Korean J. Chem. Eng., 38(9), 1843-1858 (2021)
DOI: 10.1007/s11814-021-0802-8

pISSN: 0256-1115
eISSN: 1975-7220

Adsorption of heavy metal ions via apple waste low-cost adsorbent: Characterization and performance

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(*Received 24 November 2020 • Revised 4 April 2021 • Accepted 11 April 2021*)

Abstract−This research focuses on the enhancement of the biosorption process via apple waste (a cheap adsorbent) for the treatment of heavy metals (including Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}). The apple pomace modified by potassium permanganate (ACAPMP), apple pomace modified by sodium hydroxide (APMSH) and activated carbon apple pomace (ACAP) were synthesized as adsorbents for the removal of heavy metals. The prepared biomass adsorbents were analyzed by FTIR, BET, EDS and FE-SEM. The Box-Behnken design was applied to optimize the process. The influence of pH, the time of removal, the type of adsorbent and concentration of heavy metal on the adsorption performance were investigated by batch experiments. The results revealed that ACAP, APMS and ACAP adsorbents were able to remove approximately 95% of zinc, cadmium, lead and copper from wastewater. The ACAPMP indicated the best performance compared to other adsorbents in optimal condition. Also, the results exhibited excellent removal performance for Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} with maximum adsorption percent 99.72%, 99.28%, 99.18% and 96.45%, respectively. To define the best correlation, the equilibrium data for adsorption were studied by using Langmuir and Freundlich isotherm models. The FTIR, BET and EDS characterization of functional groups and morphology confirm the suitable preparation of ACAPMP, ACAP and APMSH. The adsorption results indicate that apple waste as low-cost and high surface capacity adsorbents can be used.

Keywords: Heavy Metal Ions, Apple Waste, Removal, Box-behnken Design

INTRODUCTION

One of the major problems facing society is environmental pollution that is caused by various pollutants in urban and industrial wastewater. One of these pollutants includes heavy metals in the wastewater, which are frequently very toxic and harmful and cause major damage. Some heavy metals are essential for the body, but excessive consumption of them can be very harmful and dangerous. About 0.01% of heavy metals benefit an average human body that weighs 70 kg [1]. Copper, zinc, arsenic, cadmium, mercury and lead ions have the highest levels of environmental issues due to their widespread use in industry, and these six elements are very similar to sulfur compound pollution [2]. These heavy metals have a strong affinity for sulfur, as they usually bind by thiol groups (-SH) that cause serious disease [2]. Mineral wastes, sewage and industrial wastes, agricultural wastewater, electrical industries, paints, papermaking and batteries are potential sources of high waste metal production [1,3]. Some effects of heavy metal as follows.

Zinc is widely consumed as the fourth most metal in the world [4]. In 2018, the annual global production of lead was about 11.6 million tons, over half of which was the result of recycling [5]. Its relative abundance and low cost have resulted in its extensive use in construction, plumbing, batteries, bullets, solder and alloys [6]. Lead enters the bloodstream through aspiration. It is a neurotoxin that accumulates in tissues and bones, damages the nervous system, biological enzyme performance, finally leading to neurological disorders [7].

Copper is one of the few metals that can be employed naturally as pure metal. It is used as a conductor of electricity and heat in buildings [6]. Wilson disease causes copper to remain in the body and prevents it from entering the bile by the liver [8].

In 2020, the annual global production of cadmium was about 20 million tons [9]. The main use of cadmium is in the construction of nickel-cadmium rechargeable batteries [10]. Cadmium is one of the six components that have been forbidden via the European Union's Restriction of Hazardous Substances (RoHS) directive [11]. The most dangerous ways that cadmium enters into the body is by inhaling smoke, dust, eating and drinking cadmium-soluble compounds, so cadmium is a hazardous ion. Iron and steel production, cement production and related activities, production of non-ferrous metals and incineration of urban solid waste, can be ways to produce it [12]. The maximum contaminant level or permissible limits of zinc, cadmium, lead and copper ions in drinking water are identified by WHO organization and it was announced by directive as 5, 0.005, 0.05 and 0.05 ppm, respectively [12,13]. Excess amounts can have a negative influence on human health, such as cancer, kidney and liver disease, insomnia, nervous system damage, cramps, convulsions, skin irritations, vomiting and anemia [12,13].

There are many methods to remove and reduce heavy metals in urban and industrial wastewater, including chemical precipita-

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Table 1. Summary of adsorbents biomass-based of heavy metal ions

Biosorbent	Ion heavy metal	Adsorption capacity		Conditions	Reference
		q_m (mg/g)	%		
Apricot shells	Fe^{2+}		97%	pH=2-11	[29]
	Pb^{2+}		88%	T=25 °C	
	Cu^{2+}		81%	t=120 min	
Hickory wood	Pb^{2+}	153.1		Dose=0.01-0/1 g/l	[30]
	Cd^{2+}	34.2		T=0-200 °C	
	Ni^{2+}	28.1		pH=2-8	
Wood apple shell	Cr^{6+}		95%	pH=1.5	[45]
				T=300 K	
				pH=1-7	
				C=0-40 mg/L	
				t=0-90 min	
Shea nut shells	Pb^{2+}	16.1		pH=3-8	[46]
	Cd^{2+}	5.46		t=0-90 min	
Cashew shells	Pb^{2+}	2.61		C=10-50 mg/L	
	Cd^{2+}	2.87			
Shea nut shells and Cashew shells	Pb^{2+}	3.46			
	Cd^{2+}	3.06			
Camphor leaf	Cd^{2+}	62.42		Dose=0.05-0.35 g	[47]
	Cu^{2+}	49.96		pH=1-5.5	
	Ni^{2+}	26.42		C=200 ppm	
				t=5-90 min	
				T=30 °C	

tion, membrane filtration, ion exchange, electrodialysis, coagulation and flocculation [14,15]. These conventional methods, however, are expensive, produce a large amout of sludge, are pH dependent, with difficulty of separation, needing chemical materials, produce sludge and sediment, have limited life useful membrane, ability to remove a limited heavy metal, excessive use of chemicals, need considerable space, and are time consuming [14].

Now, in scientific and industrial societies, surface adsorption has been accepted as an effective and economical method for removing heavy metals from wastewater [16]. It is noteworthy that, adsorption properties like the presence of functional groups on surface and porosity can help to enhance the adsorption process [17]. Activated carbon is one of the most popular and widely applied surface adsorbents. Commercial activated carbon sorbent has been frequently employed to remove heavy metals from wastewater. Activated carbon, which has a high specific surface area and good size pore distribution, has the necessary conditions for a suitable adsorbent [18,19]. However, small changes in the chemical structure of an activated carbon may cause significant changes in the capacity for absorbing activated carbon [20]. The characteristics of activated carbon include great specific surface area, high porosity, lack of solubility in solvents, high adsorption capacity compared to inorganic adsorbents, such as zeolite adsorbent commercial activated carbon is relatively expensive [20].

Therefore, the use of low-cost and available adsorbent as a replacement for commercial activated carbon has become a top priority in research. So far, many studies have been done on low-cost adsorbents, and agricultural wastes and residual-based adsorbents, and biomass comprise a large part of these researches [17]. Many agricultural wastes have been reported to be used as adsorbents to remove heavy metal ions from wastewater. Previous sources, such as rice, wheat and barley bran, egg shells, Moringa pods, bamboo leaf powder, nut shells, palm shells and fruits, have a great capacity to remove heavy metals from wastewater [17,21]. Table 1 summarizes the adsorptions synthesized based on various biomasses.

Apple is one of the biomasses that could be applied for synthesis as adsorbent of heavy metal ions. Chand and Pakadeh in 2015 modified apple pomace (AP) with hydroxyapatite nanoparticles. The maximum adsorption capacity for lead, cadmium and nickel was 303, 250 and 100 mg/g, respectively. The adsorbent is also environmentally-friendly, fast, and cost-effective [22]. Chand et al. modified apple pomace by xanthan. Maximum adsorption capacity for lead, cadmium and nickel was reported at pH 2 to 8, 178.57, 112 and 51 mg/g. The advantages of this adsorbent include high adsorption capacity, reaction rate, cost-effectiveness and real wastewater treatment [23]. In a more recent study, apple pomace was polymerized by methyl acrylate. Maximum adsorption capacity by adsorbent for lead, cadmium and nickel in operating conditions of adsorbent dose 1 g/l, pH 2-9, contact time of 2 h and a concentration of 50-350 mg/L was equal to 106, 34.12 and 19.45 mg/g, respectively [24]. Also, Heraldy et al. applied sodium hydroxide in surface modification of apple. The maximum adsorption capacity of lead by adsorbent under operating conditions pH 2-10, contact time of 15-90 min and concentration of 20-100 mg/L was equal to 108 mg/g [25]. Another work synthesized an adsorbent based on activating carbon by apple peels. The maximum absorption of hexavalent chromium was 36.01 mg/g [26]. In 2019, Jangde et al. employed fixed-bed column to synthesize xanthan-modified apple pomace. The maximum adsorption capacity of the lead was 188-192 mg/g. The results show that the advantages of this adsorbent include high adsorption capacity and regeneration [27].

As can be understood, based on previous work, apples are a suitable sorbent for removing heavy metals from wastewater. Annually, 300,000 tons of apples are harvested in Maragheh, a city in the north-west part of Iran, 70,000 tons of which are discarded due to the lack of processing technology and industry that culled apple waste (fallen and bruised apples). Also, apple waste is a perishable and dangerous waste in the environment [28]. The price of each kilo apple waste (fallen and bruised apples) is 3.5 to 4.5 US cents. Because the produced biomasses were fallen apples, it was observed that, for every 12 kg, approximately 1 kg of biochar is produced. Therefore, its approximate price is 45 cents, which is very affordable compared to other absorbers.

The aim of this work was to study the biosorption of heavy metal via fallen apples. Also, based on the abundant advantages of chemical activation, focused on preparing biomass via chemical modification. Three types of biomass sorbents (biochar) were synthesized based on apple waste (fallen apples) and experimental design was performed using response surface methodology (RSM). The effective parameters in the adsorption process of heavy metal from wastewater were investigated and different prediction models were obtained based on the experimental design. The Langmuir and Freundlich adsorption isotherm models were employed to correlate the adsorption equilibrium data for apple wastes. Also, various analyses were employed to study the physical structure of the synthesized adsorbents to investigate the adsorption of heavy metals by apple adsorbent.

MATERIALS AND METHODS

1. Materials and Equipment

Sodium hydroxide (NaOH) and nitric acid (HNO_3) were supplied from Loba Chemie Co. and potassium permanganate ($KMnO_4$) was supplied from Dr Mojallali Co.; these were applied to synthesize apple-biomass. Copper (Cu), cadmium (Cd), zinc (Zn) and lead (Pb) elements with CAS number 7440-50-8, 7440-43-9, 7440-66-6 and 7439-92-1 (respectively) from Merk Co. were utilized to produce synthetic wastewater. The residual concentrations of Zn(II), Cd(II), Pb(II) and Cu(II) ions were estimated by atomic absorption spectrophotometer (AAS) Shimadzu AA-6300, Japan. The specific surface area (S_{BET}) and pore size distribution of the adsorbents were measured by means of nitrogen physisorption using BELSORP MINI II, Japan. FTIR was used for detecting functional groups on the surface of adsorbents which were characterized by using Bruker Vector 22, Germany. The morphology of adsorbents before and after the modification was studied by field emission scanning electron microscope (FE-SEM), and energy dispersive spectroscopy (EDS) was employed to analyze the surface elements using Tescan mira3, Czech Republic. Heating and removing the moisture were conducted by using oven oc55 Day tajhiz aryan paya, I.R.Iran. The dilution and solution processes were run by magnetic stirrers RCT basic Ika, Germany. Distributing nanometer particles in solution was done by ultrasonic homogenizer UHP-400 Tosa'aeh mafooghsoot, I.R.Iran. The shaking process was conducted by shaker orbital 2015 Parzan pajouh, I.R.Iran. The pH of solution was detected using pH meter AZ-86502 AZ Instrument, Taiwan. Carbonization was done by furnace VM2L-1200 Azar furnace, I.R.Iran. Grinding and making powder were conducted using planetary Ball Mill NARYA-MPM 2*250H Amin asia fanavar pars, I.R.Iran. The mills, cups and balls were made of stainless steel. This mill has four cups with the capacity of 250 mL and rotation speed of 600 rpm.

2. Adsorbent Synthesis Method

First, some apple waste (fallen apples) from gardens in Maragheh, Iran was prepared and peeled. Then, the apple pomace was sliced and washed several times with distilled water to a point that extractive impurities were removed and suitable pH of about 6.8 was achieved. The apple pomace was then oven dried at 105 °C for 24 h by removing moisture. Finally, it was ground under argon gas by ball mill for 3 h at 320 rpm (ratio 1 : 13, AP to balls).

Chemically assisted treatment can enhance the biosorption performance of biochar. To synthesize apple pomace modified by sodium hydroxide adsorbent, the dried AP was mixed with 0.1 M sodium hydroxide solution, stirred for 24 h at room temperature on magnetic stirrer at 600 rpm, then solution dried at 105 °C for 24 h by removing moisture. Since the utilization of sodium hydroxide removes natural fats and waxes from the surface of the biomass, this treatment promotes the effective surface area available [29]. The powder was taken out from the oven and washed several times with distilled water to reach a neutral pH. The powder was put back in the oven at 105 °C for 12 h to remove moisture. To synthesize ACAP adsorbent, AP slice was dried and placed in the crucible for preparation, which was filled with graphite to prevent oxidation. It was then maintained in a furnace at 500 °C for 2 h. To synthesize ACAPMP adsorbent, apple pomace was modified by potassium permanganate and the dried AP was mixed with 0.1 M potassium permanganate solution. Potassium permanganate is a strong oxidizing agent that can also achieve surface oxidation. The oxidation reaction may increase the incorporation of the precursor into the feedstock. This forms a novel engineered biochar after treatment [30]. The solution was then dispersed using ultrasonic homogenizer with 300 W for 20 min. This was divided into 10 (2-minute periods) due to a decrease in power of the device's waves after a few min and in order to be able to emit the same waves from the device. Due to ultrasonic homogenizer generated locally high temperature (especially at the head of the probe), therefore, an ice bath should be employed to keep the fixed temperature of the solution. The temperature of the solution was usually kept constant at about 30 to 35 °C by using an ice bath. After this step, the sample was dried at 105 °C for 24 h by removing the moisture. After that, the powder was placed in crucible for activation. The crucible was filled with graphite to prevent oxidation. It was finally maintained in a furnace at 500 °C for 2 h. All of the samples were ground via ball mill for 3 h at 320 rpm under argon gas (ratio 1 : 13, adsorbents to balls).

3. Adsorption Investigations

The concept of isotherm is employed for equilibrium curves for the adsorption process, that the isotherm is characteristics for a specific system at a special temperature. The adsorption capacity (q) of heavy metals onto adsorbents was determined by the following equation:

$$q_t = \frac{(C_0 - C_t)}{m} V \tag{1}$$

where q_t (mg/g) is the adsorption capacity of heavy metal at time t, C_0 (mg/L) and C_t (mg/L) indicate the initial heavy metal concentration and the concentration of heavy metal at time t, respectively. V (L) is the volume of solution, and m (g) stands for the mass of the adsorbent.

Langmuir and Freundlich are two common isotherms which are applied to determine the adsorption isotherm parameters. Langmuir isotherm is defined as linear and non-linear form. The non-linear Langmuir isotherm equation is described as [31]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is adsorption capacity in equilibrium state (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of heavy metal (mg/L) and K_L is the Langmuir constant correlated to the adsorption equilibrium (L/mg) [31]. The Freundlich isotherm equation is written as follows [32]:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F (mg/g) and n are the Freundlich constants and indicate adsorption capacity at unit concentration and adsorption intensity, respectively. Both K_F and n can predict the feasibility of heavy metal adsorption process [32].

4. Design of Experiments

Successful application of the design in the development of the

Table 2. Experimental ranges and levels of the independent test variables

Independent variables	Factor (Xi)	Ranges and levels		
		−1	Center	+1
Adsorption type	(X_1)	APMSH	ACAP	ACAPMP
Time (h)	(X_2)	1	3	5
Concentration (ppm)	(X_3)	10-50	25-125	40-200
pH	(X_4)	6		9

Table 3. The 4-factors BBD in together with the observed responses of zinc, cadmium, lead and copper

Order of running experiment	Level value of each variable in the experimental run				Removal efficiency (%)			
	X_1	X_2	X_3	X_4	Zinc	Cadmium	Lead	Copper
10	ACAP	5	10-50	6	98.90	94.04	99.60	97.22
11	ACAP	1	40-200	6	94.18	87.16	98.68	97.51
24	ACAP	5	40-200	9	98.65	96.45	99.50	99.18
5	APMSH	3	10-50	6	93.40	77.07	97.10	95.66
6	ACAPMP	3	10-50	6	93.60	81.00	96.90	95.98
19	APMSH	3	40-200	9	92.53	93.70	99.18	98.82
22	ACAP	5	10-50	9	99.20	95.70	99.70	97.30
20	ACAPMP	3	40-200	9	98.03	94.15	99.23	98.84
9	ACAP	1	10-50	6	89.10	72.50	96.50	94.26
2	ACAPMP	1	25-125	6	94.52	88.46	98.20	97.00
8	ACAPMP	3	40-200	6	97.75	93.81	99.18	98.82
12	ACAP	5	40-200	6	98.53	95.85	99.38	99.16
18	ACAPMP	3	10-50	9	93.80	81.85	97.40	96.44
15	APMSH	5	25-125	9	98.52	96.26	99.60	98.74
1	APMSH	1	25-125	6	93.56	87.07	98.00	96.18
13	APMSH	1	25-125	9	94.08	87.11	98.24	96.63
14	ACAPMP	1	25-125	9	95.08	88.72	98.32	97.58
4	ACAPMP	5	25-125	6	99.12	96.34	99.64	98.77
23	ACAP	1	40-200	9	94.70	90.46	98.70	97.60
7	APMSH	3	40-200	6	97.50	93.67	99.15	98.69
21	ACAP	1	10-50	9	89.20	73.92	96.50	94.48
17	APMSH	3	10-50	9	93.60	80.98	97.30	95.44
3	APMSH	5	25-125	6	98.12	95.22	99.28	98.82
16	ACAPMP	5	25-125	9	99.28	96.44	99.72	98.87

production process can basically reduce the time and costs of production and lead to processes and products that have better performance and reliability than those obtained by using other methods. DOE method can be used in most processes to improve quality. In most industries, correct and effective application of DOE leads to increase in efficiency, reduces variability and delay time of the design and develops better products and finally leads to customer satisfaction. For this study, to minimize the number of experiments and to optimize the effective parameters, the Box-Behnken design was used based on response surface methodology [33].

4-1. Box-Behnken Design

In this study, a BBD based on RSM was employed to obtain an appropriate mathematical model for prediction of removal heavy metals. From among the four subordinate methods of RSM (i.e., Box-Behnken design, central composite design, circumscribed central composite and inscribed central composite), BBD involves fewer experiments in designing processes with three or four factors [33]. To remove heavy metals from wastewater, the effective variables in this study include type of adsorbent, time and concentration as continuous factors and pH as categorical factor. As shown in Table 2, the type of adsorbent (X_1) ranged from APMSH, ACAP and ACAPMP, time (X_2) ranged from 1 to 5 (h), concentration (X_3) ranged from 10-50 to 40-200 (ppm) and pH (X_4) ranged from 6 to 9. Based on this data, 24 experiments were designed for each metal.

RESULTS AND DISCUSSION

Table 3 indicates the results of DOE and removal of zinc and cadmium from wastewater. Also, as shown in this table, the rates of removal of zinc, cadmium, lead and copper were different in the three adsorbents adsorptions and their performance varied.

Fig. 1 shows the removal capacity percent of the heavy metal ions, which had the highest removal value for the zinc in experi-

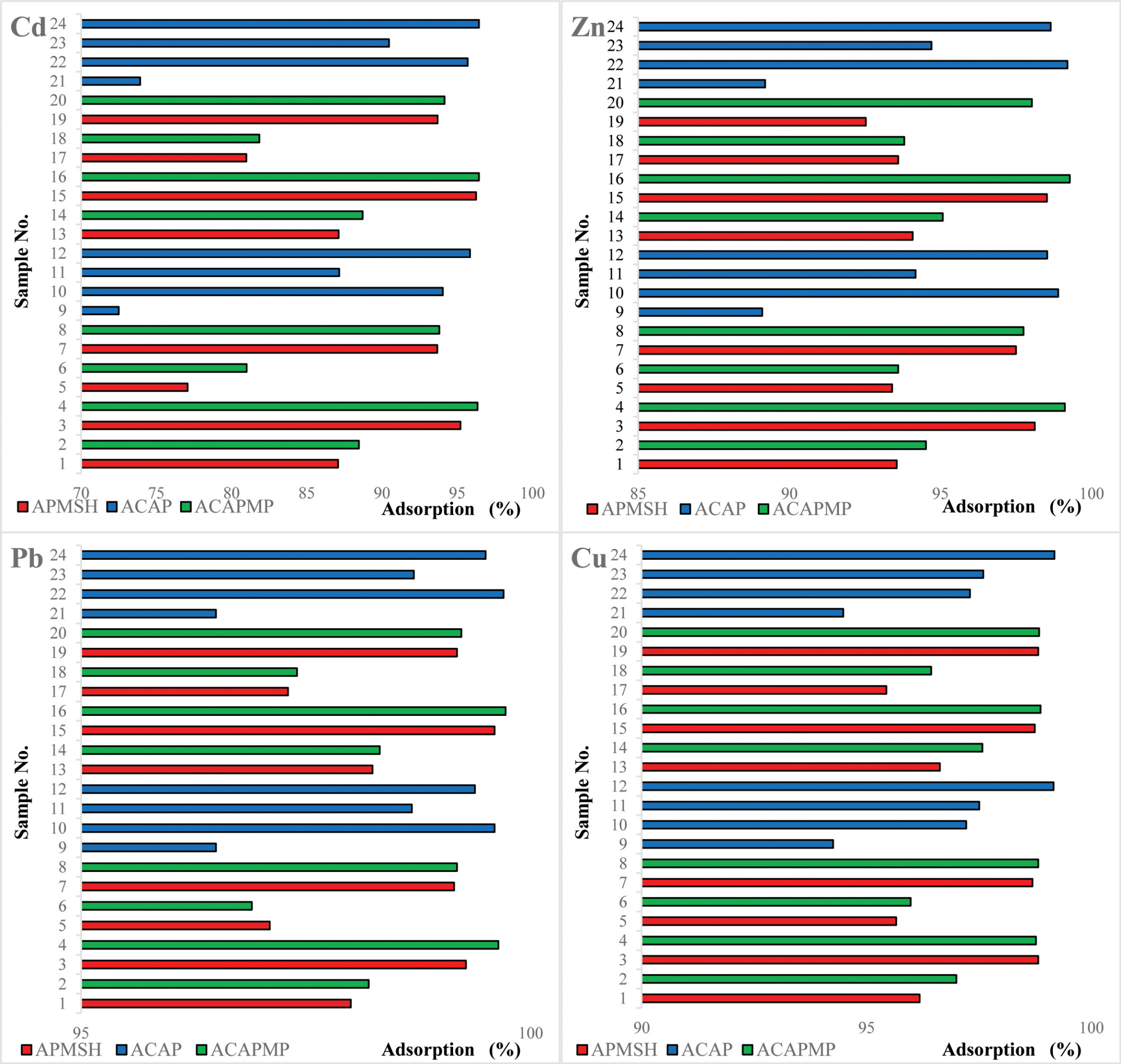

Fig. 1. Bar chart of efficiency percentage of heavy metal ion removal.

ment No.16 such that the adsorbents removed 95.62% of zinc. Also, the highest removal value for the cadmium was in experiment No. 24 where the adsorbents could remove an average of 89.08% of cadmium. Further, the highest removal value was for lead in experiment No. 16 where the adsorbents could remove an average of 98.54% of lead. Also, the highest removal value was for copper in experiment No. 24 where the adsorbents could remove an average of 97.41% of copper. Table 3 demonstrates the highest affinity of the adsorbents towards lead than the other heavy metal ions (Cu^{2+}, Zn^{2+} and Cd^{2+} respectively), in line with the predictions of some researchers. For example, Papageorgiou et al. proposed that the interactions of metals with ligands are influenced by three factors, such as the ion radius of heavy metal, electronegativity, and charge [34]. So, it can be predicted that the strength of covalent bonds between lead ion and adsorbent is higher than other heavy metals. In addition, the difference in heavy metal binding capability in the adsorption process may be described based on the classification of heavy metal ions. The lead element can be categorized as an intermediate acid while zinc, copper and cadmium are recognized as "soft" acids, (according to the hard-soft-acid-base (HSAB) concept) [34] and also, adsorbents have the "hard" carboxyl base. Therefore, the adsorption efficiency would exhibit a higher removal affinity towards lead compared to other heavy metals (zinc, copper and cadmium, respectively).

Table 4. ANOVA results for the zinc, cadmium, lead and copper removal

Source of variations	The Zinc removal			
	DF	Mean square	F-value	P-value
Model	12	7.67728	19.82	0.000
Linear	4	7.25098	56.17	0.000
X_1	1	0.10081	3.12	0.105
X_2	1	5.94141	184.09	0.000
X_3	1	1.17722	36.48	0.000
X_4	1	0.03154	0.98	0.344
Square	2	0.18276	2.83	0.102
Error	11	0.35501		
Total	23	8.03230		

Source of variations	The Cadmium removal			
	DF	Mean square	F-value	P-value
Model	12	27.2048	35.74	0.000
Linear	4	21.5731	85.02	0.000
X_1	1	0.5151	8.12	0.016
X_2	1	18.1806	286.61	0.000
X_3	1	2.5339	39.95	0.000
X_4	1	0.3436	5.42	0.040
Square	2	0.2098	1.65	0.016
Error	11	0.6978		
Total	23	27.9061		

Source of variations	The Lead removal			
	DF	Mean square	F-value	P-value
Model	12	12.1537	17.93	0.000
Linear	4	12.0603	53.39	0.000
X_1	1	0.6241	7.41	0.020
X_2	1	22.4913	267.15	0.000
X_3	1	2.6002	30.88	0.000
X_4	1	0.2542	3.02	0.344
Square	2	0.0681	0.60	0.102
Error	11	0.6213		
Total	23	12.7750		

Source of variations	The Copper removal			
	DF	Mean square	F-value	P-value
Model	12	29.5159	29.22	0.000
Linear	4	25.9698	77.12	0.000
X_1	1	0.0689	1.22	0.293
X_2	1	10.5625	187.02	0.000
X_3	1	1.2939	22.91	0.001
X_4	1	0.1350	2.39	0.150
Square	2	1.3462	7.99	0.007
Error	11	0.9261		
Total	23	30.4420		

1. Analysis of Variance

Analysis of variance is a collection of statistical models and their associated estimation procedures used to analyze the differences among group means in a sample. That includes degree of freedom, sum of squares, F-value and P-value for each factor. ANOVA for each heavy metal, zinc, cadmium, lead and copper, are shown in Table 4, respectively, for model adequacy checking. Mutual effect of variables and responses, used by ANOVA was analyzed. The influence interaction of F-value will be better when the amount of P-value is low (For proving model adequacy, quantity P-Value must be less than 0.05.) [33]. Table 4 demonstrates that quantity P-value of the model for all heavy metals is less than 0.0001. The obtained results confirm that the impact of all parameters (independent test variables) cannot be ignored and are important in experiments. Also, the used model could be an efficient model for predicting experimental values. Furthermore, bigger quantity F-value was another reason to prove the model adequacy. F-value model for zinc is 19.82, for cadmium is 35.74, for lead is 17.93 and for copper is 29.22, that shows the proper performance of the model presented for data analysis.

Table 5 illustrates the correlation coefficient values of adsorption of heavy metals (zinc, cadmium, lead and copper). R^2, adjusted R^2, and predicted R^2 values is close to 100%, adjusted R^2 and predicted R^2, that shows authority of model prediction, less than 20% different. Therefore, these values are acceptable. As a result, all of these

Table 5. Correlation coefficient values for heavy metal ions removal

Heavy metal ions	R^2 values		
	R^2	R^2_{adj}	R^2_{perd}
Zinc	95.58%	90.76%	78.96%
Cadmium	97.50%	94.77%	83.31%
Lead	95.14%	89.83%	76.85%
Copper	96.96%	93.64%	85.52%

Table 6. Heavy metal adsorption linear equations at pH=6, 9

Heavy metal ions	linear equations	
	pH=6	pH=9
Zinc	% Removal (y)=$0.732+0.474\ X_1-0.309\ X_2+0.0404\ X_3$ $-0.1262\ X_1 * X_1+0.0216\ X_2 * X_2+0.0031\ X_1 * X_2$ $-0.00217\ X_1 * X_3-0.00558\ X_2 * X_3$	% Removal (y)=$0.684+0.467\ X_1-0.292\ X_2+0.0379\ X_3$ $-0.1262\ X_1 * X_1+0.0216\ X_2 * X_2+0.0031\ X_1 * X_2$ $-0.00217\ X_1 * X_3-0.00558\ X_2 * X_3$
Cadmium	% Removal (y)=$2.111+0.223\ X_1+0.048\ X_2+0.0185\ X_3$ $-0.024\ X_1 * X_1-0.0528\ X_2 * X_2-0.0774\ X_1 * X_2$ $+0.01608\ X_1 * X_3-0.00636\ X_2 * X_3$	% Removal (y)=$2.296+0.028\ X_1+0.100\ X_2+0.0108\ X_3$ $-0.024\ X_1 * X_1-0.0528\ X_2 * X_2-0.0774\ X_1 * X_2$ $+0.01608\ X_1 * X_3-0.00636\ X_2 * X_3$
Lead	% Removal (y)=$2.039+0.057\ X_1-0.203\ X_2+0.00413\ X_3$ $-0.013\ X_1 * X_1-0.0297\ X_2 * X_2-0.0156\ X_1 * X_2$ $-0.00033\ X_1 * X_3+0.000125\ X_2 * X_3$	% Removal (y)=$1.893+0.089\ X_1-0.222\ X_2+0.00404\ X_3$ $-0.013\ X_1 * X_1-0.0297\ X_2 * X_2-0.0156\ X_1 * X_2$ $-0.00033\ X_1 * X_3+0.000125\ X_2 * X_3$
Copper	% Removal (y)=$4.918-0.775\ X_1-1.298\ X_2+0.01396\ X_3$ $+0.049\ X_1 * X_1+0.1313\ X_2 * X_2+0.1237\ X_1 * X_2$ $+0.00017\ X_1 * X_3-0.002975\ X_2 * X_3$	% Removal (y)=$4.497-0.795\ X_1-1.214\ X_2+0.01398\ X_3$ $+0.049\ X_1 * X_1+0.1313\ X_2 * X_2+0.1237\ X_1 * X_2$ $+0.00017\ X_1 * X_3-0.002975\ X_2 * X_3$

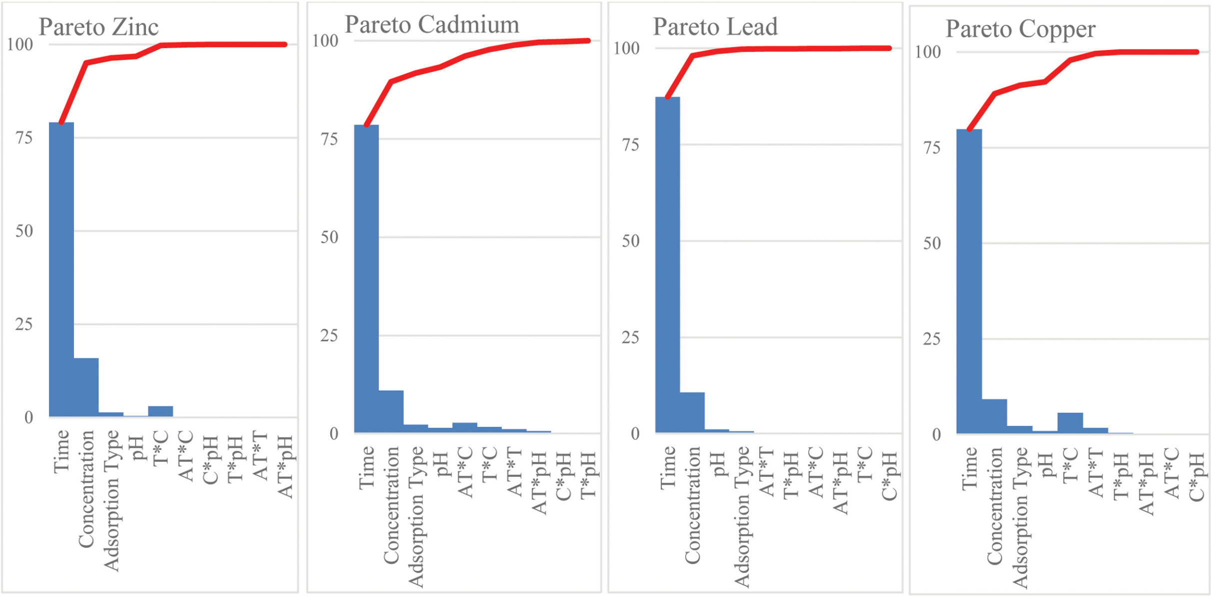

Fig. 2. Pareto graphic analysis.

statistical criteria prove the model as an appropriate model for fitting data [33].

According to experimental results, an empirical relationship (the quadratic polynomial) between the independent variables (type of adsorbent (X_1), time (X_2) and concentration (X_3)) and response (heavy metals removal efficiency) at pH=6 and pH=9 was obtained. Table 6 indicates the linear equations at various pH. The difference in linear equations between heavy metals is noticeable. But for each heavy metal, there is no imperceptible difference at various pH. Note that the negative and positive sign before the coefficient (in the quadratic polynomial) displays the antagonistic and synergistic effect, respectively [35]. According to Table 6, concentration (X_3) has synergistic effects in all of the quadratic polynomial, while type of adsorbent (X_1) indicates synergistic effects commonly. Also, time (X_2) exhibits an antagonistic effect commonly in the equations.

Pareto graphic analysis is presented in Fig. 2. As can be seen, all four chosen independent variables have a different effect on the efficiency of pollution adsorption process. Among the variables, time with an average of 80% created the main effect on the efficiency of heavy metals removal.

2. Effect of Variables

The effect of synthetic adsorbents on the adsorption of heavy metals is shown in Fig. 3. Generally, the impact of synthetic adsorbents on heavy metal adsorption is approximately uniform. But what can be seen from Figs. 1 and 3 and Table 3, ACAPMP adsorbent commonly has the highest effect on heavy metal adsorption and ACAP adsorbent has the lowest removal of heavy metals; that is the reason it can be chemically assisted treatment. According to previous works [29,30], the chemical treatment enhances the effective surface area available and also causes the forming of the novel engineered biochar. The equilibrium time is one of the important

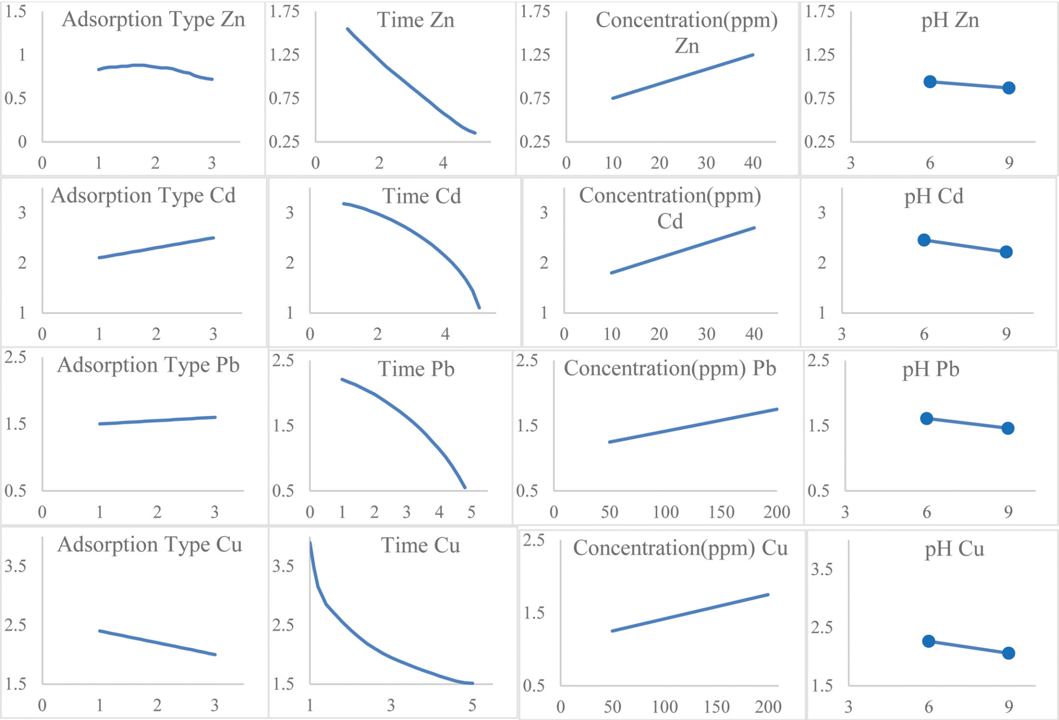

Fig. 3. Plot of the factors effect on the results of heavy metal adsorption.

factors to design a low-cost wastewater treatment system. It is obvious that the adsorption capacity will increase as more contact time is given to the samples. The adsorption of zinc and cadmium at various initial concentrations (10, 25, and 40 mg/L) and for lead and copper at various initial concentrations (50, 125, and 200 mg/L) was investigated as a function of contact time to determine the necessary adsorption time. In different times (1, 3 and 5 h) for zinc is achieved 93.05, 95.03 and 98.79% removal for average all three zinc concentrations, respectively. Also, for other heavy metals in time 1, 3 and 5 h, respectively, is achieved 84.43, 87.01 and 95.79% for cadmium, 97.89, 98.18 and 99.55% for lead and 96.40, 97.34 and 98.51% removal heavy metals. Based on achieved result, maximum level of adsorption is observed for 5 h and minimum level of adsorption for 1 h. The equilibrium adsorption increases from 6.15 mg/g to 14.07 mg/g while % removal of zinc observed in similar behavior, as increases from 93.85 to 96.48% when initial concentration is increased from 10 mg/L to 40 mg/L. The equilibrium adsorption increases from 17.87 mg/g to 27.38 mg/g while % removal of cadmium observed in similar behavior, as increases from 83.91 to 93.16% when initial concentration is increased from 10 mg/L to 40 mg/L. The equilibrium adsorption increases from 11.88 mg/g to 17.50 mg/g while % removal of lead observed in similar behavior, as increases from 97.63 to 99.13% when initial concentration is increased from 50 mg/L to 200 mg/L. The equilibrium adsorption increases from 20.76 mg/g to 28.45 mg/g while % removal of copper observed in similar behavior, as increases from 95.85 to 98.58% when initial concentration is increased from 50 mg/L to 200 mg/L. The solution pH is a prominent factor controlling adsorption of metal ions onto adsorbent. It was found that high adsorption capacity of heavy metals occurs at pH 9 and 6, respectively. As seen in Fig. 3, adsorption capacity increased from 95.55 to 95.69% for zinc, 82.90 to 88.52% for cadmium, 98.47 to 98.62% for lead and 97.34 to 97.49% for copper when the solution pH was increased from 6 to 9.

3. Residual Analysis

Fig. 4 exhibits a residual plot of heavy metal adsorption, which is used for model adequacy checking. Four assumptions are raised to prove model adequacy. The first assumption is to discuss the normality of data or remaining values, which are examined using normal probability plot. Residual values are almost normal. Second assumption is to discuss variance fixed assumption. Fig. 4 also indicates versus fitted value plots adsorption of heavy metals. As can be seen in the plot, the data do not follow a specific trend, and it can be said that data variance is almost fixed. The third assumption for model adequacy checking is data independence over time assumption. Also, Fig. 4 shows versus observation order plot of adsorption heavy metals, Points on the plot do not show a specific trend, so it can be said that the data is independent of time. The fourth assumption for model adequacy checking is model accuracy assumption, which uses Table 4 (ANOVA Tables) and amount of R^2s to model accuracy checking. This assumption was examined above.

Fig. 5(a) shows the effect between time and concentration on zinc adsorption, which has high level adsorption at 5 h and concentration of 10 ppm. Fig. 5(b) shows the effect between time and concentration on cadmium adsorption, which has high level adsorption at 5 h and concentration of 10 ppm. Fig. 5(c) shows the effect between time and concentration on lead adsorption, which has high level adsorption at 5 h and 50 ppm. Fig. 5(d) shows the effect between time and concentration on copper adsorption, which

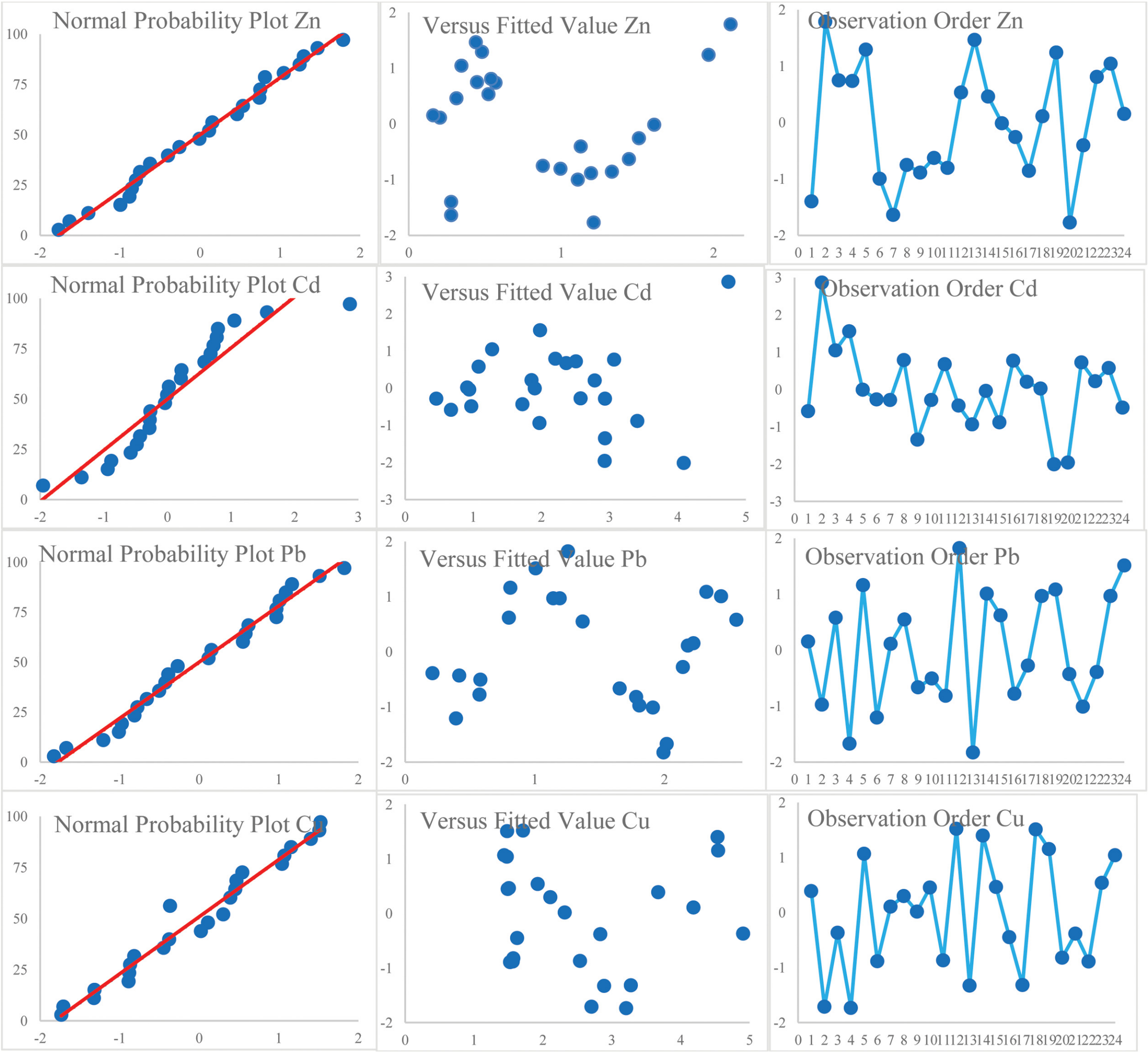

Fig. 4. Residual Plot of heavy metal ions adsorption.

has high level adsorption at 5 h and concentration of 50 ppm.

4. Optimization

The main purpose of DOE is to determine the optimal values of factors for achieving the maximum response value. Optimization is aimed at finding conditions in which the experiment is best responding. The optimal value of factors shows the degree of the vicinity to the chosen amount and shows the degree of the probability by considering how close the interaction is between them. Proximity of utility function to the value of 1 indicates the possibility of a greater predictability of real optimal response. Proximity of the value of utility function to zero indicates that the proposed optimal response is inappropriate and far from a real optimal response [36]. Fig. 6 illustrates optimal response plot for heavy metal adsorption. Value y is the value of optimal sample response, which is also indicated by blue horizontal line, and value of Cur, which is the abbreviation of current factor, shows optimal response in each factor as red vertical lines. According to obtained consequences in section 3.2 and Fig. 6, it can be concluded that ACAPMP adsorbent has the highest effect on the adsorption of heavy metals.

5. Adsorption Isotherms

Table 7 presents parameters of Langmuir (K_L and q_m) and Freundlich (K_F and 1/n) isotherms as well as the regression coefficients (R^2) for the adsorption of the heavy metals. Furthermore, the fitting heavy metals isothermal adsorption process on Langmuir and Freundlich adsorption isotherms models is displayed in Fig. 7. The Freundlich model is applied to explain heterogeneous systems and Langmuir model describes the surface as homogeneous. Also, this model is a monolayer adsorption model [37]. Fig. 7 exhibits adsorption capacity (q_e) versus the equilibrium concentration (C_e) for zinc, cadmium, lead and copper with the correlation coefficient of 0.94, 0.73, 0.85 and 0.99, respectively (for Langmuir isotherm). The monolayer adsorption capacity calculated for zinc, cadmium, lead and copper is 27.52, 30.76, 19.69 and 32.88 mg/g, respectively (for the Langmuir model). Based on the Freundlich model, adsorption capacity (q_e) against the equilibrium concentration (C_e) for zinc, cadmium, lead and copper with the correlation

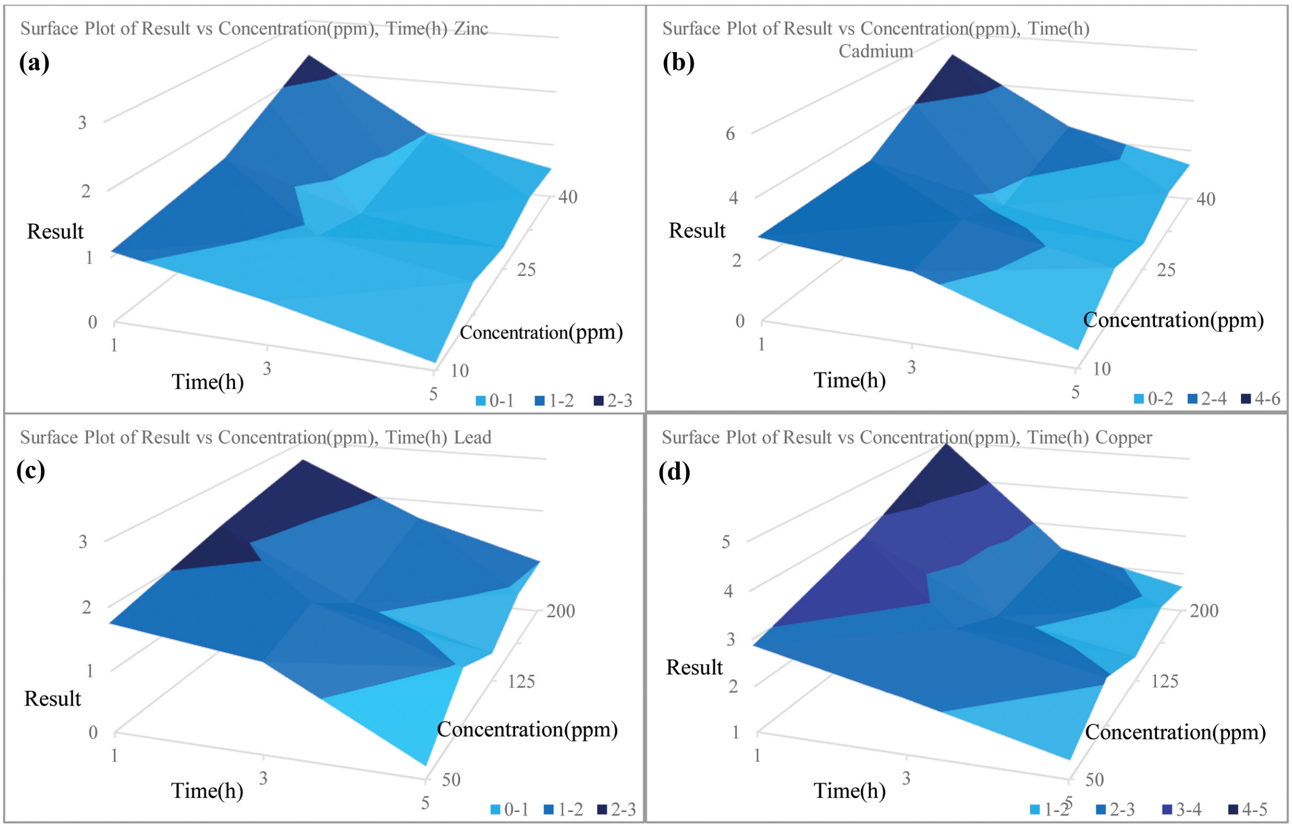

Fig. 5. 3D Surface plots of heavy metal ions adsorption.

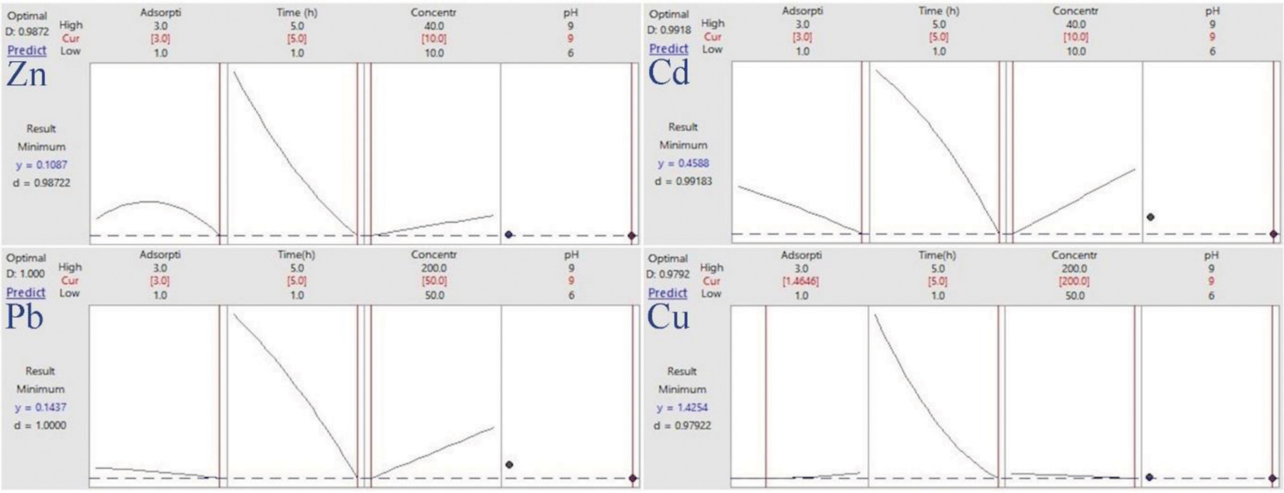

Fig. 6. Optimization plots of heavy metal adsorption.

Table 7. Parameters of isotherm models for adsorption of heavy metals by adsorbents

Heavy metal ions	Langmuir			Freundlich		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F (mg/g)	1/n	R^2
Zinc	0.0244	27.52	0.94	1.32	0.6333	0.92
Cadmium	0.1197	30.76	0.73	8.13	0.3157	0.83
Lead	0.0278	19.69	0.85	3.82	0.2821	0.93
Copper	0.0349	32.88	0.99	8.70	0.2279	0.95

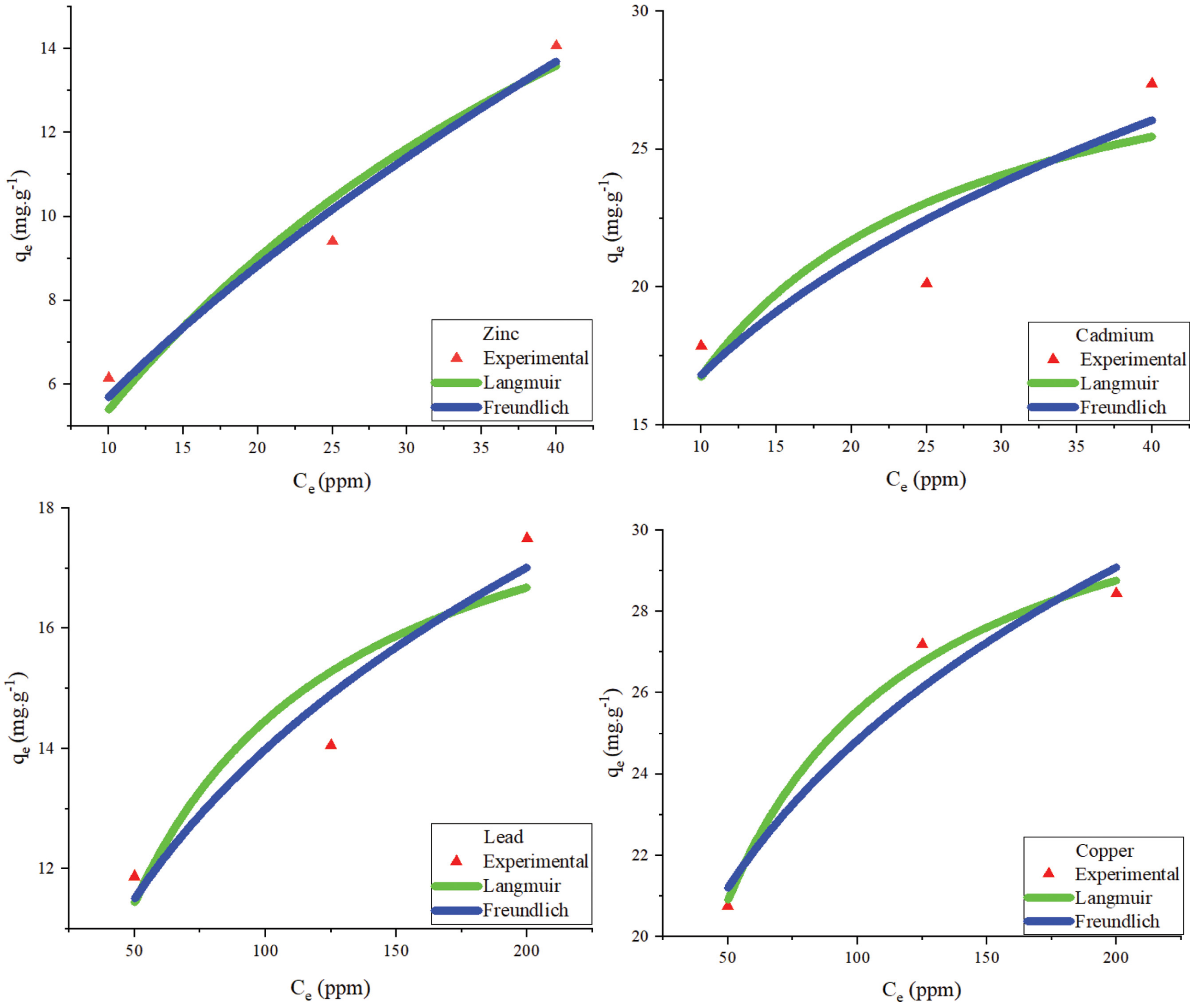

Fig. 7. The equilibrium adsorption of adsorption of heavy metals by adsorbents.

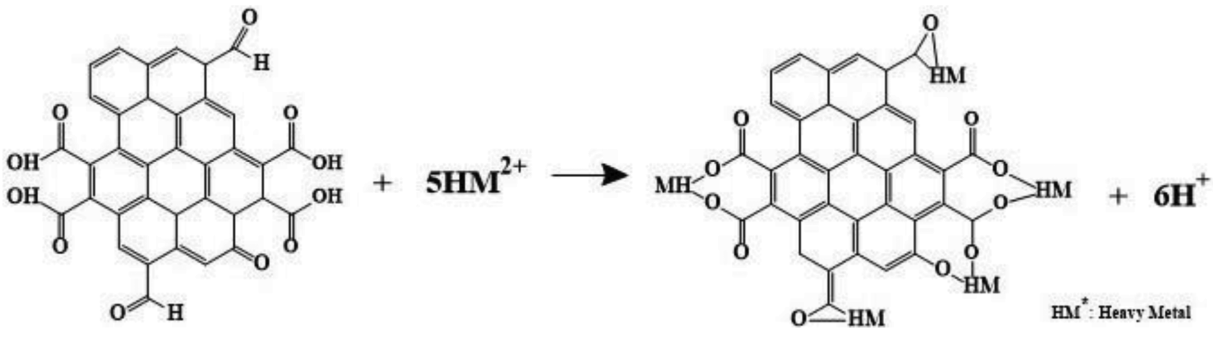

Fig. 8. Schematic of adsorption mechanism of heavy metals (zinc, cadmium, lead and copper).

coefficient of 0.92, 0.83, 0.93 and 0.95 was achieved. Due to the Freundlich parameter, 1/n should be between 0 and 1 which confirms that the adsorption is linear and uniform throughout the adsorbent surface [37]. According to Table 7, the Freundlich parameter 1/n for zinc, cadmium, lead and copper is 0.633, 0.316, 0.282 and 0.228.

Strong correlation coefficients (R^2) demonstrated both the Langmuir and Freundlich isotherms models agreed with experimental data of heavy metals removal. For copper both Langmuir and Freundlich gave the best correlation compared to other metals. Among the two isotherm models, the Freundlich isotherm indicates the best fit for all heavy metals. The regression coefficient values demonstrated that the Freundlich model (R^2>0.91 averagely) fitted better than the Langmuir model (R^2>0.88 averagely).

Fig. 8 demonstrates the adsorption reaction between heavy metals ions and functional groups. Since the reaction of lead ion by absorbents (apple-based) occurs with carboxyl groups, commonly. Therefore, it can result in that the other heavy metal ions are obliged to react with surface functional groups, especially carboxyl groups. A previous study showed that carboxyl groups (COOH) on carbonized surfaces (biochar) can react with lead ions [38]. Note that surface modification (treatment) causes to break holes in the wall of macropores and expands mesopores and micropores. Therefore, the surface area available and functional groups such as carboxyl, ketone, phenol and ester of the adsorbents increased after treatment process.

6. Brunauer-Emmett-Teller (BET) Analysis

The porous characteristics analyzed by the BET are presented in Table 8. According to Table 4, BET surface areas and pore size were changed with the treatment of adsorbents. The evaluation of adsorbents shows that with the use of chemical-assisted treatment the specific surface areas of the samples (especially of ACAPMP

Table 8. Pore structures of the adsorbents

Sample	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
ACAP	26.299	0.03722	5.6611
APMSH	54.187	0.03998	5.1283
ACAPMP	128.681	0.04213	4.3297

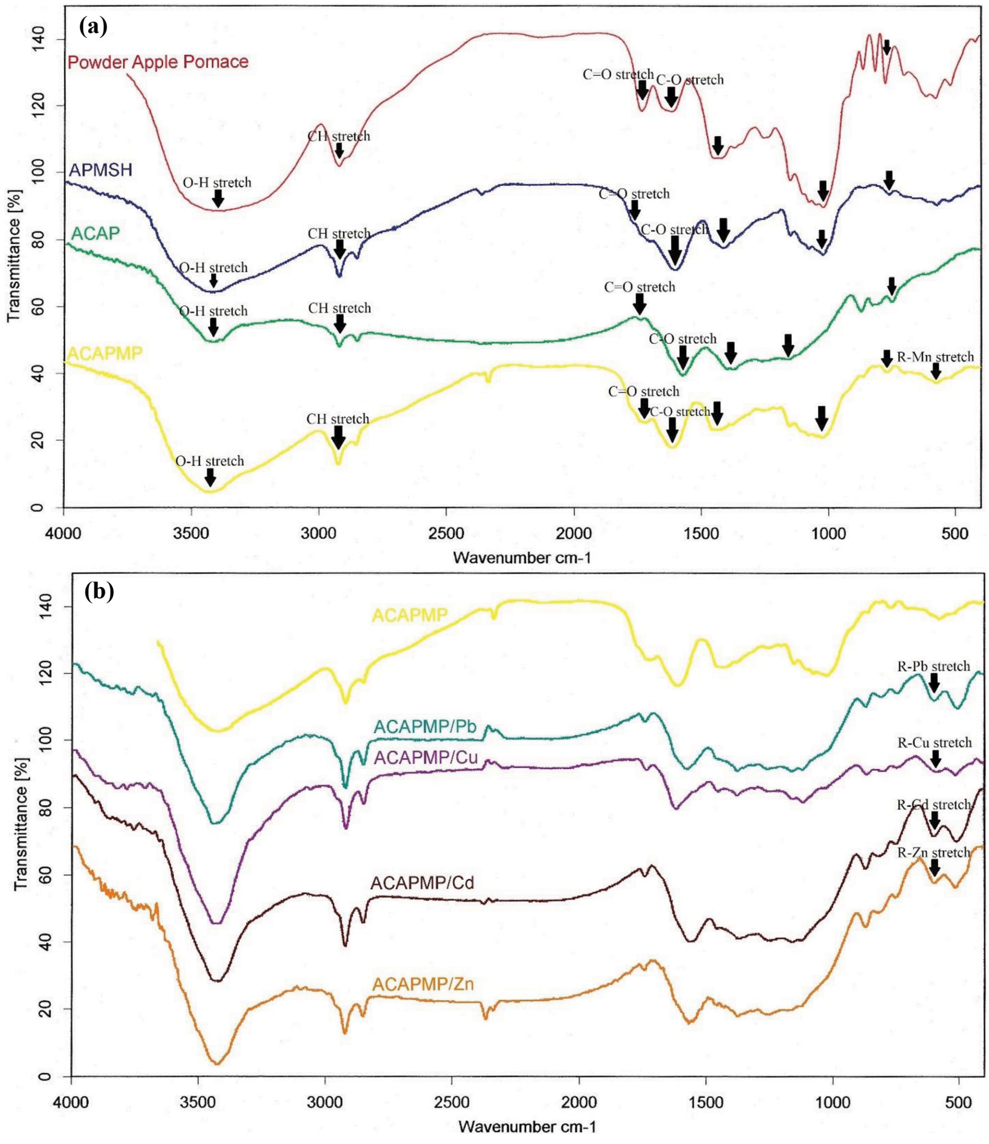

Fig. 9. FTIR spectra of (a) apple powder, APMSH, ACAP and ACAPMP adsorbents (b) Heavy metals adsorbed by ACAPMP adsorbents.

adsorbent) were improved. The reason can be the presence of plenty of micropores and mesopores after activation and modification due to oxidation process [39].

7. Fourier Infrared Transmission Spectroscopy

FTIR spectra of AP and three adsorbents before the adsorption process and also ACAPMP are shown in Fig. 9(a), (b), respectively. The peaks of the area (3,000-3,500 cm^{-1}) are related to (-OH) hydrogen bonds, including alcohols, phenols, and acids of carboxylic acid in pectin, cellulose, hemicellulose, lignin, and adsorbed water (moisture). The peaks of the area (3,000-2,800 cm^{-1}) are related to symmetrical and asymmetrical stretching in ketone and phenolic compounds (-CH) in groups CH$_2$ and CH$_3$. The peaks of the area (1,750-1,600 cm^{-1}) are related to stretching of amide functional group (-C=O) in the structure of lignin rings. The peaks of the area (1,600-1,500 cm^{-1}) are related to the stretching of carboxylic acid functional group (-C-O). The peaks of the area (1,500-

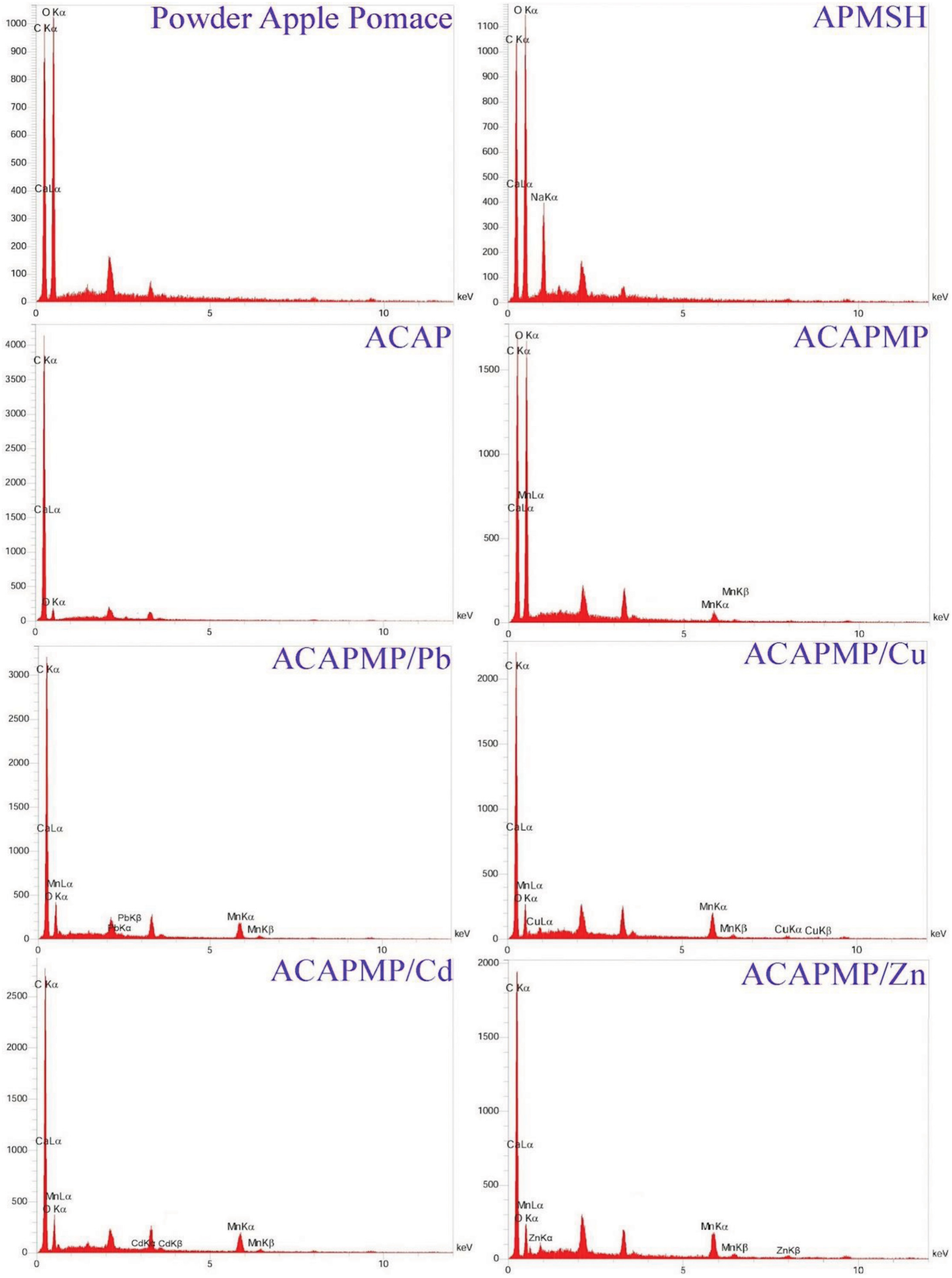

Fig. 10. EDS spectra of apple powder, APMSH, ACAP and ACAPMP adsorbents and heavy metals adsorbed by ACAPMP adsorbents.

1,400 cm^{-1}) are related to the stretching of aromatic group (-C-C). The peaks of the area (1,385-1,375 cm^{-1}) are related to the stretching of alkane. The peaks of the area (1,300-1,000 cm^{-1}) are related to the stretching (-C-O) in alcohol, ester, ether and carboxylic groups. Increased peak intensity in 1,600-1,000 cm^{-1} range is because of the carbon bonding. The FTIR peak of aromatic rings (-C-H) is (880-700 cm^{-1}). The peaks of the area (700-500 cm^{-1}) indicate symmetrical stretching. The peak intensity is decreased in this range because of cation-exchange [40].

In spectra of 1-4 in the above range, no significant peak is observed except in the ACAPMP spectrum, at (576 cm^{-1}) which is related to the manganese peak. In spectrum (ACAPMP/Pb) in the range (600-500 cm^{-1}), peak (597.52 cm^{-1}) is related to the presence of lead element and shows that lead in wastewater is adsorbed by adsorbent. In spectrum (ACAPMP/Cu) in range (600-500 cm^{-1}), peak (592 cm^{-1}) is related to the presence of copper element and shows that copper in wastewater is adsorbed by adsorbent. In spectrum (ACAPMP/Cd) in the range (600-500 cm^{-1}), peak (599 cm^{-1}) is related to the presence of cadmium element and shows that cadmium in wastewater is adsorbed by adsorbent. In spectrum (ACAPMP/Zn) in the range (600-500 cm^{-1}), peak (596 cm^{-1}) is related to the presence of zinc element and shows that zinc in wastewater is adsorbed by adsorbent. Therefore, by comparing spectra from 1-4 with spectra from 5-8, the peaks (597, 592, 599, and 596 cm^{-1}) are related to heavy metals that have been successfully adsorbed by the adsorbent [40-44].

7. Energy Dispersive Spectroscopy

Fig. 10 demonstrates EDS spectra of PAP and APMSH, ACAP, and ACAPMP adsorbents. The main components of apple are carbon and oxygen. In PAP spectrum, oxygen and carbon peaks are well represented. Due to the addition of sodium hydroxide to PAP, there have been changes in AMPSH spectrum compared to the previous spectrum: oxygen peak has increased and also sodium peak has been observed in this spectrum. PAP is placed in a crucible when charcoal and area around PAP in crucible is insulated with graphite to prevent oxidation when turning into charcoal; for this reason, as can be seen in ACAP spectrum, due to the charcoal process of PAP, carbon peaks have risen and oxygen peaks have declined, carbon and oxygen peaks have risen alike, indicating oxidation of sample. Also, manganese peaks are seen in this spectrum.

Fig. 10 indicates EDS spectra of heavy metals which are adsorbed by ACAPMP adsorbent. Heavy metals peaks show that heavy metals are well adsorbed (in Fig. 12). In addition, as for FTIR spectra of adsorbents and heavy metals adsorbed by ACAPMP adsorbent, there are good results and good overlap between FTIR and EDS spectra.

8. Field Emission Scanning Electron Microscopy

In Fig. 11A, PAP morphology is well seen; PAP is a spherical shape and has limited cavities. In Fig. 11B, with addition to sodium hydroxide to PAP, APMSH has crystalline form and morphology changes. In Fig. 11C, PAP is converted to charcoal, particle size is reduced and adsorption cross section is increased. Also, the shape of the particles is changed from spherical to crystalline. In Fig. 11D, compared to Fig. 11C, due to the carbon activation by potassium permanganate and the oxidation of the sample, adsorbent pores have increased. Morphology of APMSH, ACAP, and ACAPMP adsorbents has completely changed in comparison to PAP.

In Figs. 12A and 12B, ACAPMP adsorbent surface can be seen; there is no heavy metal on adsorbent surface. Figs. 12C to F are from ACAPMP adsorbent surface, which has adsorbed heavy metals (lead, copper, cadmium and zinc), respectively. As can be seen

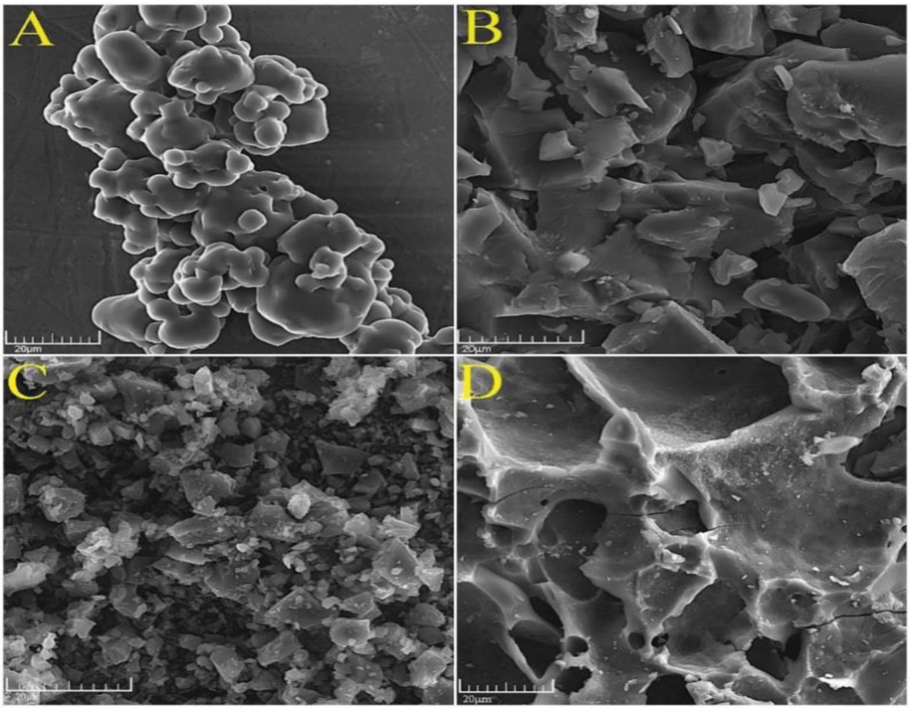

Fig. 11. FESEM images of apple powder and APMSH, ACAP and ACAPMP adsorbents.

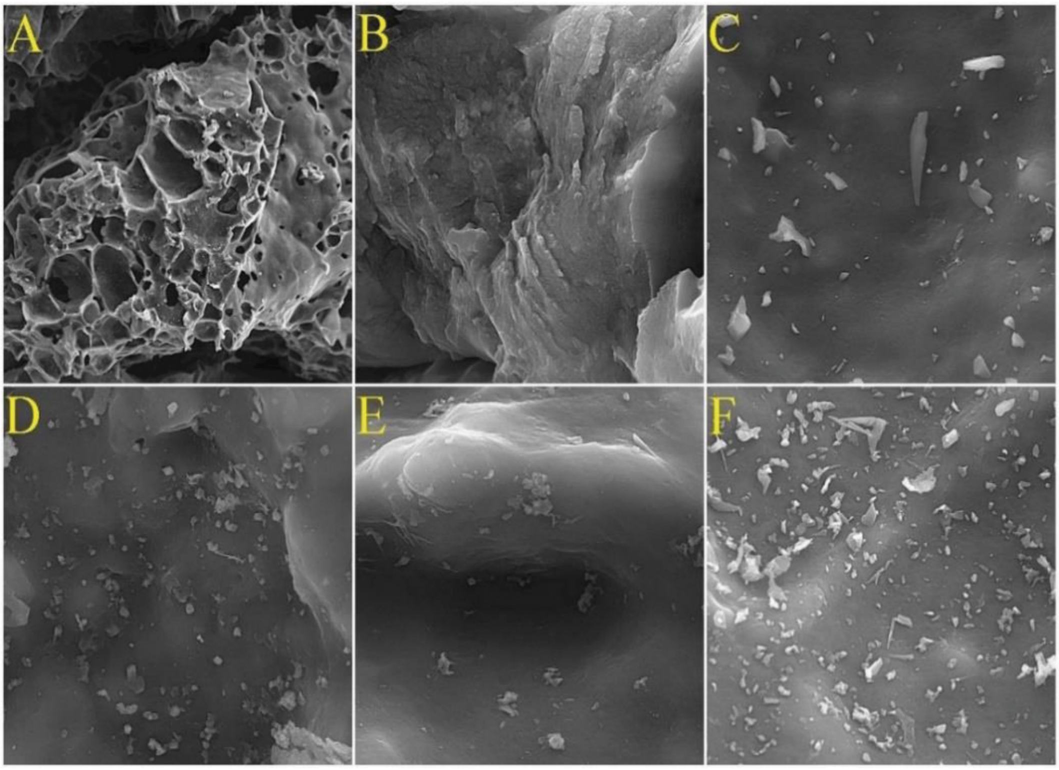

Fig. 12. SEM images of the ACAPMP adsorbent surface before and after heavy metal adsorption.

in the figures, small particles of heavy metals sit on adsorbent surface and confirm that adsorbing heavy metals by adsorbent has been successful, which corresponds to FTIR and EDS spectra.

CONCLUSION

The conclusions of this work can be drawn as follows:

- Three adsorbents of APMSH, ACAP and ACAPMP were synthesized using apple waste pomace with various methods. These biomass adsorbents were employed for removing four heavy metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}).
- BBD was applied for the experimental optimization and modeling. The time of removal, pH of solution, the type of adsorbent and concentration of heavy metal on the adsorption performance were chosen as independent of variables.
- ANOVA tables reported a high correlation coefficient for all heavy metals. As for zinc, cadmium, lead and copper ions, correlation coefficient achieved was $R^2_{adj}=0.908$, $R^2_{adj}=0.948$, $R^2_{adj}=0.898$ and $R^2_{adj}=0.936$, respectively. Also, based on ANOVA results, time is a significant variable among independent variables. The Pareto charts also illustrated that time has a notable effect on adsorption.
- The actual experiments indicated 89.10-99.28%, 72.50-96.45%, 96.50-99.72% and 94.26-99.18% heavy metal ions removal for Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}, respectively. Although APMSH and ACAP show appropriate adsorption potential for heavy metal ions, it is noteworthy that ACAPMP adsorbent was identified as the best removal for the heavy metal ions at optimal operation.
- The adsorption isotherms demonstrated that the Freundlich isotherm is favorable. The Freundlich parameter 1/n for all heavy metals was between 0 and 1.
- APMSH, ACAP and ACAPMP were characterized by BET, FTIR, FE-SEM and EDS before and after adsorption of heavy metal ions. BET consequences presented that the ACAPMP sample has a suitable surface area and pore size compared to other adsorbents. FTIR and EDS analyses exhibited functional group Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+} bond in the samples. FE-SEM images confirmed good preparation of ACAPMP adsorbent, so that surface morphology was altered. Also, FE-SEM showed high porosity of ACAPMP in comparison to other samples.
- Finally, this adsorption process has various preferences such as low cost, high active surface, availability of raw materials, and ease of synthesis.
- Due to the limitations in measuring heavy metals in atomic absorption apparatus (Shimadzu AA-6300), it is recommended to evaluate the efficiency of this adsorbent for the removal of urban wastewater in different conditions.

NOMENCLATURE

C_e	: the equilibrium concentration of heavy metal [mg/L]
C_t	: indicate the concentration of heavy metal at time t [mg/L]
C_0	: initial concentration of metal [mg/L]
HM	: heavy metal (zinc, cadmium, lead and copper)
K_F	: constant feature of the Freundlich equation [mg/g]
K_L	: constant feature of the Langmuir equation [L/mg]
m	: mass of the adsorbent [g]
n	: constant feature of the Freundlich equation
q_e	: adsorption capacity in equilibrium state [mg/g]

q_m : the maximum adsorption capacity [mg/g]
q_t : adsorption capacity of heavy metal at time t [mg/g]
R^2 : coefficient correlation
V : volume of metal solution [mL]
X : independent variables

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