.0	6.00	-	30.0	109.9	[48]
Agro waste and bacterial biomass	25.0	6.00	3.50	60.0	49.79	[49]
Activated carbon from walnut shell modified by sepiolite	20.0	5.00	0.05	25.0	269.67	This Study

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