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Research article

Efficient removal of lead and arsenic using macromolecule-carbonized rice husks

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ABSTRACT

The adsorption process using inexpensive adsorbents is one of the methods to remove contaminants from aqueous solutions. Biomass porous carbon based materials are among the most widely used adsorbents in this field. Rice husk is a bio-based adsorbent material for pollutant removal. In this study, the porous carbon material obtained from the rice husk was used for the adsorptive removal of lead (Pb) and arsenic (As) from aqueous solutions. Silica was removed from rice husk structure through the one-step reaction using PTFE. The morphological and crystallographic characteristics of the adsorbent surface were determined by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The removal efficiency was investigated under different conditions of pH (3–9), contact time (3–90min), adsorbent amount (0.5–6 g/l) and initially adsorbed concentration (10–100 μg/l) by changing the parameters in the adsorption reactions. The Response Surface Method (RSM), a Box-Behnken design (BBD), was used to optimize adsorption of Lead and Arsenic by Rice husk. The removal efficiency was finally calculated using analysis of variance. According to the adsorption analysis results, the removal efficiency of Pb and As in aqueous solutions increased (up to 97%, 85% for Lead and Arsenic) under optimum conditions.

1. Introduction

Nowadays, the frequency of pollution in the water systems is a major problem because of the seawater, lake or river flows [1,2].Different types of aquatic pollutants, such as organic, mineral and heavy metals threaten human health. Heavy metals such as lead and arsenic can have toxic effects on humans, plants, and animals; even at low concentrations because of their low biodegradability [3,4,5]. Lead enters water through ores, metal electroplating and leaded gasoline [6]. Arsenic is also found in natural environments in both organic and inorganic forms and is generally produced in processes that require high temperatures. High amounts of inorganic arsenic can be found in deep wells due to the natural geological contamination [5,7].

There are various methods for the removal of organic pollutants, salinity, water hardness and acidity in polluted waters such as reverse osmosis, electro dialysis, chemical precipitation, ion exchange, solvent extraction, and reduction. Membrane distillation (MD), the combination of membrane and thermal methods, is widely used to remove pollutants from water [8,9].

Adsorption is also a technique whereby pollutants and contaminants can be removed by the adsorbent surface. Porous carbon compounds are suitable adsorbents for removing pollutants from aquatic environments. Biomass, as an environment-friendly, inexpensive, renewable and abundant source of adsorbent, has been shown to produce porous carbon compounds. Various bio sorbents have been used for contaminants removal in the literature and acceptable results have also been achieved [2,10]. The following materials can be used as adsorbents for removal of pollutants from polluted water: maize, pussy flower, coffee waste [12] natural zeolites, and activated carbon charcoal produced from the coconut leaf [13], rice husk and its ash [11,12,13,14,15,16,17,18]. Moringa olefina is also used as a carbon precursor to produce porous carbon nanosheets derived from biomass and has shown suitable porous carbon properties with two-dimensional structure, good electrical conductivity and short ion diffusion paths [12].

Rice husk (RH) is an inexpensive and environment-friendly adsorbent for removing pollutants and heavy metals. It contains large amounts of fiber, protein and functional groups such as carboxyl, hydroxyl, and amidogen that make the adsorption process possible [14,18,19,20]. The

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use of rice husk biochar depends on the characteristics of biochar and its interaction mechanisms with heavy metals [14].

Commonly, it has low performance when it is directly used to remove heavy metals. Thus, an activation process is necessary for obtaining high porosity Carbon (HPC) from rice husk biomass. Many studies have been conducted to modify the RH surface to enhance adsorption efficiency [15,16].

The response surface methodology (RSM) has been widely used as an optimization tool in various kinds of analytical chemistry, applied chemistry, and industrial and biological processes. Three common multilevel designs, central composite design (CCD), Box–Behnken design (BBD), and Doehlert matrix (DM) have been frequently utilized for the final optimization of desired processes [21]. The BBD has been widely applied in bioengineering processes as it decreases the number of experimental runs. Such designs have proved to be economical and useful in expensive experimental runs [22].

RSM is a simple, effective, and low-cost mathematical and statistical method for designing experiments and can be used for developing and optimizing processes. Another advantage of this method is the ability of variance analysis to determine the final formula of elimination and theoretical optimal conditions [23,24].

Peng et al. (2017) [16] investigated the use of graphene oxide and its composites for the removal of heavy metals (Pb (II), Cd (II), Co (II)), and found out that functionalization with oxygenated functional groups, the type of metal ions in the solution, graphene thickness, pH, contact time and reaction temperature have a great influence on the removal process [25].

Arab-Ahmadi and Ghorbami (2017) [5] used polythiophene as the base matrix and added rice husk to the matrix during the polymerization process. They concluded that Rice husk with Surface modification could increase the adsorption efficiency of Pb (II) from aqueous solutions (up to 96.58%) due to obtaining a mesoporous structure and increasing the specific surface area [5].

Samad et al. (2016) investigated the effect of heating reaction on rice husk for arsenite removal in groundwater. They increased the reaction temperature from 80 °C to 300 °C and observed that the removal efficiency was 75% in 150 °C, which indicated a significant increase relative to efficiency in environment temperature that was 54% [1].

Alimohammadi et al. (2017) [25] used eucalyptus leaves to remove arsenic and mercury from aqueous solutions and calculated the optimal removal conditions used the equations of response surface. The results showed that the removal of heavy metals from aqueous solution was more efficient by eucalyptus leaves available in Iran than other reports [21].

Liang et al. (2017) [13] produced high-porosity carbons by mixing Polyethylene Tetra Fluoro Ethylene (PTFE) powder and RH. These carbons can produce HF for silica removal during carbonization reaction and HF application steps for silica removal and rinsing with NaOH. The carbon surface area reached 2051 m^2/g without any chemical activation, which is 20 times more porous than the traditional methods of producing carbon from rice husk [16].

In this study, an inexpensive biomass source (rice husk) was used with a simple method for the preparation of porous carbon compounds that remove silica by application of poly tetra fluoro ethylene (PTFE) in the reaction of rice husk carbonization, in situ [13]. Raw rice husk was obtained from western shales of Golestan province, Iran as a local sample. Due to the presence of heavy metals (As, Pb) in prepared rice in this geographical area [22,26,27]; these elements were removed in the adsorbents produced by the digestion process. It was found that despite the presence of high amounts of lead and arsenic in the prepared adsorbent and purification by digestion, the adsorbent has a very high ability to readsorb these elements. Simultaneously Box-Behnken Desine can help to reduce the number of experiments in the future and ultimately reduce costs. Due to the limitations of this project, the Researchers team decided to use a simple reactor that they designed. This typical furnace works by installing nitrogen gas inlets like industrial furnaces under nitrogen atmosphere.

In this study, the effect of parameters such as changes of pH, contact time, adsorbent amount and adsorbed concentration on Pb and As were investigated on the removal efficiency.

The Response Surface Methodology (RSM) based on Box-Behnken design was used to optimize the removal of Pb and As and the access to appropriate response levels, because it has many advantages such as reducing the number of experiments, time and cost. In addition, the analytical statistical method (ANOVA) was used and the elimination equation was determined. (ANOVA statistical procedure was used to determine the elimination equation).

2. Materials and methods

2.1. Chemical materials

Certain chemicals with analytical grade were used in this study including PTFE powder, hydro fluoro acid (HF), hydrochloric acid (HCl), and sodium hydroxide (NaOH) from Merck Co. The Lead and Arsenic standard solutions with a concentration of 1000 μg/ml from Varian Co. were used and diluted with deionized distilled water for adsorption tests and measurement of Pb and As concentrations.

2.2. Absorbent preparation

In this study, raw rice husk as a raw material was obtained from western shales of Golestan province, Iran. The raw samples were first washed with deionized distilled water to remove contaminants then heated at 105 °C for 2h in the oven and sifted to obtain homogeneous and uniform materials. Rice husk (5 gr) was carbonized via the nitrogen flow at 750 °C for 2h resulting in the black product (0.865 g). The obtained product (CS-1) was dissolved in 3.5 ml of hydrofluoric acid (40%) in a plastic lid container for 24 h to complete digestion of silica material. Then, Atomic Absorption (Table 1) calculated the mass percentage of Si in the product.

Rice husk (5 gr) was also mixed with PTFE powder (1:2) and heated up in the presence of nitrogen from 650 °C to 900 °C with the heat rate of 1.5 °C/min in the furnace. Then, the mass percentage of Si and concentration of Pb(II) and As(V) in the carbonized black product (CS-2) was also calculated after complete digestion of silica material [9] (Tables 1 and 2).

The morphology and surface crystallographic characteristics of CS-1 and CS-2 samples were determined by field emission scanning electron microscopy (SEM) and X-ray diffraction (XRD) (Figures 1 and 2).

2.3. Adsorption tests

All the tests were performed in 250 ml Erlenmeyer flasks containing 100 ml of different concentrations of lead and arsenic, with different values of adsorbent (CS-2), at different pH and variable contact times. A magnetic stirrer was used to prepare a uniform mixture of the adsorbent and the adsorbed at a constant speed (300rpm). The working solutions were prepared from Standard reference solution (1000 μg/ml). The pH of solution was adjusted using HCl (0.1N) and NaOH (0.1N), as well.

After the certain contact time, the solution was filtered using a 0.45 μm-syringe filter and the residual concentrations of lead and arsenic were measured using inductively coupled plasma Optical Emission Spectrometer (ICPE-OES) method. In order to evaluate the influence and

Table 1. Mass percentage of Si/product in the samples CS-1 and CS-2.

Sample name	mass of rice husk	Atmosphere	mass of PTFE	mass of product	Volume of Hf	Si/product (Mass percentage)
CS-1	5g	N_2	-	0.865g	3.5ml	40.32%
CS-2	5g	N_2	10g	1.745g	3.5ml	0.294%

Table 2. Concentration of Pb(II) and As(V) in the samples CS-1 and CS-2.

Sample name	Pb(II) befor digestion (mg/kg)	Pb(II) after digestion (mg/kg)	As (V) befor digestion (mg/kg)	As (V) after digestion (mg/kg)
CS-1	38	0	9	0
CS-2	32	0	7	0

efficiency of each factor, the experiments were performed by changing one or two parameters and keeping the other parameters constant.

2.4. Batch experiments

2.4.1. Optimization by changing a parameter in lead removal

Four independent variables, contact time (CT) (3, 5, 10 and 20 min), pH (3, 5, 7 and 9), Adsorbent concentration (A.C) (0.5, 1, 1.5, And 2 g/l) and the initial concentration of adsorbent (C0) (10, 20, 40 and 100 μg/l) were selected for the lead experiments. The percent of Pb removal is given in Table 3.

2.4.2. Optimization by changing a parameter in arsenic removal

Four independent variables of contact time (20, 40, 60 and 90 min), pH (3, 5, 7 and 9), adsorbent concentration (1, 2, 4 and 6 g/l) and the

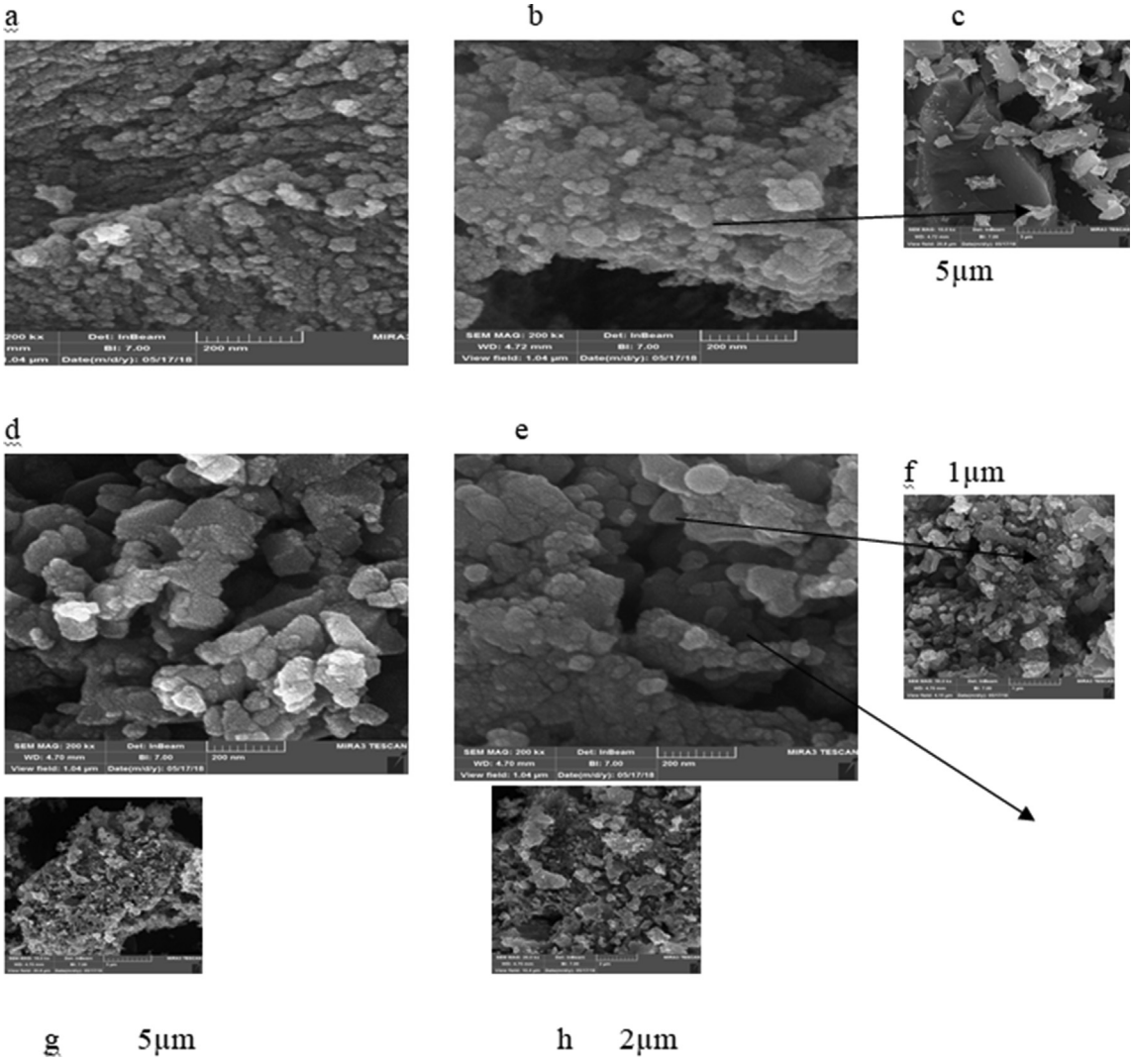

Figure 1. (a, b, c) SEM images of sample CS-1, (d, e, f, g, h) of sample CS-2.

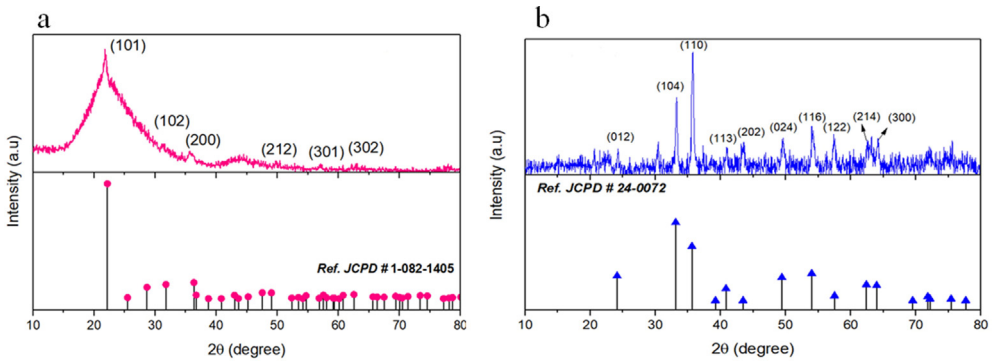

Figure 2. (a) XRD spectrum of sample CS-1, (b) sample CS-2.

Table 3. Removal percentage of Pb and As for Optimization by changing a parameter.

Pb					As				
pH	C.T	A.C	I.C	elimination%	pH	C.T	A.C	I.C	elimination%
3	20	1	100	82.6	3	40	4	100	82.5
5	20	1	100	91.8	5	40	4	100	71.9
7	20	1	100	97.7	7	40	4	100	78.4
9	20	1	100	86.7	9	40	4	100	83.61
7	5	1	100	86.1	9	20	4	100	32.9
7	**10**	**1**	**100**	**98.38**	9	40	4	100	44.3
7	20	1	100	96.4	**9**	**60**	**4**	**100**	**86.03**
7	30	1	100	96.4	9	90	4	100	75.3
7	10	0.5	100	86.4	9	60	1	100	6.9
7	**10**	**1**	**100**	**98.38**	9	60	2	100	40
7	10	1.5	100	96.5	**9**	**60**	**4**	**100**	**86.4**
7	10	2	100	96.4	9	60	6	100	81
7	10	1	10	75	9	60	4	10	26.6
7	10	1	20	80.5	9	60	4	20	28
7	10	1	40	79.5	9	60	4	40	61.5
7	**10**	**1**	**100**	**98.38**	**9**	**60**	**4**	**100**	**86.1**

The bold values are shown maximum adsorptions.

initial concentration of adsorbed (10, 20, 40 and 100 μg/l) were selected for arsenic experiments. The percent of As removal is shown in Table 3.

2.4.3. Optimization by changing two-parameter and Box-Behnken design in lead removal

The number of experiments required by the response surface methodology is calculated by applying the Box-Behnken model through the following equation:

$$N = 2K\,(K-1) + C \quad \text{(Eq. 1)}$$

In which; N, K, and C are the number of experiments, the number of variables and the number of central points, respectively. Each of the response variables for elimination percent (Y) is presented as a function of independent variables in the form of the polynomial regression model, as:

$$Y = ß_0 + \Sigma ß_i X_i + \Sigma ß_{ii} X_{ii}^2 + \Sigma ß_{ij} X_i X_j + \varepsilon \quad \text{(Eq. 2)}$$

In which: Y is the response variable (the percent of elimination) ß0 is intercept or constant coefficient and ßi, ßii, ßij are linear, quadratic and interaction coefficients, respectively [25,28].

Four independent variables of contact time (3, 16.5 and 30 min), pH (5, 7 and 9), adsorbent amount (A.D) (0.05, 0.1 and 0.15 mg in 100ml) [or A.C (0.5, 1 and 1.5 g/l)] and adsorbed initial concentration of lead (10, 55 and 100 μg/l) were selected for lead experiments at three levels, high (+1), medium (0) and low (-1). The percentage of Pb removal is given in Table 3. The variance analysis and regression coefficients for finding the quadratic equation are tabulated in Table 4.

2.4.4. Optimization by changing two-parameter and Box-Behnken design in arsenic removal

Four independent variables of contact time (45, 65 and 90 min), pH (3, 6 and 9), adsorbent dose (0.1, 0.15 and 0.2 mg in 50 ml) [or A.C (2, 3 and 4 g/l)] and adsorbed initial concentration of As (10, 55 and 100 μg/l) were selected for Arsenic experiments at three levels, high (+1), medium (0) and low (-1). The percentage of As removal is given in Table 4. The variance analysis and regression coefficients for finding the quadratic equation are tabulated in Table 5.

3. Result and discussion

3.1. Adsorbent characteristics

Atomic Absorption calculated the mass percentage of Si in the ash of samples CS-1 and CS-2 and the results are presented in Table 1.

The analysis result of Pb (II) and As (V) in the samples CS-1 and CS-2 are presented in Table 2.

Figure 1 (a, b, c) shows the SEM images of CS-1 sample which show a poorer dispersion and uniformity than Figure 1 (d, e, f, h) for FESEM images after rice husk carbonization through a PTFE syringe filter and

Table 4. Results of Box-Behnken design experiments for Lead and Arsenic Removal.

Run Order	Pb						As					
	pH	C.T	A.D	C_0	C_t	Removal%	pH	C.T	A.D	C_0	C_t	Removal%
1	**7**	**16.50**	**0.05**	**10**	**7.00**	**30.00**	3	65	0.15	100	17	83.00
2	7	30.00	0.10	10	1.50	85.00	**6**	**90**	**0.15**	**10**	**7**	**30.00**
3	7	30.00	0.05	55	12.00	78.18	6	40	0.10	55	27	50.91
4	7	30.00	0.15	55	7.00	87.27	6	65	0.15	55	21	61.82
5	7	16.50	0.15	10	1.50	85.00	9	40	0.15	55	21	61.82
6	7	30.00	0.10	100	12.00	88.00	6	90	0.15	100	35	65.00
7	7	3.00	0.15	55	12.00	78.18	9	65	0.10	55	21	61.82
8	5	16.50	0.10	100	18.00	82.00	6	65	0.15	55	23	58.18
9	9	16.50	0.10	10	1.50	85.00	3	65	0.20	55	11	80.00
10	7	3.00	0.10	100	19.00	81.00	6	40	0.15	10	5	50.00
11	5	16.50	0.15	55	7.00	87.27	6	65	0.10	10	5	50.00
12	7	16.50	0.10	55	4.00	92.73	6	90	0.10	55	21	61.82
13	5	16.50	0.10	10	4.00	60.00	3	65	0.15	10	2	80.00
14	9	16.50	0.05	55	14.00	74.55	9	65	0.20	55	12	78.18
15	7	16.50	0.05	100	18.00	82.00	6	40	0.20	55	17	69.09
16	5	3.00	0.10	55	14.00	74.55	6	65	0.10	100	27	73.00
17	**9**	**16.50**	**0.15**	**55**	**1.50**	**97.27**	6	65	0.20	10	2	80.00
18	9	30.00	0.10	55	7.00	87.27	3	40	0.15	55	17	69.09
19	7	16.50	0.10	55	7.00	87.27	9	90	0.15	55	21	61.82
20	**7**	**3.00**	**0.10**	**10**	**7.00**	**30.00**	9	65	0.15	100	17	83.00
21	7	16.50	0.10	55	7.00	87.27	6	40	0.15	100	21	79.00
22	5	30.00	0.10	55	12.00	78.18	9	65	0.15	10	5	50.00
23	7	3.00	0.05	55	14.00	74.55	3	65	0.10	55	17	69.09
24	9	3.00	0.10	55	12.00	78.18	**6**	**65**	**0.20**	**100**	**15**	**85.00**
25	5	16.50	0.05	55	14.00	74.55	6	65	0.15	55	17	69.09
26	7	16.50	0.15	100	10.00	90.00	6	90	0.20	55	11	80.00
27	9	16.50	0.10	100	12.00	88.00	3	90	0.15	55	15	72.73

The bold values are shown maximum adsorptions.

concentration in a nitrogen evaporator (CS-2). The particle diameter ranged from 19 to 26nm (Figure 1a) and 13–15nm (Figure 1d).

Figure 2 (a) and (b) show the XRD spectrum of samples (CS-1 and CS-2), respectively. There are two distinct peaks at 25° and 43°, which are described as (101) and (200) planes, respectively (Figure 2a). The 101 plane indicates that the crystallinity was not entirely performed for graphitic layers, and the 200 plane indicates amorphous and disordered graphitic carbon (Ref.JCPD#1-082-1405). After carbonization with PTFE, the two peaks were diminished and had a very low intensity (Figure 2b), that suggests the graphite layers disappeared, and the porosity and degree of irregularity were simultaneously increased (Ref.JCPD#24–0072) [28].

Table 5. Regression coefficients of surface response model for lead and arsenic removal percentages.

Term	Pb				As			
	coef	SE Coef	T	P	Coef	SE Coef	T	P
Constant	89.09	5.30	16.80	0.00	63.03	4.95	12.75	0.00
pH	4.48	2.65	1.69	0.12	-4.77	2.47	-1.93	0.08
C.T	7.29	2.65	2.75	0.02	-0.71	2.47	-0.29	0.78
A.D	9.27	2.65	3.50	0.00	8.80	2.47	3.56	0.00
C_0	11.33	2.65	4.28	0.00	10.67	2.47	4.31	0.00
pH*pH	-1.03	3.98	-0.26	0.80	7.12	3.71	1.92	0.08
C.T*C.T	-6.83	3.98	-1.72	0.11	-5.20	3.71	-1.43	0.18
A.D*A.D	-4.53	3.98	-1.14	0.28	5.60	3.71	1.53	0.15
C_0*C_0	-11.13	3.98	-2.80	0.02	1.80	3.71	0.49	0.64
pH*C.T	1.36	4.59	0.30	0.77	-0.90	4.28	-0.21	0.84
pH*A.D	2.50	4.59	0.54	0.60	1.30	4.28	0.32	0.76
pH*C_0	-4.75	4.59	-1.04	0.32	7.50	4.28	1.75	0.11
C.T*A.D	1.36	4.59	0.30	0.77	0.00	4.28	0.00	1.00
C.T*C_0	-12.00	4.59	-2.61	0.02	1.50	4.28	0.35	0.73
A.D*C_0	-11.75	4.59	-2.56	0.03	-4.50	4.28	-1.05	0.31

3.2. Adsorption by batch method

The removal efficiency (Y) of lead and arsenic from aqueous solutions was determined by the following equation;

$$Y\ \% = [(C_0–C_e)/C_e]*100 \quad \text{(Eq. 3)}$$

Where, C_0 and C_e are the adsorbed initial concentrations at zero and the adsorbed concentrations after contact time, respectively.

The data in Table 3 show that the highest (98.38%) of the removal percentage of Pb was at pH = 7, t = 10 min, adsorbent concentration = 1 g/l and initial concentration of Pb = 100 μg/l. Amen et al used The biochar rice husk for lead and cadmium removal and found out the lead (Pb^{+2}) and cadmium (Cd^{+2}) removal percentages were 96.41% and 94.73% respectively [29]. An increase in adsorbent dosage resulted in an increase in lead removal efficiency. This was because of the increase in adsorbent mass with more surface area available for adsorption, resulting in a greater availability of reactive groups or an increase in the number of available binding sites [30].

As can be seen in Table 3, the highest removal percentage of As occurred at the following conditions: pH = 9, t = 60 min, adsorbent concentration = 4 g/l and initial concentration of As = 100 μg/l. The positive influence of the adsorbent contact time enhancement on the efficient removal of heavy metals can be related to the fact that the higher contact time leads to the provision of more adsorption sites [31].

It can also be attributed to the fact that when the adsorption time increases, the heavy metal ions initially adsorb on the exterior adsorption sites on the surface of the adsorbent materials exhibiting significant removal of heavy metals at the initial stage [29]. Agrafioti et al realized that Biochars derived from rice husk were effective in adsorbing Cr (III), As (V) and Cr (VI) from aqueous solution. The maximum removal achieved was 42%, 25% and 18% respectively [32].

3.3. Simultaneous optimization by Box–Behnken design

Box-Benken design by using Minitab 16 software package (Minitab Ltd., Coventry, UK) was used to optimize the adsorption process. The effect of the four main parameters comprising X1 = pH, X2 = contact time, X4 = adsorbent concentration and X3 = initial concentration of Pb and As on the removal of Pb and As was investigated using carbonized rice husk. The response surface methodology (RSM) and Box-Benken design were performed for optimization. Implementing a four-factor (K), three-level (C) requires 27 runs (N). (Equation1).

The results of the analyses are presented in Table 4. The variance analysis of data was performed to determine the final formula and the optimal theoretical conditions using Box-Behnken design (Table 5). Regarding Table 4, the highest and lowest percentage of lead removal by Box-Behnken design were found to be 97% and 30%, respectively As for arsenic, these percentages were 85% and 30%, respectively.

Anna et al applied A Box-Bssehnken experimental design to establish the combined effect of three selected parameters on the biosorption process of three heavy metals and to determine optimal values for the method. Initial concentration of metals, pH of the reaction environment and concentration of the biosorbent were included in the study. The following removal levels were achieved: Cd 44, 67%; Cu 63, 32%; Pb 78, 23% in the optimal condition [33].

The analysis of variance results are presented in Table 5. Using equation 2, equation 4 was obtained, which denoted the mathematical relationship between the independent and dependent parameters for the lead.

$$Y = 89.09+(4.48*pH)+(7.29*C.T)+(9.27*A.D)+(11.33*I.C)+(-1.03*pH*pH)+(-6.83*C.T*C.T)+(-4.53*A.D*A.D)+(-11.13*IC*IC)+(1.36*pH*C.T)\ (2.5*pH*A.D)+\ (-4.75*pH*IC)+(1.36*C.T*A.D)+\ (-12*C.T*IC)+\ (-11.75*A.D*IC) \quad \text{Eq. 4}$$

Quadratic Eq. (5) also shows the mathematical relationship between the arsenic parameters using the response surface method.

$$Y = 63.0303+(-4.77*pH)+(-0.71*C.T)+(8.8*A.D)+(10.67*I.C)+(7.12*pH*pH)+(-5.2*C.T*C.T)+5.6*A.D*A.D)+(1.8*IC*IC)+(-0.9*pH*C.T)+(1.3*pH*A.D)+(7.5*pH*IC)+(1.5*C.T*IC)+(-4.5*A.D*IC) \quad \text{Eq. 5}$$

The positive sign in front of the parameters indicates the synergy of the interaction effect on the model and the negative sign indicates the decreasing effect or opposite effect on the model.

When one variable is increased, the other one also follows, resulting in a positive correlation coefficient that indicates a synergy, and when one variable is decreased, the other one also decreases, producing a negative correlation coefficient that indicates disengagement.

3.3.1. Comparing the simultaneous effect of pH and contact time on lead removal efficiency

Figure 3(a) depicts the visualization and comparison of the combined effects of the two variables of pH and contact time on the rate of Pb removal in response surface methodology using the backbone design. The removal efficiency increased with the increase of pH and the adsorption rate was almost high in both the neutral and alkaline conditions. In addition, the removal efficiency increased with the increase in contact time (10 min and even up to 20 min) until the optimum time was obtained in univariate analysis.

Thus, there was a synergistic positive effect among the simultaneous change of pH and contact time parameters based on the equation of elimination and the bivariate analysis in the removal of lead [33].

3.3.2. Comparing the effect of simultaneous change of the amount of adsorbent and adsorbate concentration on lead removal efficiency

Figure 3(b) shows the simultaneous effect of changes in adsorbent dosage and adsorbate concentration on lead removal rate. As shown in both the equation of removal and the diagram, the initial adsorbate concentration had a greater effect on the efficiency [22].

3.3.3. Comparing the effect of simultaneous change of pH and adsorbate concentration on lead removal efficiency

Pb removal efficiency was high at neutral pH (optimum pH obtained in univariate analysis) and alkali values and according to adsorption equation and Figure 3(c), it is clear that the effect of adsorbate initial concentration was greater than pH [22].

3.3.4. Comparing the effect of simultaneous change of pH and contact time on arsenic removal efficiency

Using Figure 3 (d), the simultaneous effect of the two variables of pH and contact time on the rate of arsenic removal was observable and compared at one point. In the optimum pH range obtained from the 2-b diagram (pH = 9), the adsorption value was high and the time change had no effect. In addition, the removal equation shows that the pH effect was greater than the contact time.

3.3.5. Comparing the simultaneous effect of adsorbent amount changes and adsorbate concentration on arsenic removal efficiency

Regarding Figure 3(e), the simultaneous effect of the two variables, namely the amount of adsorbent and the adsorbate concentration was visible and was compared to the percentage of arsenic removal. As the equation and figure of removal show, the initial adsorbate concentration has a greater effect on the removal efficiency [22,33].

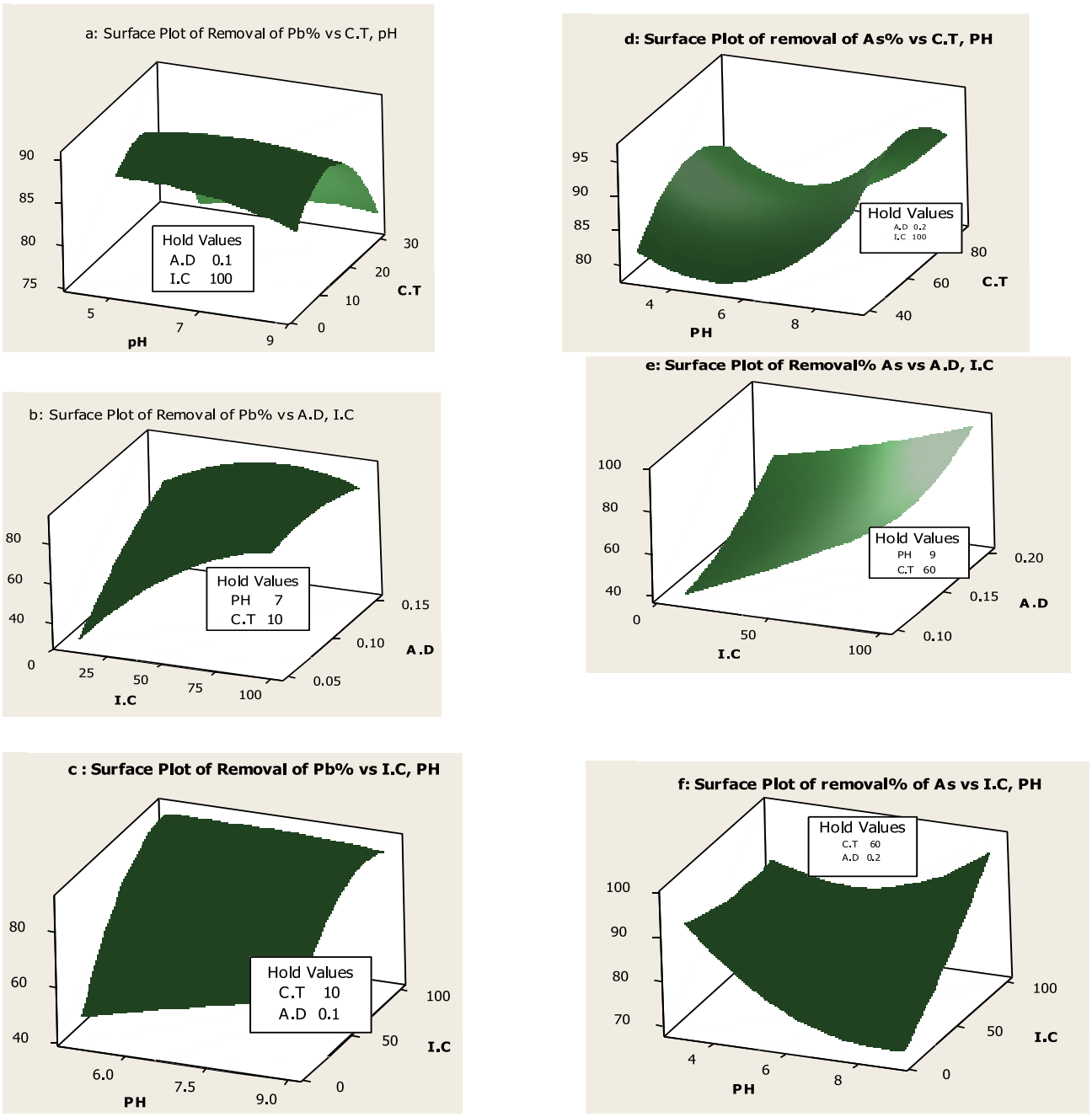

Figure 3. 3D response surface diagrams showing the effects of the mutual interactions between pH, C.T, A.D and I.C on removal efficiency of Pb (a, b, c) and As (d, e, f).

3.3.6. Comparing the effect of simultaneous change of pH and adsorbate concentration on arsenic removal efficiency

As shown in Figure 3(f), the simultaneous effects of changes in pH and adsorbate concentration on the arsenic removal rate can be observed. As Figure 3(f) shows and the removal equation confirmed, the adsorbed initial concentration and pH had a synergistic effect on efficiency.

Parmar et al used The Box-Behnken design (BBD), a Response Surface Method (RSM) to optimize biosorption of metals by V. alginolyticus PBR1. The three major factors, namely pH, biosorbent dosage and metal concentration were optimized to remove the metals efficiently. The removal efficiencies of 59.78 % and 82.20 % were observed for Cd and Pb, respectively in the optimum conditions [22].

4. Conclusion

Based on the obtained results and considering the reasonable performance and proper removal of heavy metals by biomass adsorbent, this adsorbent must be used as a low cost, high-performance adsorbent for the removal of heavy metal contaminants in water and wastewater treatment processes.

Furthermore the optimal amount obtained from the univariate diagram (maximal efficiency: 98.38%, 86.03% for Pb and As) is in accordance with maximal efficiency obtained in the simultaneous change of two parameters in Response Level Methodology (97.27%, 85% for Pb and As); the Level of importance of each parameter in increasing the efficiency is indicated by the software. In addition, Elimination equations indicate synergy and disengagement effects. Therefore, the design of

experimental (DOE) method is an efficient way to reduce costs and the number of tests and must help investigators to better understand the interaction of variables for the simultaneous optimization and investigation of variables. Thus, the use of this inexpensive adsorbent and DOE method in the removal of other contaminants such as dyes, toxins and other heavy metals is recommended.

Declarations

Author contribution statement

Fariboz Kaveh, Zeinab Babazad, Mehdi Ebadi, Ramin Zafar Mehrabian and Mohammad Habibi Juibari: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Additional information

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