I-Optimal Design of Numerous Metals Adsorption by Agro-Waste Activated Carbon

Ali A. Hanoon[1], **Sami D. Salman**[1*]

[1]Biochemical Engineering Department, Al-Khwarizmi College of Engineering, University of Baghdad, Baghdad 47024 Iraq
Corresponding Author [1*] E-mail: sami.albayati@gmail.com
sami@kecbu.uobaghdad.edu.iq

Abstract

This article presents the simultaneous adsorption of numerous metal ions Pb^{2+}, Cu^{2+}, and Zn^{2+} from synthetic solution by activated carbon produced from pomegranate peel (PP) using sulfuric acid and microwave activation. The raw material and pomegranate peel activated carbon (PPAC) were characterized by Brunaure-Emmett-Teller (BET), Field Emission Scanning Electron Microscopy (FESEM), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The effect of absorption time, pH, metal ions concentration, and activated carbon dose on the capacity and adsorption efficiency were investigated. The experimental data of activated carbon preparation and heavy metals adsorption were analyzed by Design-Expert software with I-optimal approach. The statistical analysis for removal efficiencies of Cu^{2+}, Pb^{2+} and Zn^{2+} indicated that the correlation models produced by the software were significant ($P < 0.05$). The maximum removal efficiencies at optimum conditions were obtained in order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$ with 99.373, 98.88 %, and 97.89%, respectively. Adsorption data at equilibrium conditions were fitted with two isotherm models; Langmuir and Freundlich as well as two kinetic models of pseudo first and second order, and, the results showed good agreement with Langmuir and second order kinetic model. The results showed that the pomegranate peel activated carbon could be used as an efficient adsorbent to remove Cu^{2+}, Pb^{2+} and Zn^{2+} from wastewater.

Keywords: Pomegranate peel; Microwave irradiation; Activated Carbon; I-optimal design

1. Introduction

The availability of potable and clean water is essential to human and animal for healthy lifestyle [1]. The environment has a variety of water sources. likes wells, rivers, lakes, ponds, marshes, seas, and oceans possess different qualities and properties. These properties are significantly impacted by human activities and environmental conditions including weather, water location, morphological properties, and vegetations availability in the environment. The weather and climate change affected in water quality (physical, chemical, and biological) due to temperature and rainfall [2]. The criteria of water quality for animals' protection from the effects of bio accumulative elements depends on their relative sensitivities and should be lower than that affected to the aquatic living organisms [3]. Water pollution due to the presence of nonmetals and metals in addition to bacteria or viruses is harmful to the human being health [4-6]. There are two types of heavy metals which can be classified as essential and non-essential metals depend on its concentration, the essential metals at low-concentration are considered as nontoxic or relatively nontoxic and its useful for the biological activities, various enzymatic reactions, oxygen utilization, bimolecular synthesis, …etc [7]. The essential heavy metals like Copper (Cu), Cobalt (Co), Iron (Fe), Manganese (Mn), and Zinc [8-10]. Whereas the non-essential heavy metals like Arsenic (As), Chromium (Cr), Cadmium (Cd), Lead (Pb), Mercury (Hg), and Selenium (Se) [11-14]. The presence of heavy metals in sources of water have motivated the researchers to find efficient methods of treatment to eliminate these metals from water sources [15-19]. Therefore, different methods were applied to remove heavy metals from water including adsorption, advanced oxidation, electrochemical, Electro-Fenton process, ion exchange, precipitation, and reverse osmosis [20-24]. Various studies were applied for removing heavy metal from water or wastewater by adsorption method using agricultural wastes such as beech leaves [25], charred pistachio shell [26], coconut husk [27], oil palm waste [28], rice husks [29], sawdust [30, 31], and waste tea leaves [32]. The carbon-based substance as activated carbon has high surface area, various pore structure, and different pores volume, with various functional groups likes aldehydes, carboxyl, carbonyl, phenols [33, 34].

However, the commercial activated carbon as efficient adsorber is considered as costly material [35, 36]. Several types of activated carbons were prepared from agricultural by-products, and waste using conventional and microwave methods have garnered increased interest due to their low-cost and availability. The properties of activated carbon mainly depend on the precursors and preparation techniques [37-40]. Different agricultural wastes and byproducts were used such as bamboo dust [41], coconut shell kenaf core [42], coconut shell [43], oil palm and empty fruit bunch [44, 45], pecan and almond shells [46, 47], peach stones and olive stones [48], rice husks [49], rice straw pellets, soybean hull pellets, sugarcane bagasse [50], sawdust [51, 52], Siri's seed pods [53, 54], water hyacinth [55] were used to prepared activated carbon adsorbent for various pollutants including mono and bimetals using conventional techniques. Whereas, Microwave as efficient technique was applied for activated carbon peroration using date stones [56], Ficus benjamina [57, 58], plum seed [59] and different agricultural waste [60]. The limitations of these researches including the adsorption of mono and bimetals using activated carbon prepared by microwave techniques or adsorption of multi metal with activated carbon prepared using conventional method have motivated this research. It is essential to investigate the competition impacts, affinity, and selectivity of metals adsorption using a variety of metals [61-63]. This study focuses the adsorption of multi-metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) from solution by activated carbon prepared from pomegranate peel with acid and microwave activation. Sulfuric acid was selected for chemical activation and microwave technique for heating to produce activated carbon preparation. The effect of pH, numerous metal ions concentration, adsorption time, and adsorbent dose on the capacity of adsorption and removal efficiency was investigated. The adsorption process was analyzed using the response surface method (RSM) with I optimal design methodology.

2. Materials and methods

All materials and experimental setup that used in this study are illustrated listed in Table 1.

Table 1. materials and experimental setup

Material	Chemical Formula	Purity	Origin	Application
Pomegranate peel	----	----	Local markets	Raw material
Sulfuric acid	H_2SO_4	99.999%	Germany (Sigma-Aldrich)	Chemical activation
Nitric acid	HNO_3	98%	Germany (Sigma-Aldrich)	pH adjustment
Sodium hydroxide pellets	NaOH	Pure	Germany (Sigma-Aldrich)	pH adjustment
Distilled water	H_2O	100%	Al-Khwarizmi Labs	Preparation and washing
Copper nitrate powder	$Cu\,(NO_3)_2{\cdot}6H_2O$	98%	Germany (Sigma-Aldrich)	Synthetic solution
Lead nitrate powder	$Pb\,(NO_3)_2$	99%	Germany (Sigma-Aldrich)	Synthetic solution
Zinc nitrate powder	$Zn\,(NO_3)_2{\cdot}6H_2O$	98%	Germany (Sigma-Aldrich)	Synthetic solution
Nitrogen	N_2	99.9%	Local markets	Microwave activation
Methylene Blue Dye	$C_{16}H_{18}ClN_3S$	~70 %	Germany (Sigma-Aldrich)	Methylene Blue Number (MBN)
Microwave Oven Rated Output 450 - 900 watts Microwave Frequency 2450 Hz	---	----	Made in China	Activated carbon preparation

2.1 Methylene Blue Number (MBN)

A stock solution with 50 mg/L of methylene blue dye was produced using 50 mg of the methylene blue dye with 1 liter of distilled water. Then ten samples of diluted solution ranged from 0.025 to 4 mg/L was prepared from the stock solution with distilled water, and the absorbance of the diluted solution samples were measured using UV-visible spectroscopy (λ = 660 nm). The calibration curve of the concentration with absorbance values is illustrated shown in Figure 1.

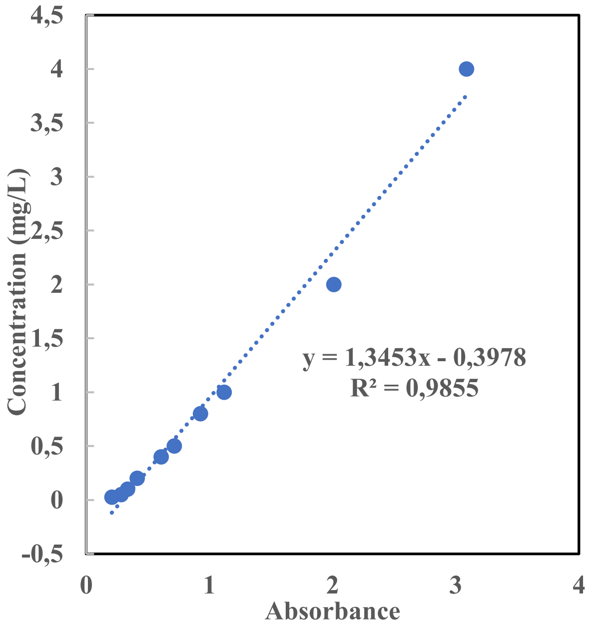


Figure. 1. Methylene blue dye calibration curve

2.2 Heavy Metals Solution

Synthetic of aqueous water was prepared for absorption experiments by dissolving metal nitrates in distilled water. A stock solution of Cu (II), Pb (II), and Zn (II) with 100 mg/L for each using annular grade copper nitrate Cu $(NO_3)_2 \cdot 6H2O$, lead nitrate Pb $(NO_3)_2$, and zinc nitrate Zn $(NO_3)_2 \cdot 6H_2O$. The desired concentration for 100 mL of metal ions was prepared from the stock solution varied (10-50) mg/L separately, then mixed together in 300 mL stopper bottles. The pH of solution was adjusted using 0.1 N of HNO_3 and/or NaOH.

2.3 Activated Carbon Preparation

Design Expert Software (13.0) with I-Optimal approach was selected as appropriate method for activated carbon preparation with multi-factor to generate a set number of experiments and reach the response of MBN with a limited number of experimental run trials, and provides a relationship between these multi factors at optimum operating conditions [64, 65]. The independent factors (multi-factor) levels selected, and number of runs in I-Optimal generated by software are shown in tables 2 and 3.

Table 2. Independent variables of activated carbon preparation

Factors	Levels		
Sulfuric acid concentration (%)	40	60	80
Impregnation ratio IR (ratio)	1:1	1:2	1:3
Impregnation time (hr)	2	4	6
Power of activation (watt)	450	720	900
Time of activation (min)	7	14	21

Table 3. I-Optimal approach for activated carbon preparation

Run	Aced concentration (%)	Impregnation ratio (ratio)	Impregnation time (hr)	Power (watt)	Activation time (min)	MBN (g/g)
1	80	3	4	720	7	24.713247
2	40	3	6	450	7	24.356002
3	40	1	2	900	7	25.13029
4	80	1	6	450	21	25.18612
5	80	1	6	900	7	25.126254
6	40	1	6	900	7	25.05159
7	60	1	4	720	14	25.120873
8	60	1	4	720	14	24.964818
9	40	1	2	450	21	24.804054
10	80	1	2	900	14	24.928629
11	60	3	6	900	14	23.626244
12	80	2	6	450	7	24.938584
13	40	2	4	720	14	24.904952
14	**60**	**3**	**6**	**450**	**21**	**25.198227**
15	40	3	2	900	21	23.677366
16	60	3	2	450	14	24.103826
17	80	1	2	450	7	24.520869
18	60	2	4	900	7	24.376922
19	40	2	4	720	14	25.188138
20	40	1	6	450	14	25.188138
21	40	1	6	900	21	24.522887
22	80	2	4	900	21	23.090949
23	80	2	2	720	21	24.524905
24	40	1	2	450	7	23.678711
25	60	2	4	900	7	24.574008
26	60	2	2	720	7	25.18612
27	60	1	4	720	14	25.079841
28	40	3	4	720	7	24.524232
29	80	3	2	900	14	23.694182
30	40	3	4	450	14	24.470353

2.4 Characterization of Raw Material and Activated Carbon

2.4.1 Brunaure-Emmett-Teller (BET)

The specific surface area, average pore diameter, and pore volume of the pomegranate peels and activated carbon were measured based the maximum value of MBN as indicated in Table 3 (Run 14) using Brunaure-Emmett-Teller technique (USA, HORIBA, SA-900 series). The BET measured data of the pomegranate peels and activated carbon are illustrated in Table 4. It’s stated from this table that the specific surface area, average pore diameter, and pore volume of the activated carbon were enhanced as compared to pomegranate peels.

Table 4. BET test for raw material and AC

Sample	surface area [m^2 /g]	Average pore diameter [nm]	Total pore volume(p/p_0=0.990) [cm^3 /g]
Pomegranate peels	8.9671	5.6405	0.012645
activated carbon	1431.8	2.5934	1.623601

2.4.2 FESEM & EDX Analysis

The surface morphologies elements composition for peels and the activated carbon produced were analyzed by field emission scanning electron microscopy and energy dispersive X-ray tests. The results of these tests were illustrated in Figures 2-3 with tables 5 and 6. Figure 2 showed that the peels have a uniform surface with large pore diameter and minimal pore sizes, and Figure 3 depicts a spongy surface with several visible porous with different shapes duo to the chemical activation with microwave irradiation. Furthermore, tables 5 and 6 stated the elements composition variation of carbon element from 38.6% to 74.5% as compared with other elements composition for peels and the activated carbon due to activation processes [65].

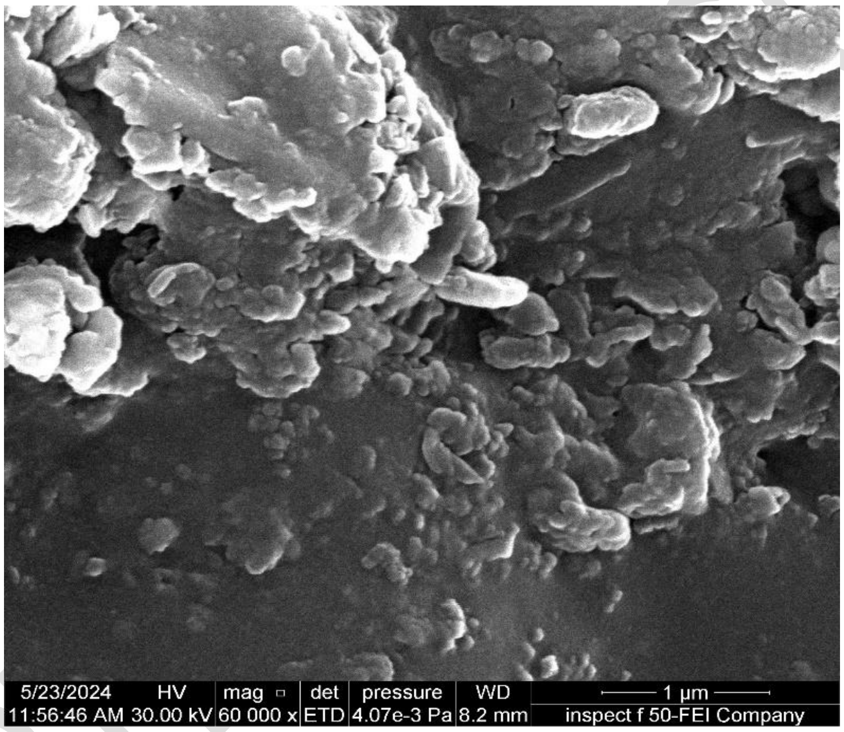


Figure 2. FESEM images of pomegranate peels

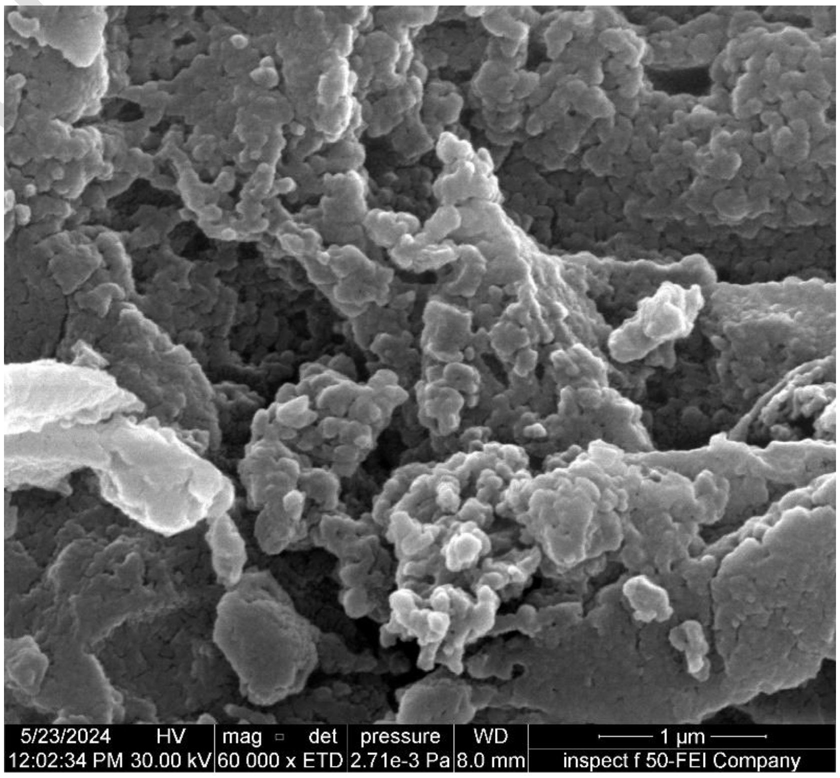


Figure 3. FESEM images of activated carbon

Table 5. Composition of pomegranate peels

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
Ca	0.2	0.0	0.5	0.0
K	0.6	0.0	1.5	0.0
C	46.2	0.3	38.6	0.3
Cl	0.2	0.0	0.5	0.0
O	52.8	0.4	58.8	0.4

Table 6. Composition of activated carbon

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
Ca	0.4	0.0	1.2	0.0
K	0.8	0.0	2.1	0.1
C	72.8	0.4	74.5	0.4
Al	0.4	0.0	0.7	0.1
O	25.4	0.5	20.3	0.6
Nb	0.1	0.1	0.7	0.6
Fe	0.1	0.0	0.5	0.1

2.4.3 X-ray Diffraction (XRD)

Analysis of peels and activated carbon using X-ray diffraction (XRD) technique as shown in Figures 4 and 5. It's from Figure 4. Figure 5 illustrates sharp peaks for activated carbon indicating that the activated carbon primarily possesses amorphous properties with a little crystalline from [66].

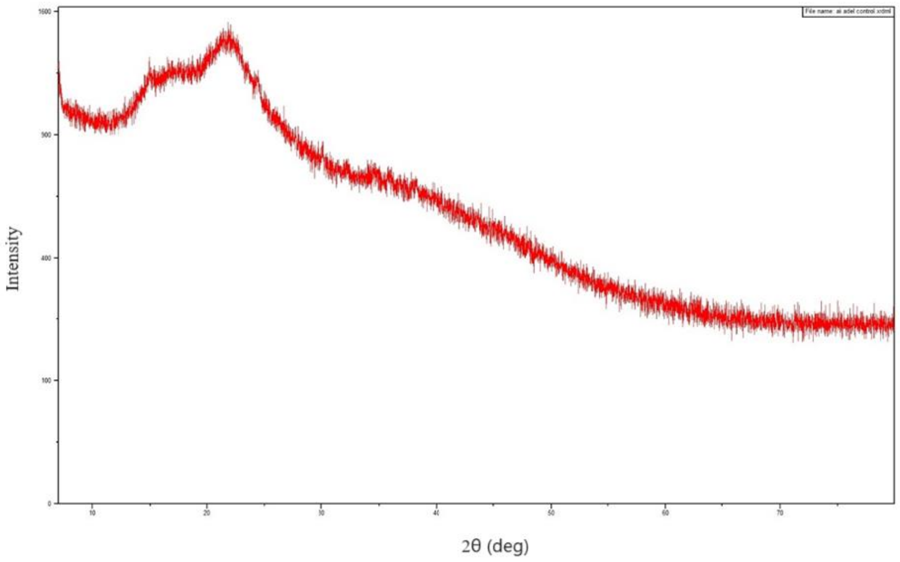


Figure 4. X-ray diffraction of pomegranate peels

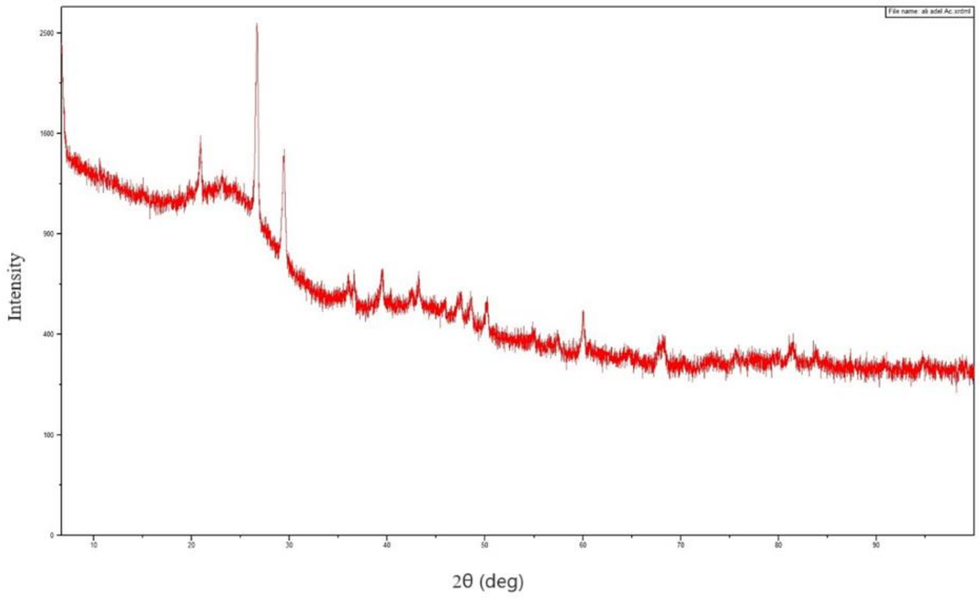


Figure 5. X-ray diffraction of activated carbon

2.4.4 FTIR Analysis

Figure 6 presents the results of the FTIR spectrum analysis for activated carbon (PPAC) and pomegranate peels (PP) between 4000 and 500 cm^{-1}. The strong peaks of the raw material spectrum reffered to thier complex nature. Alcohols, phenols, and carboxylic acids exhibit OH stretching, as indicated by the peaks between 3000 and 3500 cm^{-1} [67, 68]. The C-H group also designates the peaks between 2500 and 3000 cm^{-1} [69]. On the other hand, the peaks between 500 and 1000 cm^{-1} showed the aromatic compounds, while the peaks between 1000 and 1500 cm^{-1} correspond to phenol C=C and aldehyde C=O cm^{-1} [70, 71]. Many peak that were distiguished in the raw materials (PP) spectrum were attenuated or vanshed in PPAC spectram. This attenueation compatible with the acid to raw material impregnatation which leading to bonds breaking, and new bonds being formation as well as volatile materials emancipation with partially aromatization of non aromatic compounds due to carbonization and activation process [72]. Consequently, OH stretching of alcohols, phenols, and carboxylic acids is indicated by the peaks about 3000–3500 cm^{-1} [67, 68]. C-H bending stretching also indicates the peaks between 2500 and 3000 [69, 73]. The peaks at 1000–1300 cm^{-1} are assigned to (C–O) bonds because of the presence of hydroxy ester, while the peaks between 1500–1750 cm^{-1} are primarily indicative of alkene C–C and ketones C=O. Similarly, when alkenes are present, the peaks between 600 and 900 cm^{-1} are assigned to = C-H [74].

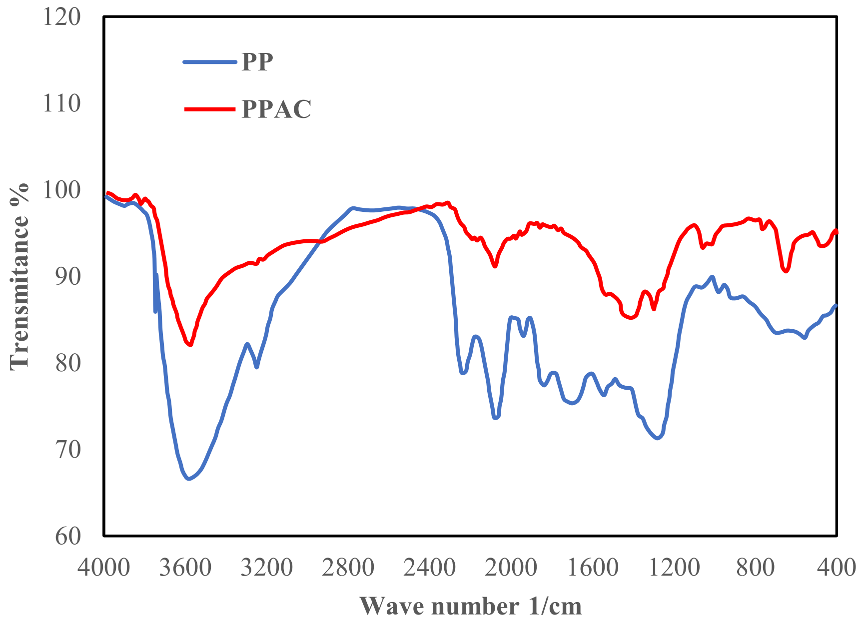


Figure 6. FTIR spectra of pomegranate peels (PP), and activated carbon (PPAC)

3. Results and Discussion

Batch experiments were carried out for adsorption of Pb^{2+}, Cu^{2+}, and Zn^{2+} from synthetic solution simultaneously with different independent factors using I-Optimal approach as efficient for design experiments are illustrated in Tables 7 and 8.

Table 7. Independent factors for metals ions adsorption [75]

Factor	Name	Unit	Levels				
A	Contact time	hr	1	2	3	4	5
B	pH	pH	2	4	6	8	10
C	Solution concentration	mg/L	10	20	30	40	50
D	Dose of AC	g/100ml	0.1	0.2	0.3	0.4	0.5

Table 8. Experimental runs using RSM with I-Optimal method [75]

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3
Run #	A: Time	B: pH	C: Conc.	D: Dosage	RE1%	RE2%	RE3%
	hr	pH	mg/L	g/100ml	Pb	Cu	Zn
1	3	6	30	0.3	99.2	98.5833	97.3267
2	5	6	20	0.1	86.98	82.475	79.615
3	1	2	20	0.1	94.268	90.335	88.31
4	3	6	30	0.3	99.368	98.5433	97.2267
5	2	6	10	0.2	92.336	90.42	86.79
6	2	10	40	0.5	83.698	79.6225	77.2575
7	1	10	10	0.3	79.248	74.06	69.41
8	1	2	50	0.4	87.5584	84.448	82.156
9	2	4	10	0.5	91.096	88.87	83.73
10	4	2	10	0.3	91.704	89.63	86.34
11	5	2	30	0.5	95.368	94.21	93.61
12	4	2	10	0.3	92.216	90.27	88.11
13	5	10	40	0.2	92.804	91.005	89.13
14	1	8	20	0.5	80.752	75.94	72.99
15	5	10	10	0.5	94.928	93.66	91.17
16	2	10	30	0.2	90.8987	88.6233	87.12
17	3	10	10	0.1	86.68	83.35	80.62
18	1	4	40	0.2	96.314	95.3925	94.2375
19	5	6	50	0.5	97.4272	96.784	96.308
20	**3**	**6**	**30**	**0.3**	**99.373**	**98.88**	**97.89**
21	1	8	50	0.1	97.0704	96.838	96.406
22	5	6	20	0.1	86.884	83.605	81.845
23	4	2	50	0.1	98.3376	97.922	97.752
24	3	6	30	0.3	98.9973	98.7467	97.58
25	5	4	40	0.3	96.438	95.5475	94.9475

3.1 Adsorption Process Optimization

The removal efficiencies of Cu^{2+}, Pb^{2+} and Zn^{2+} can be described by general quadratic equation (1);

$$Y = \beta_o + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{1 \le i \le j}^{4} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is model response for Cu^{2+}, pb^{2+} and Zn^{2+} respectively, X_i is independent factor, Ɛ is error of the model, intercept of model, β_o is intercept of model, β_i , β_{ii}, β_{ij} are linear, quadric, and interaction coefficients [76].

Based on the general quadratic equation, the empirical models for predicted removal efficiencies of Pb^{2+}, Cu^{2+}, and Zn^{2+} in coded terms are illustrated in equations 2, 3, 4, Tables 9, and the model's fit statistics are given in Table 10.

$$RE1\%(pb) = 99.13 + 2.64A - 2.03B + 2.63C - 1.12D + 2.47AB + 0.501AC + 5.37AD - 0.1348BC - 0.0165BD \\ -3.35CD - 5.64A^2 - 3.38B^2 - 1.54C^2 - 1.18D^2 \qquad (2)$$

$$RE2\%(Cu) = 98.69 + 3.41A - 2.28B + 3.55C - 1.18D + 2.77AB + 0.165AC + 6.59AD - 0.2374BC - 0.3189BD \\ -4.31CD - 4.35A^2 - 4.35B^2 - 1.34C^2 - 1.74D^2 \qquad (3)$$

$$RE1\%(Zn) = 97.46 + 3.93A - 2.46B + 4.7C - 1.53D + 2.44AB + 0.1201AC + 7.36AD - 0.4902BC - 0.1082BD \\ -4.35CD - 7.54A^2 - 4.48B^2 - 2.23C^2 - 1.65D^2 \qquad (4)$$

Table 9. Experimental runs with responses predicted values

Run #	Factor 1 A: Time hr	Factor 2 B: pH pH	Factor 3 C: Conc. mg/L	Factor 4 D: Dosage g/100ml	Response 1 RE1% (Pb)	Response 2 RE2% (Cu)	Response 3 RE3% (Zn)
1	3	6	30	0.3	99.13	98.69	97.46
2	5	6	20	0.1	87.10	83.33	81.24
3	1	2	20	0.1	94.10	90.38	88.30
4	3	6	30	0.3	99.13	98.69	97.46
5	2	6	10	0.2	92.45	90.16	86.77
6	2	10	40	0.5	83.85	79.72	77.83
7	1	10	10	0.3	79.40	74.52	70.29
8	1	2	50	0.4	87.51	84.55	82.28
9	2	4	10	0.5	91.44	89.39	84.76
10	4	2	10	0.3	91.88	89.81	86.83
11	5	2	30	0.5	95.38	94.12	93.69
12	4	2	10	0.3	91.88	89.81	86.83
13	5	10	40	0.2	92.68	90.73	88.78
14	1	8	20	0.5	80.25	75.17	71.28
15	5	10	10	0.5	94.94	93.69	91.21
16	2	10	30	0.2	91.36	89.16	87.70
17	3	10	10	0.1	86.38	82.86	79.73
18	1	4	40	0.2	96.71	95.32	94.28
19	5	6	50	0.5	97.53	96.95	96.28
20	3	6	30	0.3	99.13	98.69	97.46
21	1	8	50	0.1	96.82	96.71	96.18
22	5	6	20	0.1	87.10	83.33	81.24
23	4	2	50	0.1	98.40	97.94	97.78
24	3	6	30	0.3	99.13	98.69	97.46
25	5	4	40	0.3	96.27	95.34	94.73

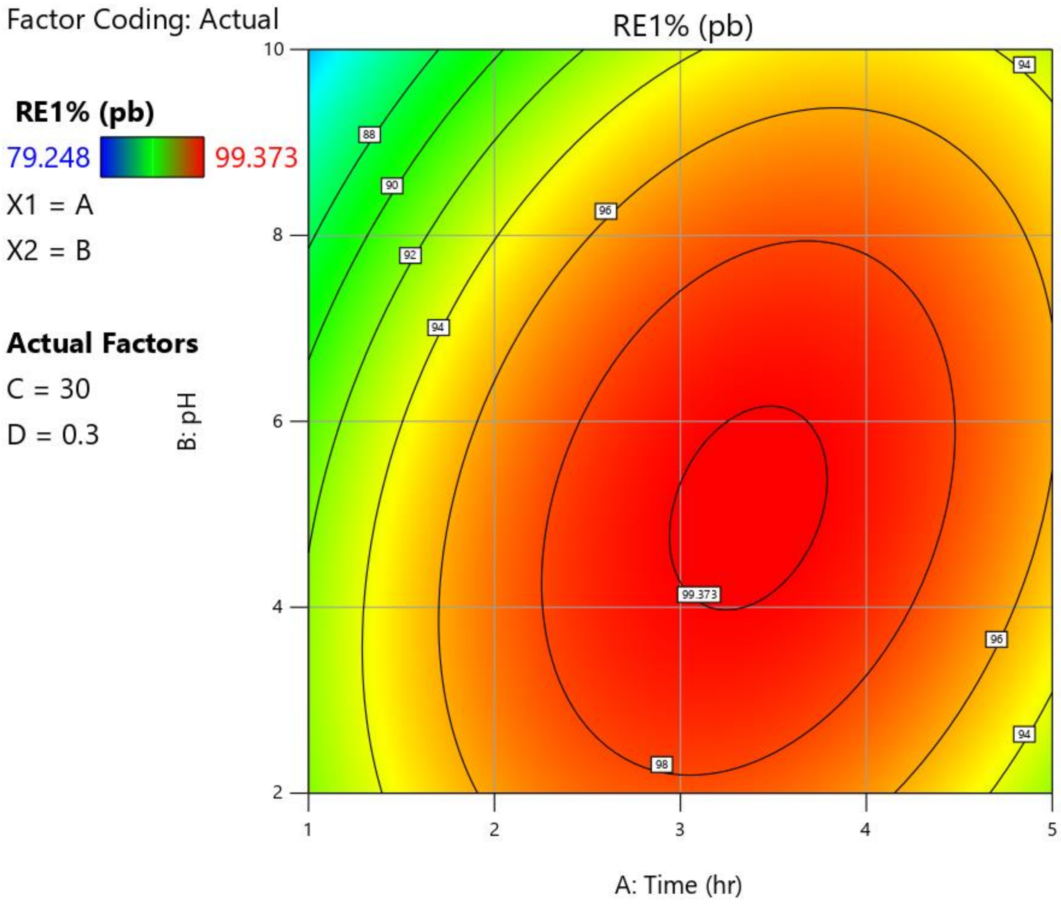
Table 10. Summary of model's Fit Statistics

RE%	Std. Dev.	Mean	CV%	R^2	Adjusted R^2	Predicted R^2	Adeq Precision
Pb	0.3729	92.4	0.4036	0.9983	0.996	0.9684	68.2884
Cu	0.5462	90.31	0.6048	0.9977	0.9944	0.968	57.1414
Zn	1.08	88.32	1.22	0.9929	0.9829	0.925	32.8762

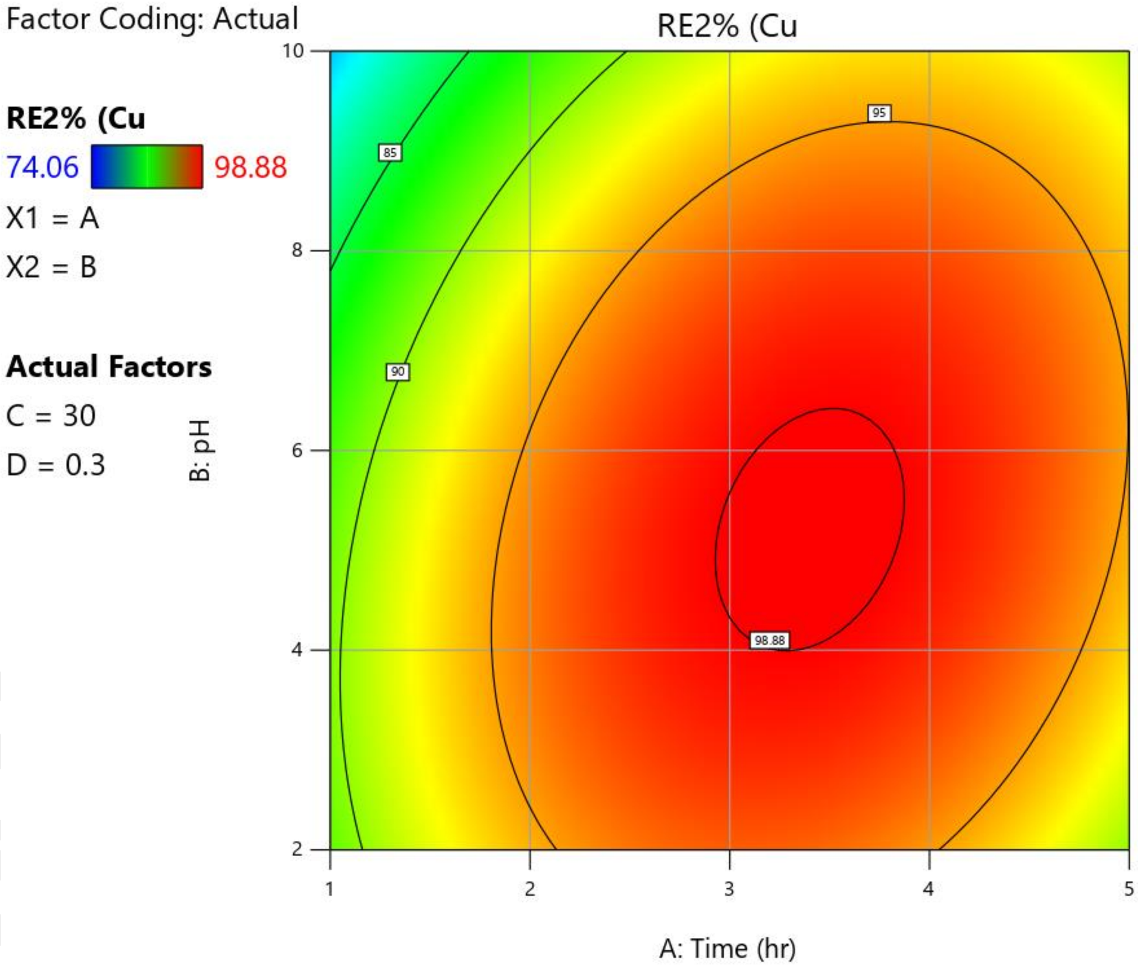
It's clearly observed from Table 10, that the adjusted and predicted R^2 are in a reasonable agreement (difference < 0.2). Signal to noise ratio for all model are greater than 4, which mean all models are applicable for design range.

3.2 Response Surface Plots

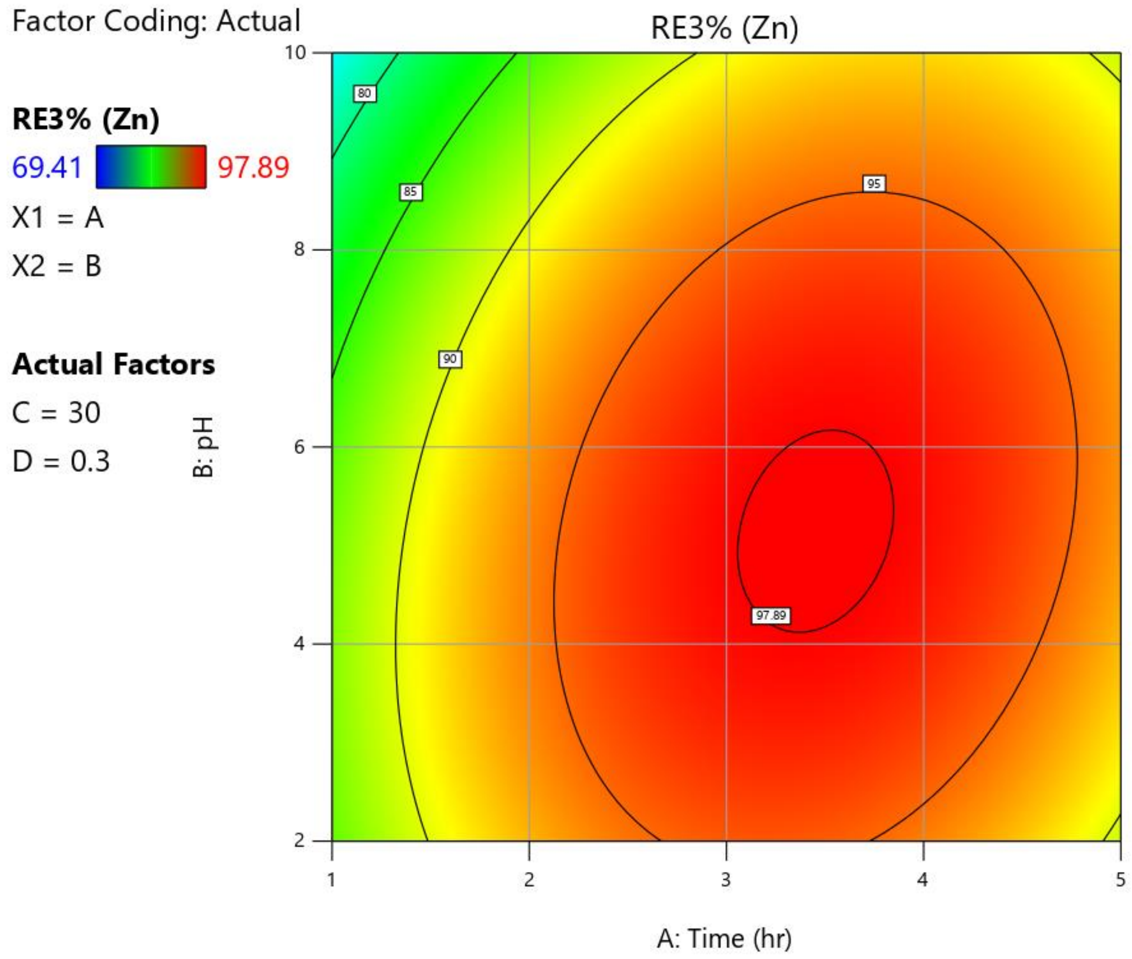
Contour plots for removal efficiencies of Pb^{2+}, Cu^{2+}, and Zn^{2+} related to the multi-independent factors was applied to explain the interactions between these factors and to validate the optimum values for each factor to obtained maximum removal efficiency of Cu^{2+}, Pb^{2+} and Zn^{2+} [59, 77, 78]. The contour plots for multi-metals removal efficiencies versus contact time, pH, metal ions concentrations, and adsorbent doses are shown in Figures 7, 8, 9, and 10. Figures 7 a, b, and c, illustrated the effect of contact time and pH on ions adsorption at constant metal ions concentrations (30 mg/L) and adsorbent dose (0.3g/100mL). It's noted from these figures the ions adsorption increased with increase in in contact time and pH up to 3 hr and pH 6. Furthermore, the adsorption decreases for contact time greater than 3 hr and pH 6. This implied that the active sites in adsorbent were occupied by heavy metal ions with increasing in desorption rate [79, 80]. Likewise, the adsorption rate for pH below 6 mean that the hydrogen ions available in solution was probably to compete with heavy metal ions and for pH greater than 6 the heavy metal ions may be precipitate as hydroxides [81]. Figures 8 a, b, and c, illustrated the effect of contact time and metals ions concentration on removal efficiency at constant pH (6) and adsorbent dose (0.3g/100mL). It's noted from these figures the removal efficiency increased with increase in contact time up to 3 hr and 30 mg/L. Whereas, the removal efficiency decreased for contact time, and concentration greater than 3 hr and 30 mg/L. This mean that the active sites in adsorbent were vacuous and ravenous for ions which then occupied by heavy metal ions with increasing of time and concentration consequently, a significant increasing in desorption rate as the contact time increased [82, 83].


Factor Coding: Actual
RE1% (pb)
RE1% (pb)
79.248
99.373
X1 = A
X2 = B
Actual Factors
C = 30
D = 0.3
B: pH
A: Time (hr)
10
8
6
4
2
1
2
3
4
5
88
90
92
94
96
98
99.373
96
94
94

(a)

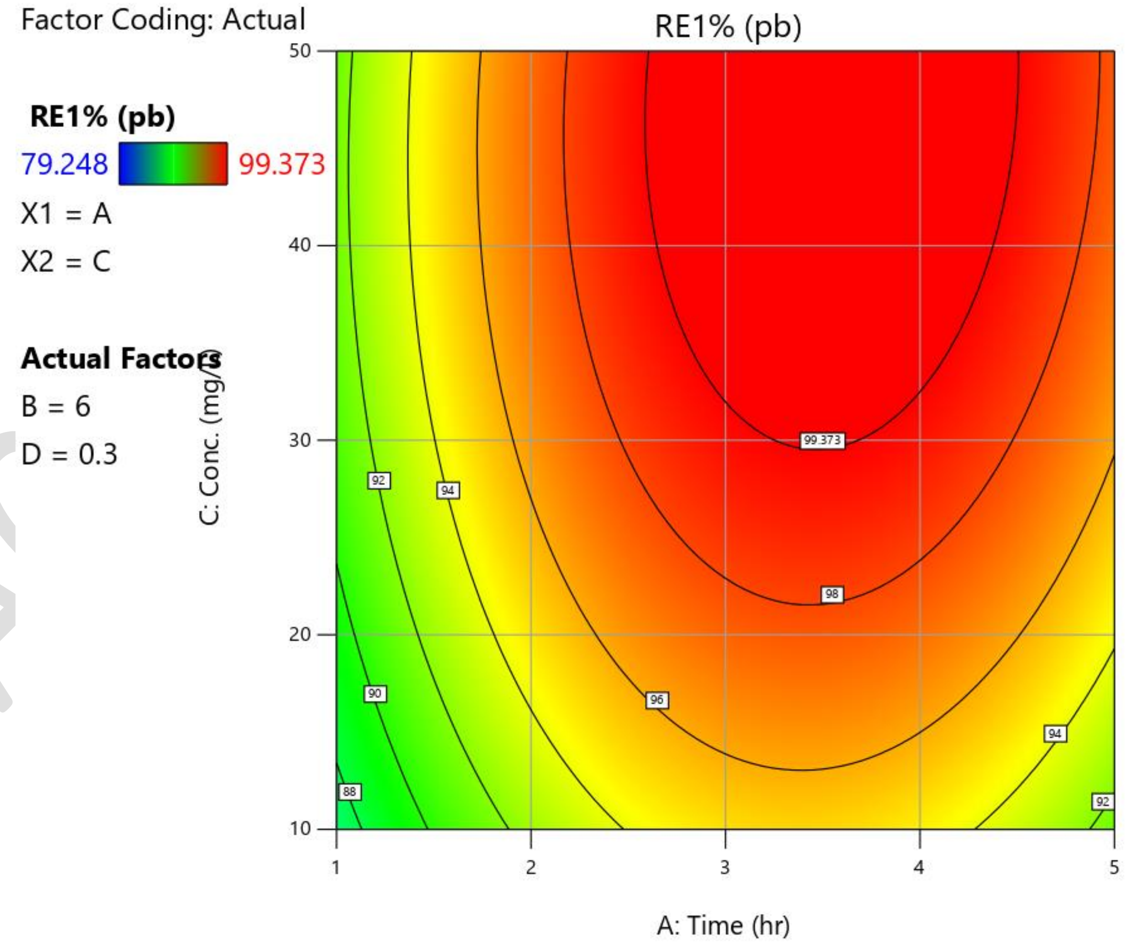

Factor Coding: Actual
RE2% (Cu
RE2% (Cu
74.06
98.88
X1 = A
X2 = B
Actual Factors
C = 30
D = 0.3
B: pH
A: Time (hr)
10
8
6
4
2
1
2
3
4
5
85
90
95
98.88

(b)

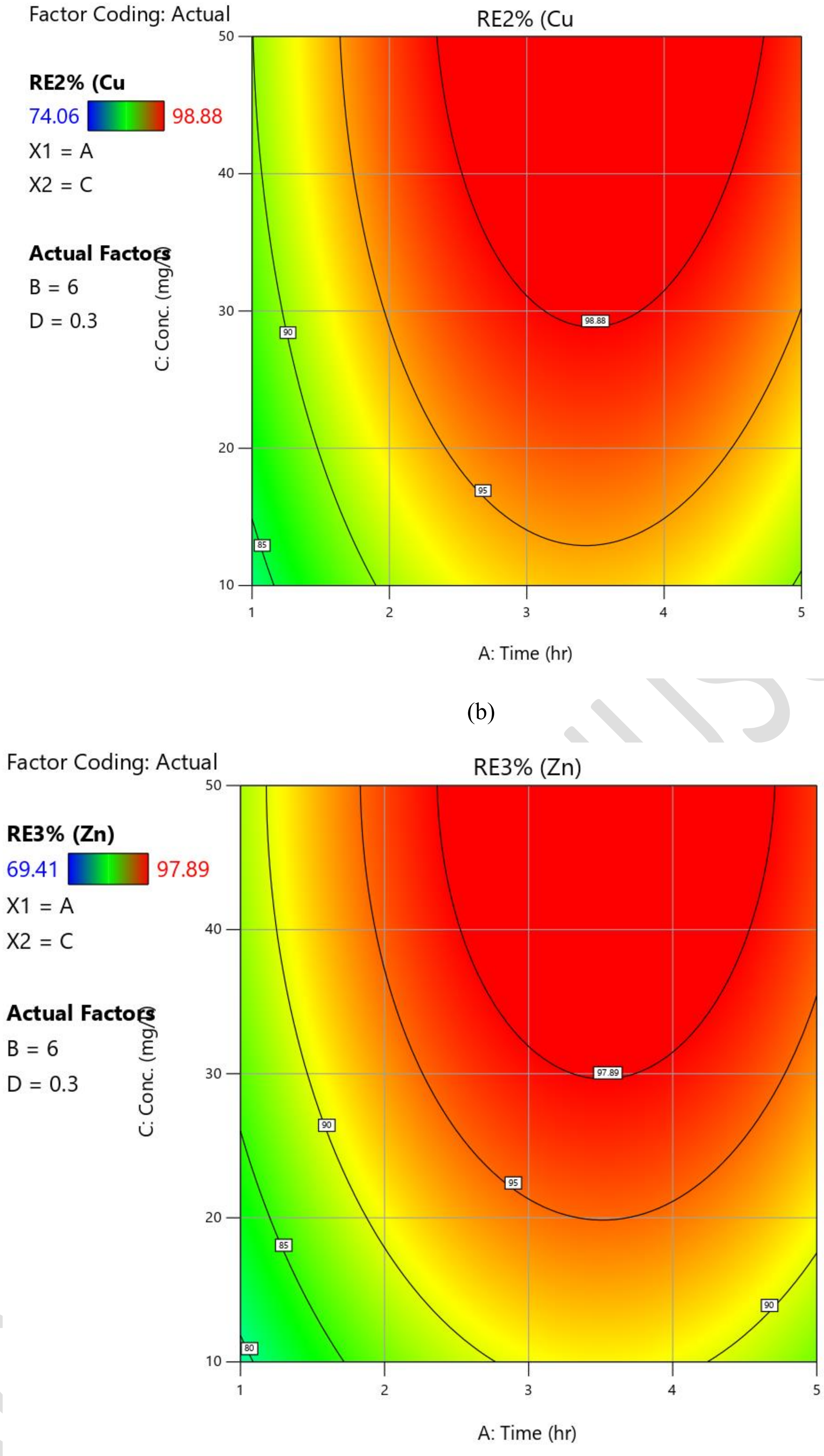


(c)

Figure 7 (a, b, c). Contour plots contact time (hr) and pH (metals concentration = 30 mg/L, adsorbent dose = 0.3 g/100 mL)



(a)

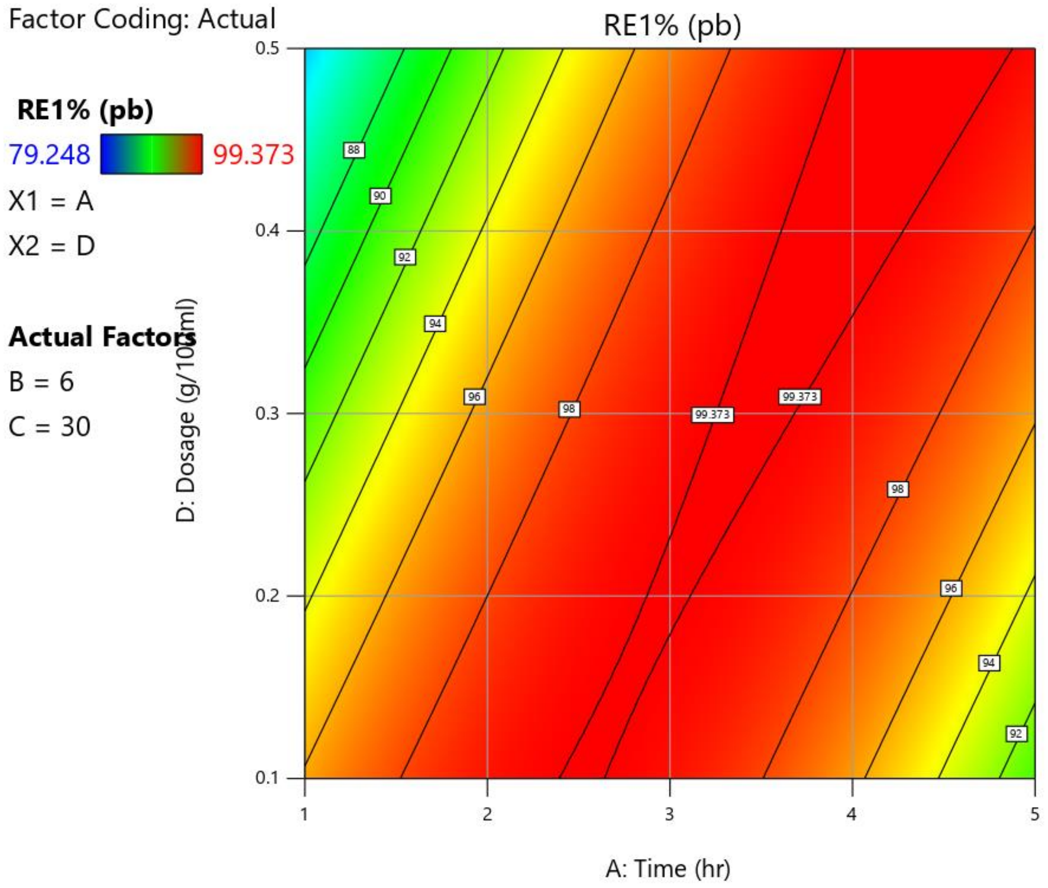


(b)

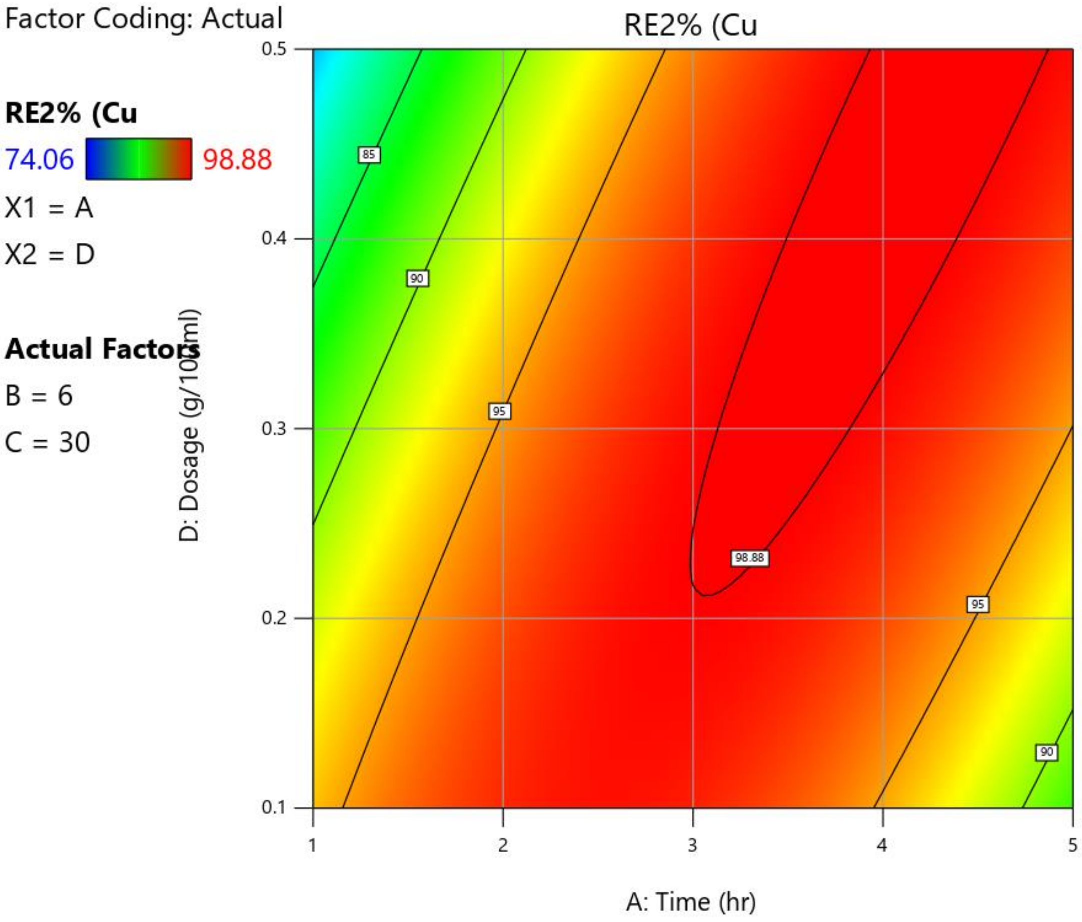
(c)

Figure 8 (a, b, c). Contour plots contact time (hr) and metals concentration (pH = 6, adsorbent dose = 0.3 g/100 mL)

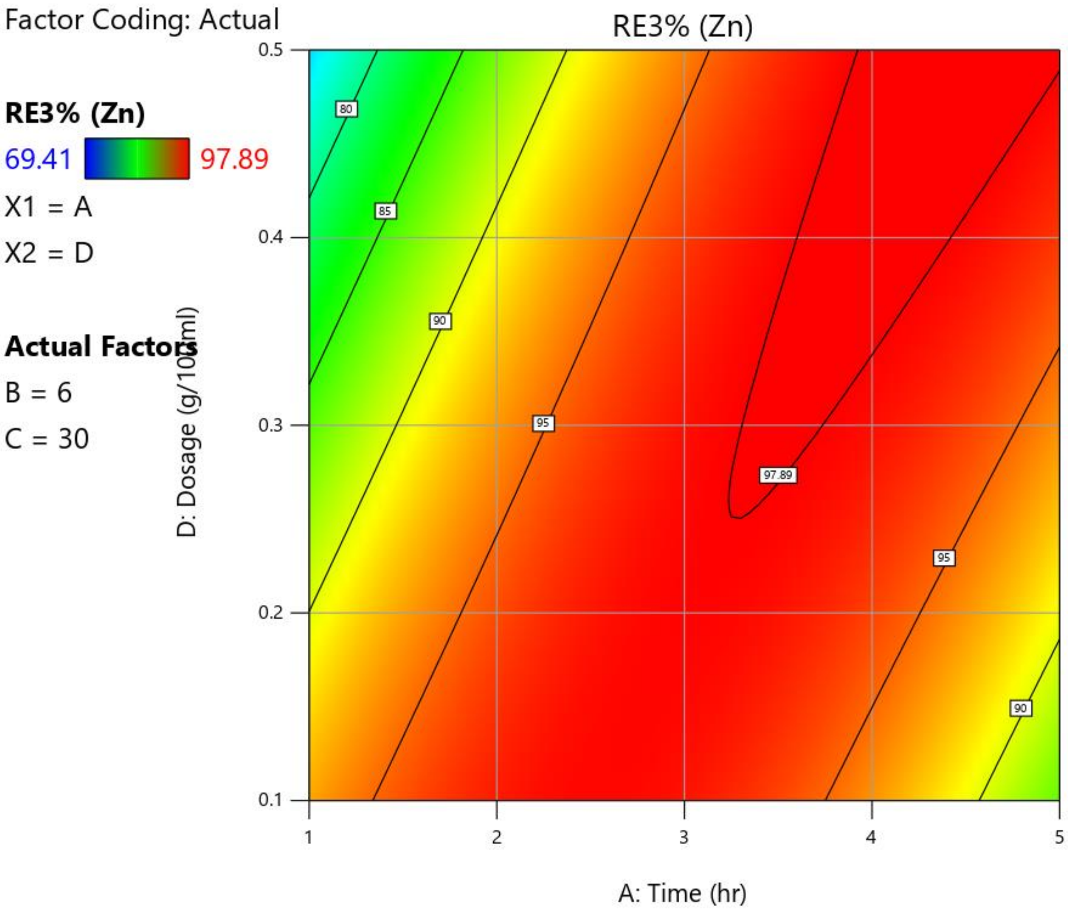
Figures 9 a, b, and c, showed the effect of contact time and adsorbent dosage on the removal efficiency at constant pH (6) and metals concentration (30 mg/L). It's observed from these figures the removal efficiency increased with increase in contact time and adsorbent dosage up to 3 hr and 0.3 g/100mL. However, the removal efficiency decreased for contact time, and adsorbent dosage greater than 3 hr and 30 mg/L. This mean that the greater dose may be produce an aggregation in adsorbent particles leading to decrease adsorbent surface area and consequently decrease the removal efficiency [84-86].


Factor Coding: Actual
RE1% (pb)
RE1% (pb)
79.248
99.373
X1 = A
X2 = D
Actual Factors
B = 6
C = 30
D: Dosage (g/100ml)
A: Time (hr)
0.1
0.2
0.3
0.4
0.5
1
2
3
4
5
88
90
92
94
96
98
99.373
99.373
98
96
94
92

(a)


Factor Coding: Actual
RE2% (Cu
RE2% (Cu
74.06
98.88
X1 = A
X2 = D
Actual Factors
B = 6
C = 30
D: Dosage (g/100ml)
A: Time (hr)
0.1
0.2
0.3
0.4
0.5
1
2
3
4
5
85
90
95
98.88
95
90

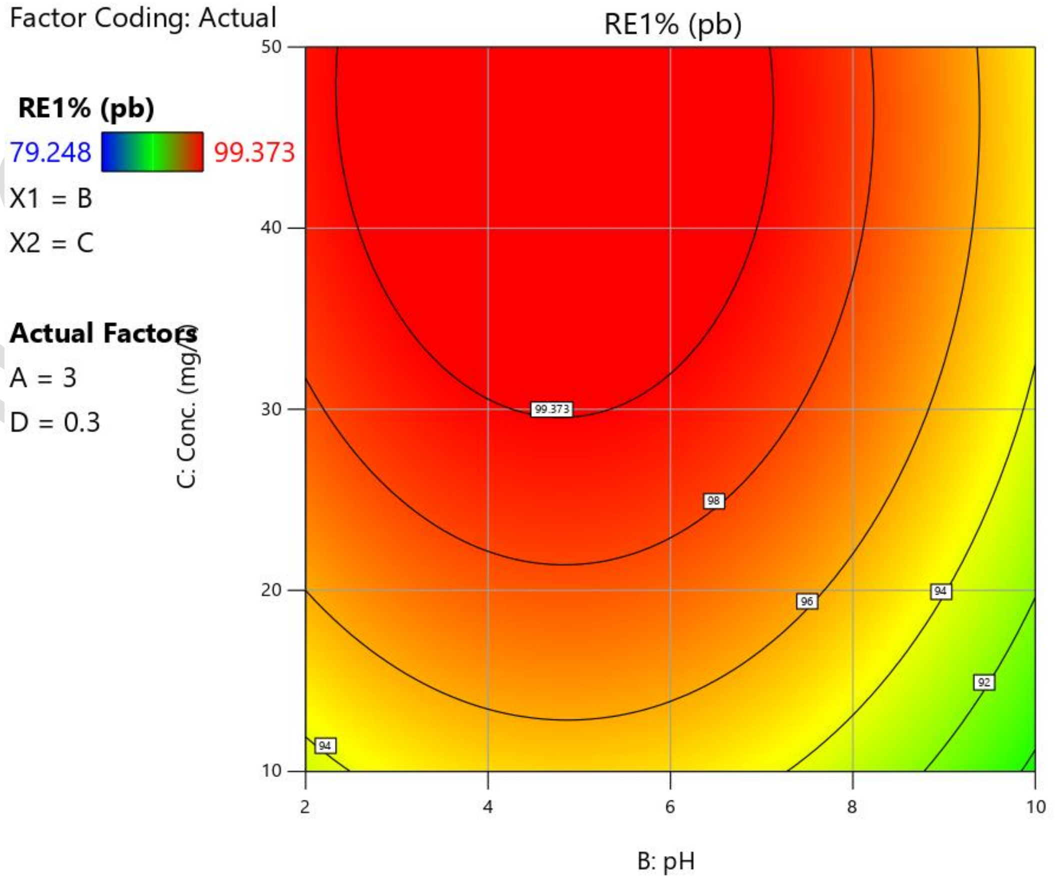
(b)



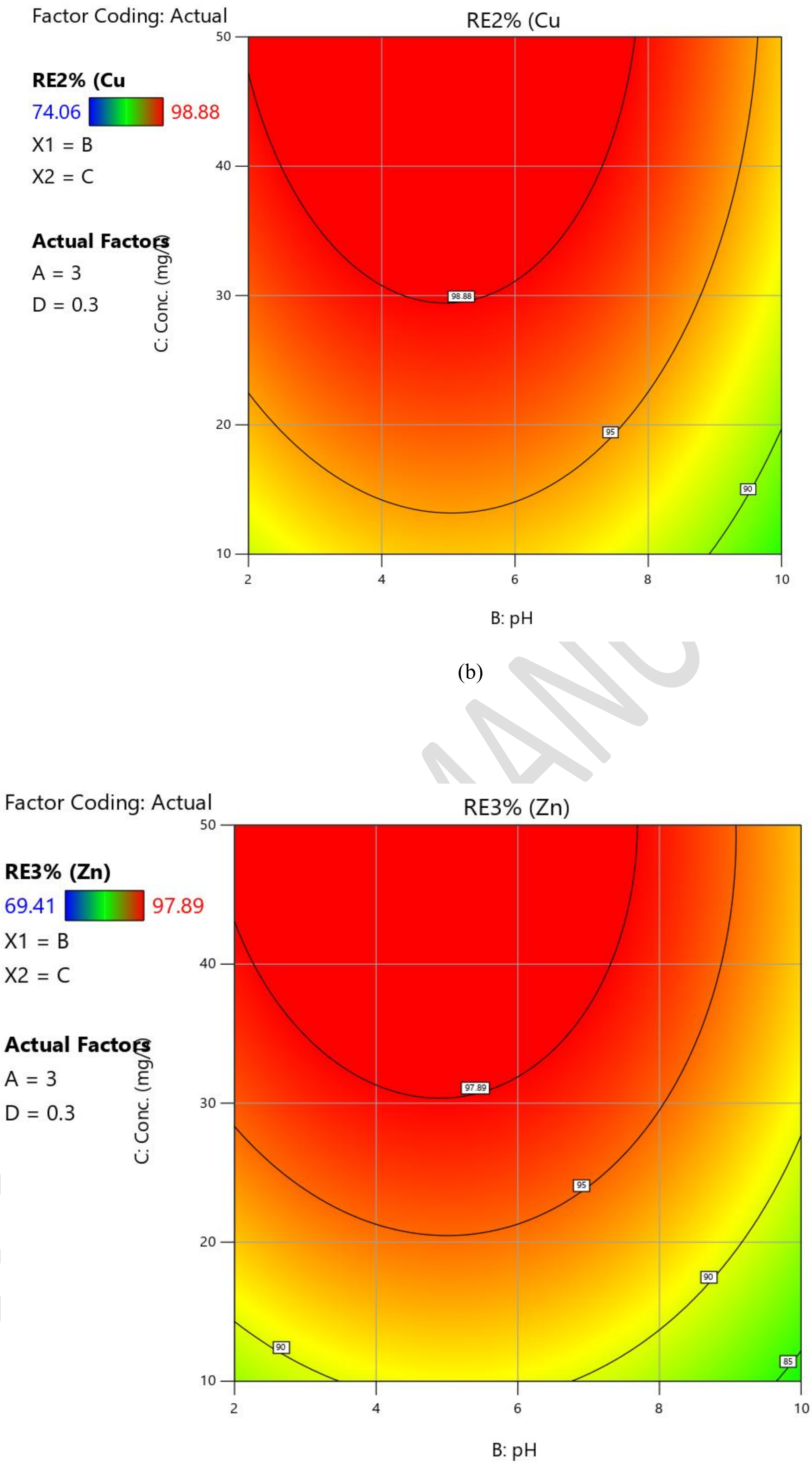
(c)

Figure 9 (a, b, c). Contour plots contact time (hr) and adsorbent dosage (pH = 6, metals concentration = 30 mg/L)

Figures 10 a, b, and c, show the effect of metal concentration and pH on the removal efficiency at constant contact time (3 hr) and adsorbent dose (0.3 g/100mL). It's noted from these figures the removal efficiency significantly increased with increase in concentration as compared with increasing of pH at its reached to the maximum removal efficiency at 30 mg/L and pH equal to 6. Then the removal efficiency decreased for further increasing of concentration and pH. This implied that a sufficient adsorbent surface area was available at low metals concentrations, which led to an increase in the removal efficiency and at high concentrations the majority of metal ions were not absorbed due adsorbent site saturation as well as the effect of pH increasing [81, 87, 88].



(a)

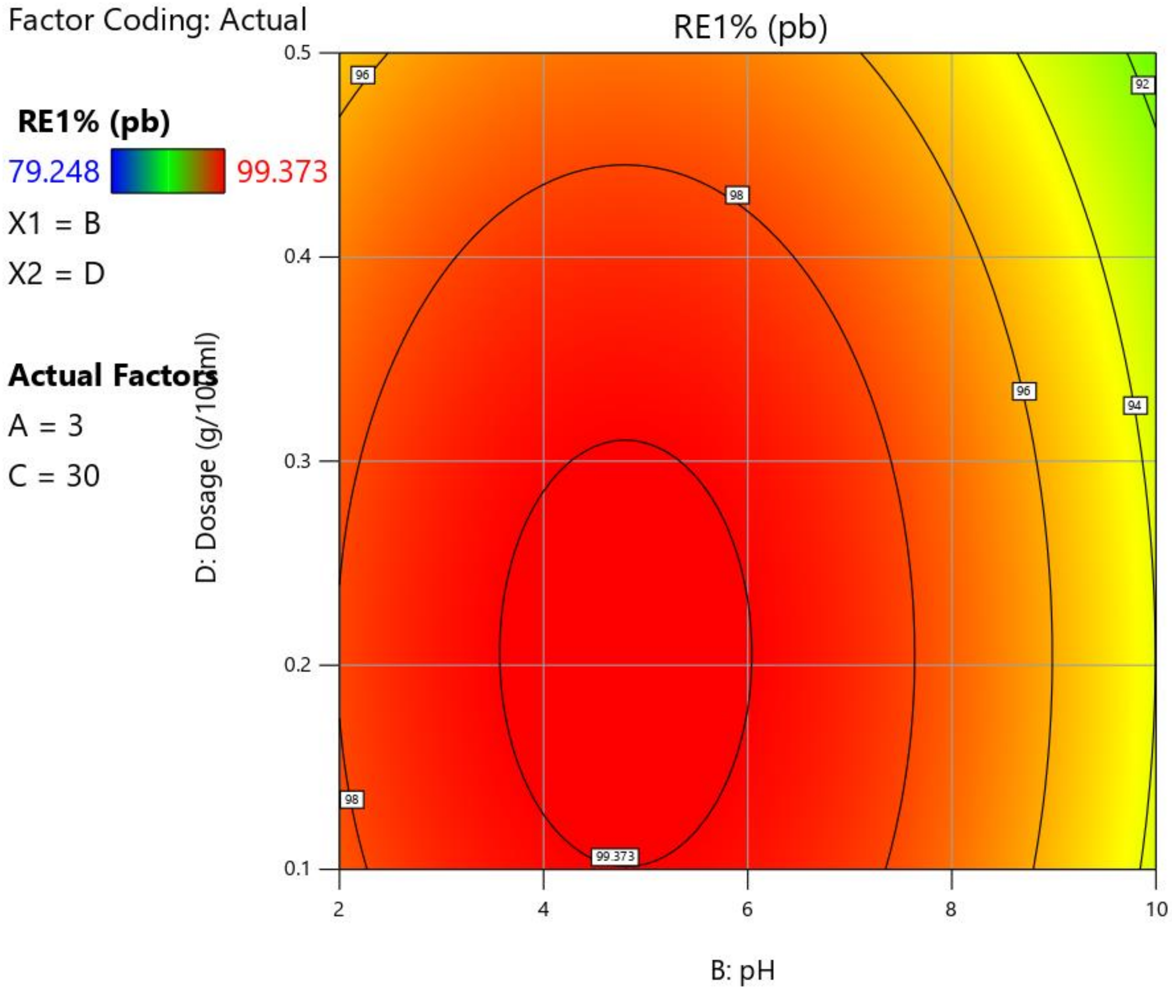


(b)

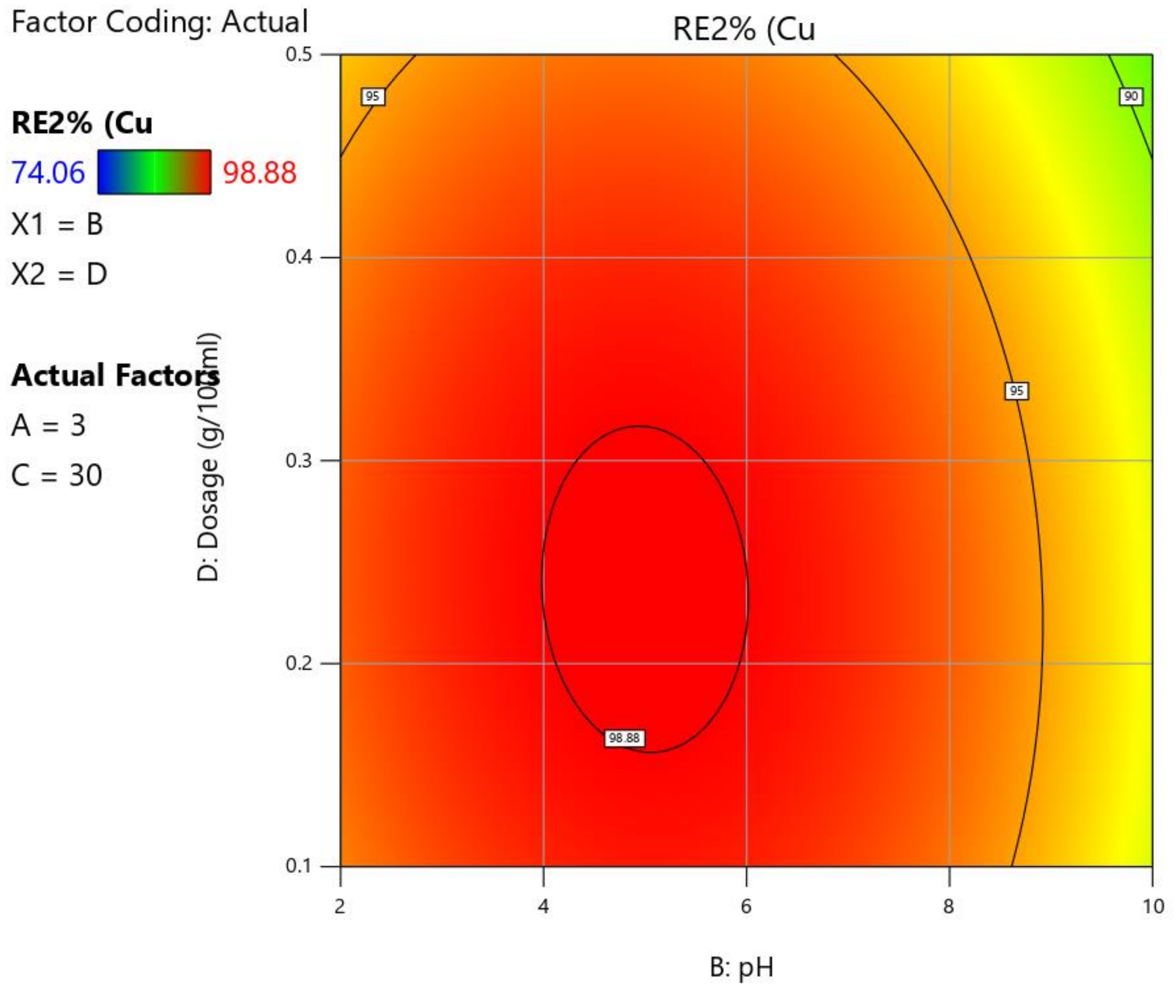
(c)

Figure 10 (a, b, c). Contour plots c metal concentration and pH (contact time =3 hr and adsorbent dose = 0.3 g/100mL)

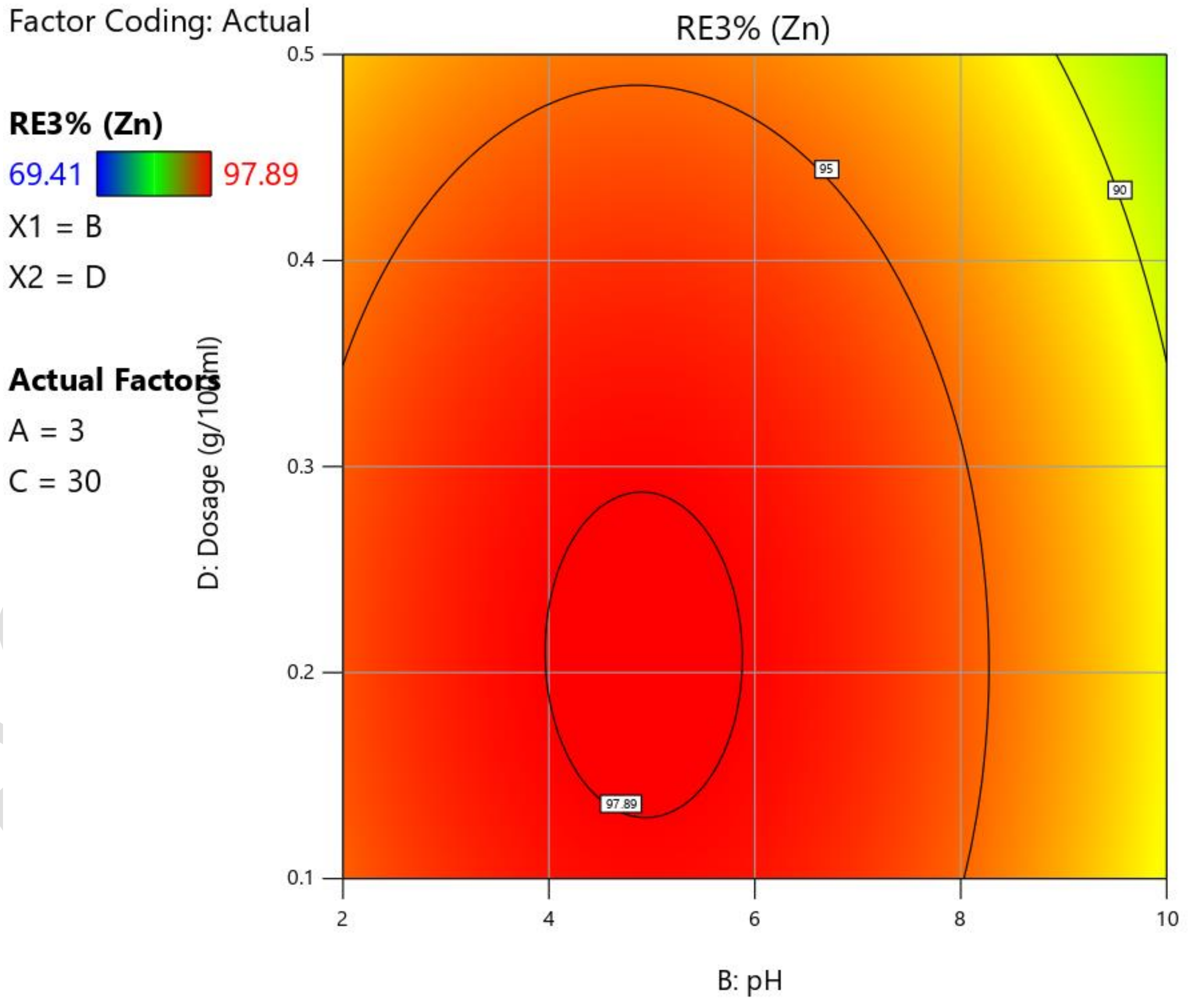
Figures 11 a, b, and c, show the effect of adsorbent dose and pH on the removal efficiency at constant contact time (3 hr) and metals concentration (30 mg/L). It's noted from these figures the removal efficiency strongly increased with increasing of adsorbent dose and of pH at its reached to the maximum removal efficiency at 0.3 g/100mL and pH equal to 6. Then the removal efficiency slightly decreased for further increasing of adsorbent dose and pH. This means that the amount of adsorbent dose may be produce an aggregation between its particles leading to decrease adsorbent surface area and consequently decrease the removal efficiency. Whereas, the heavy metal ions may be precipitate as hydroxides for pH greater than 6 [81, 86].



(a)



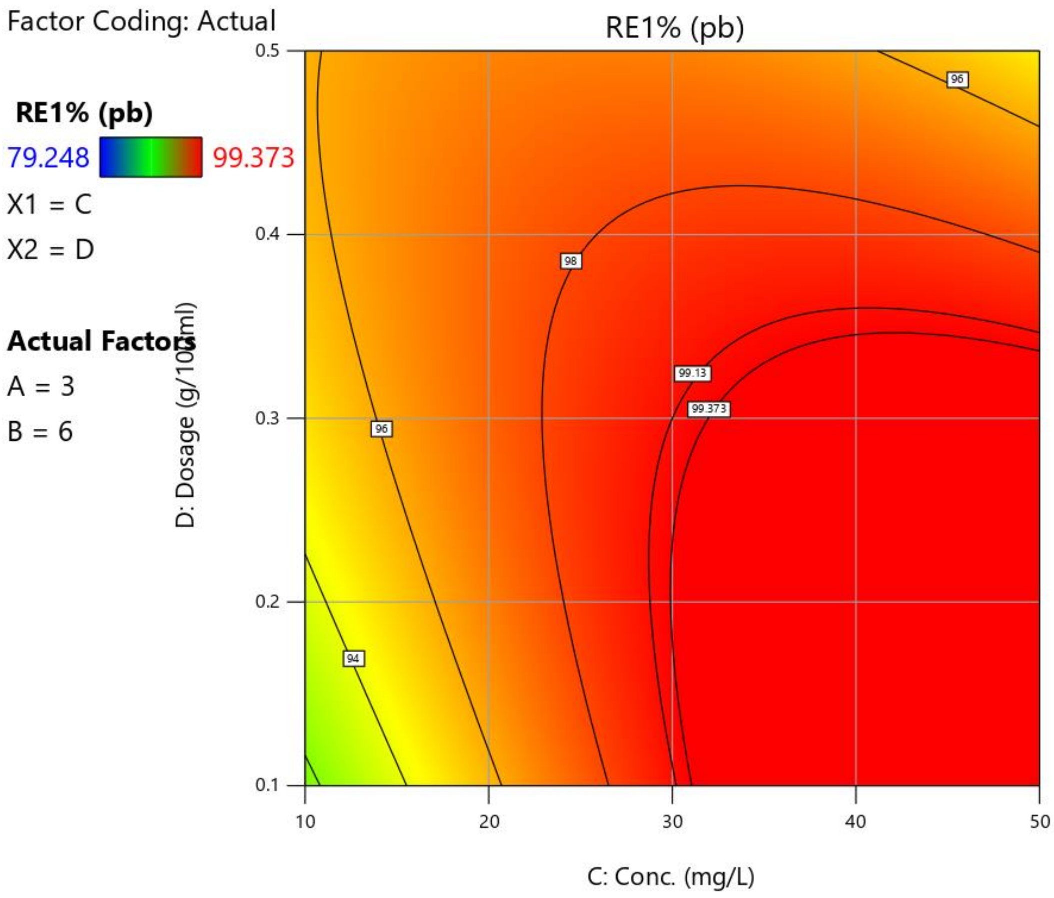
(b)



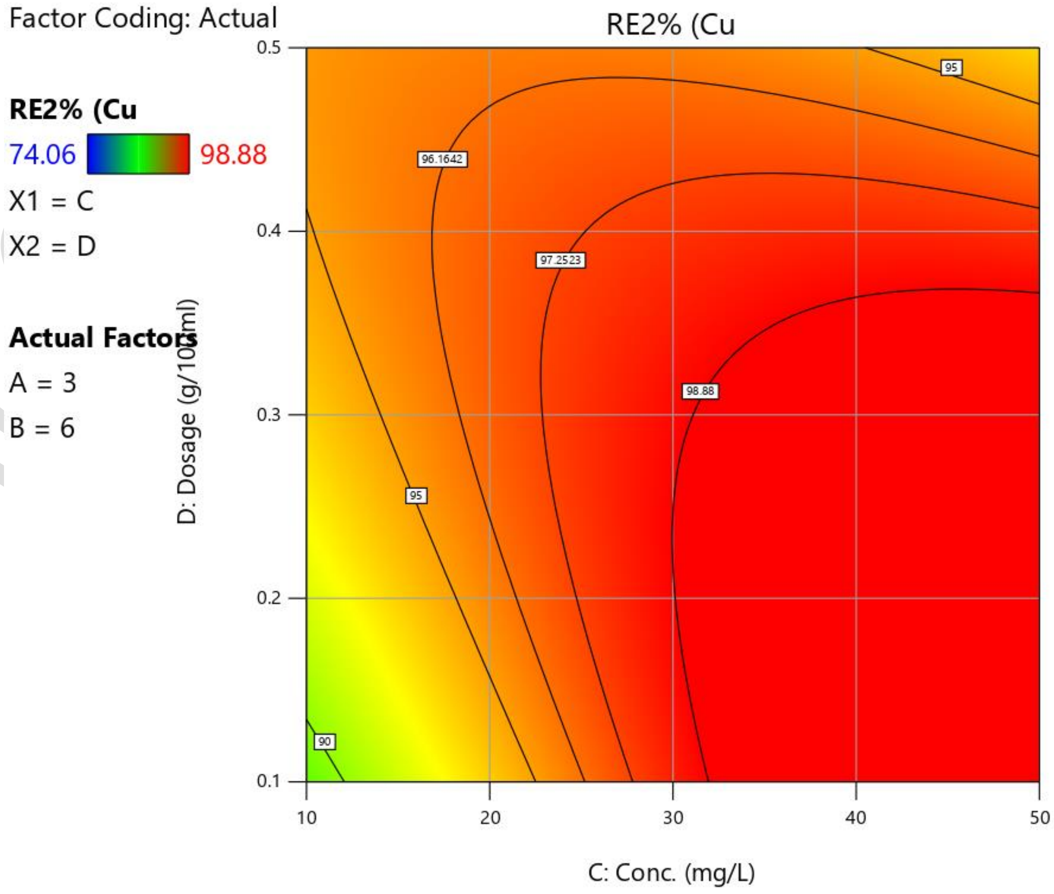
(c)

Figure 11 (a, b, c). Contour plots of adsorbent dose and pH (contact time =3 hr and metals concentration = 30 mg/L)

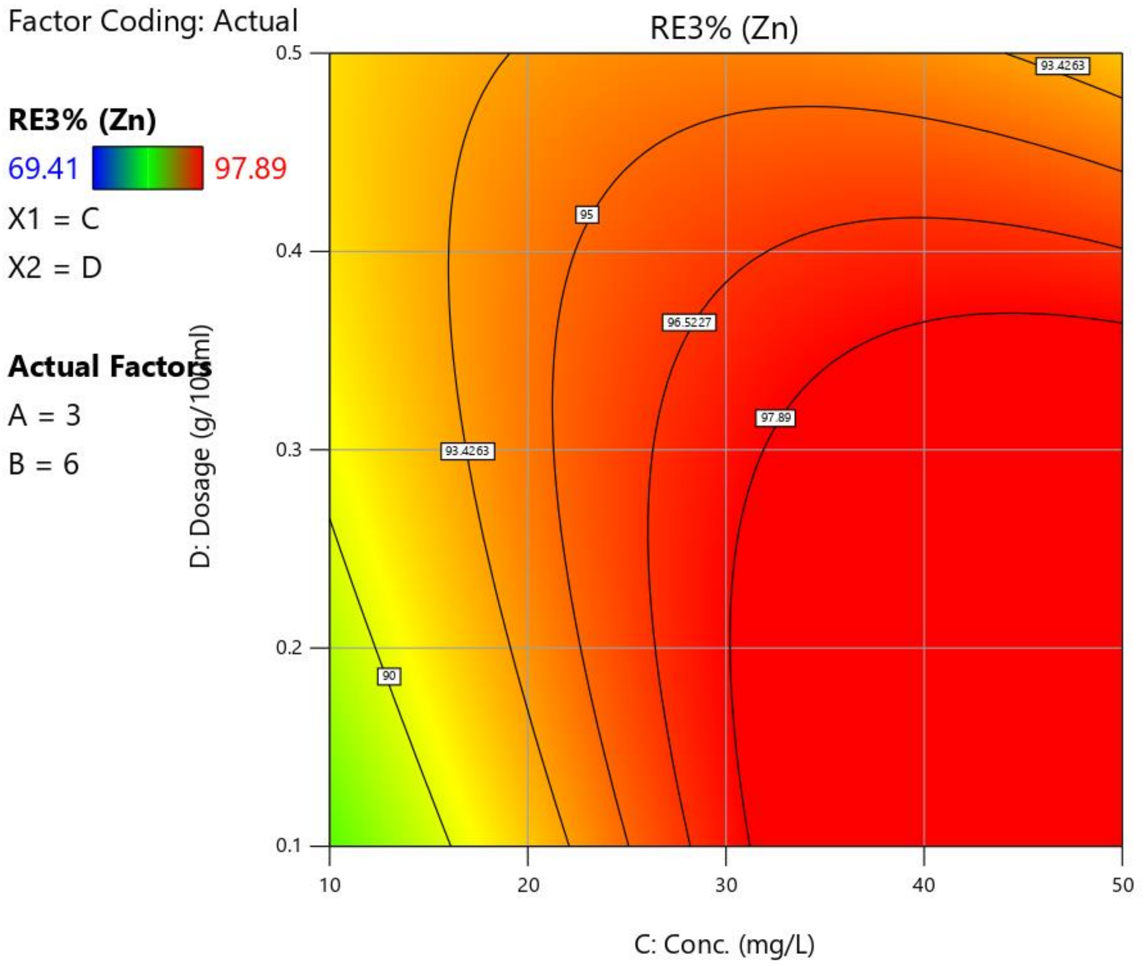
Finally, Figures 12 a, b, and c, show the effect of metals concentration and adsorbent dose on the removal efficiency at constant contact time (3 hr) and pH (6). It's noted from these figures the removal efficiency strongly increased with increasing of adsorbent dose and metals concentration to reach the maximum removal efficiency around adsorbent dose 0.3 g/100mL and metals concentration equal to 30 mg/L. Thereafter, the removal efficiency slightly decreased for further increasing of metals concentration and adsorbent dose. It's inferred that at low metal concentrations, there was enough adsorbent surface area available, increasing removal efficiency, whereas at high concentrations, the bulk of metal ions were not absorbed due to adsorbent site saturation. Whereas, the increasing in adsorbent dose may be produce an aggregation between its particles leading to decrease adsorbent surface area and consequently decrease the removal efficiency [89-91].



(a)



(b)



(c)

Figure 12 (a, b, c). Contour plots of metals concentration and adsorbent dose (contact time =3 hr and pH = 6)

3.3 Isotherm Models

Various adsorption isotherm models explained the adsorbate's dispersion into solid and phases. In order to fit experimental data for metals ions adsorption under equilibrium circumstances, Langmuir and Freundlich isotherm models were chosen for this purpose. Langmuir model as represented in equation 5 is applied to elucidate monolayer adsorption into the pores of the homogenous surface of the adsorbent at isothermal and equilibrium conditions assuming that the adsorption process occurred without any interaction between adsorbent molecules and sorption at one site is unaffected by adsorption at nearby sites. [92]. Freundlich model as elucidate in equation 6 is applied to expound multilayer adsorption into the pores of the heterogeneous adsorbent surface at isothermal and equilibrium conditions assuming that the capacity of adsorption is depend on the power of adsorbate concentration [93].

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L\, q_m\, c_e} \qquad (5)$$

$$\ln q_e = \ln k_f + \left(\frac{1}{n}\right) \ln C_e \qquad (6)$$

where q_m (mg/g) and q_e (mg/g) are the maximum capacity of the adsorption and the capacity at equilibrium conditions. Ce (mg/l) is the concentration at equilibrium condition, k_l (l/mg), (l/mg), and 1/n are the equation constants.

The data of metals concentrations (pb^{2+}, Cu^{2+} and Zn^{2+}) with adsorption capacities are plotted as shown in Figures 13 (a, b), and the isotherm models coefficients sorted from these Figures are illustrated in Table 11. It's found that the data was well fitted with the Langmuir model as compared with the Freundlich model for Pb^{2+}, Cu^{2+} and Zn^{2+} with R^2 = 0.992, 0.9841, and 0.9512, respectively. This behavior elaborated that metals adsorption were occurred in monolayer at the adsorbent surface without any interaction between metal ions, and the heat of absorption are uniform for all adsorbent sites [94, 95]

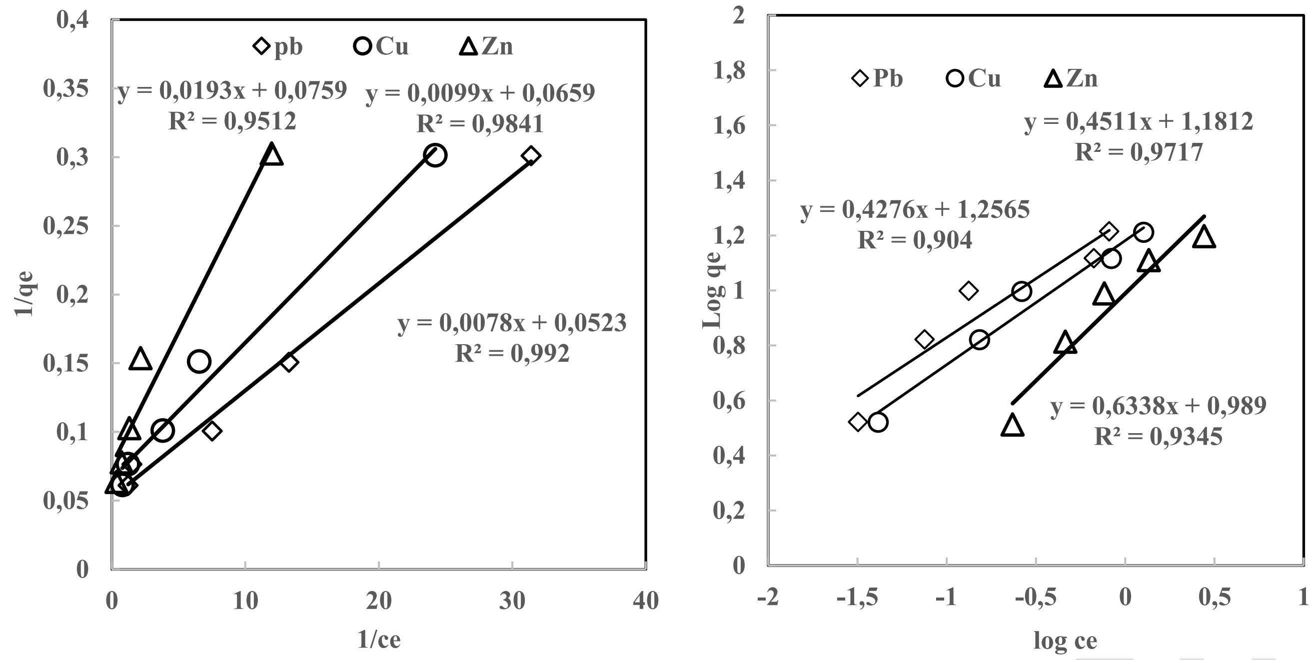


Figure 13. Plots of (a) Langmuir and (b) Freundlich isotherm models

Table 11. Correlation constants and correlation of isotherm models

	Langmuir			**Freundlich**		
Adsorbate	k_L (L/mg)	q_m (mg/g)	R^2	k_f (mg/g)	n	R^2
Pb	6.7156	19.1237	0.992	3.5131	2.3206	0.9041
Cu	6.6520	15.1766	0.9841	3.2583	2.2170	0.9717
Zn	3.9258	13.174	0.9512	2.6884	1.5778	0.9345

3.4 Adsorption Kinetic Models

Two kinetic models were chosen to explain the adsorption mechanism of Pb^{2+}, Cu^{2+} and Zn^{2+} on the surface of the adsorbent as shown in equations 7, and 8. Pseudo-first-order kinetic model applied with assumption thar the rate of ions or adsorbate molecules adsorbed onto the adsorbent is limited by physisorption. Whereas, Pseudo-second-order kinetic model applied with assumption thar the rate of ions or adsorbate molecules adsorbed onto the adsorbent is limited by chemisorption [96, 97]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

$$t/qt = (1/k_2 q_e^2) + (t/q_e) \qquad (8)$$

where q_t (mg/g) and q_e (mg/g) are the capacities of the adsorption with time and at equilibrium condition, t (min) is the adsorption time, k_l (l/min) and k_2 (mg/g.min) are model's coefficients.

The data of adsorption time for metal ions of Pb^{2+}, Cu^{2+} and Zn^{2+} were plotted with adsorption capacities at equilibrium and different intervals of metals adsorption as shown in Figures 14 (a, b), and the kinetic model coefficients sorted from these Figures are illustrated in Table 12. It's found that the data was well fitted with the pseudo-second-order kinetic model compared with the pseudo-first-order for Pb^{2+}, Cu^{2+} and Zn^{2+} with R^2 = 0.99998, 0. 0.99996, and 0.9997, respectively. This behavior elaborated that metals adsorption were conducted as chemisorption for all adsorbent sites [98-100],

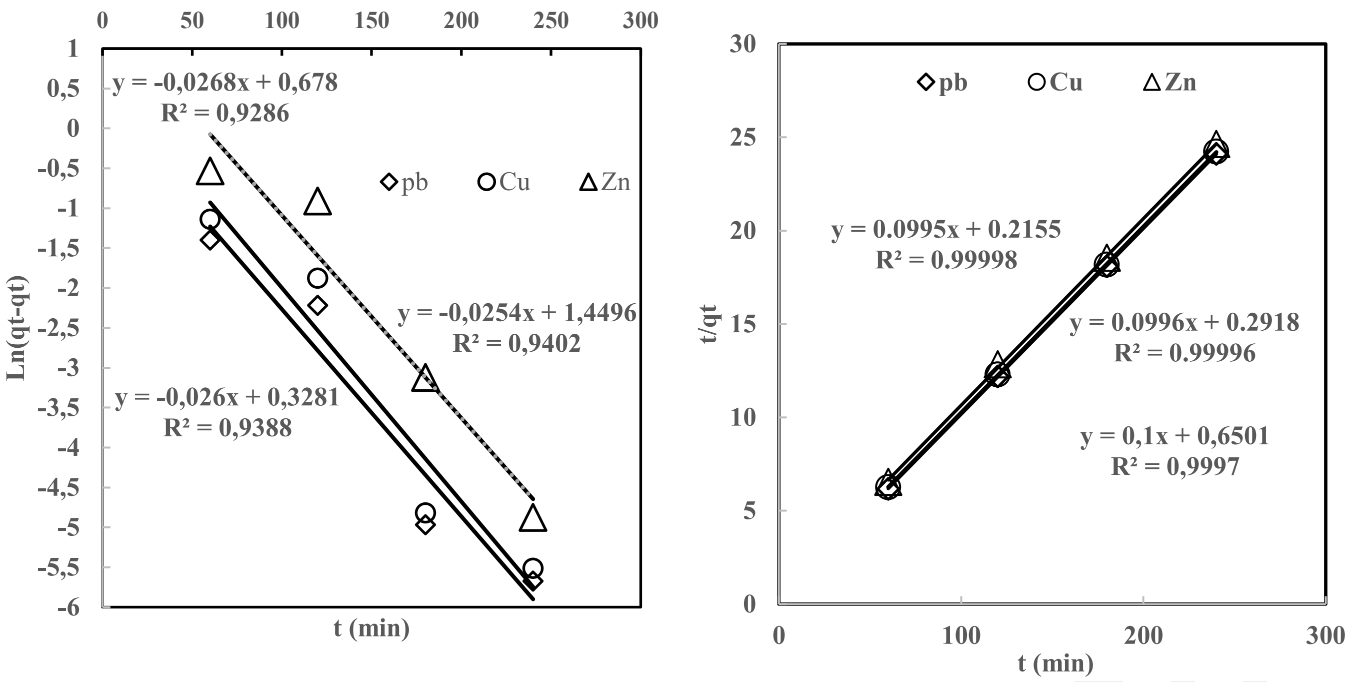


Figure 14. Kinetic model plots of (a) pseudo-first-order and (b) pseudo-second-order

Table 12. Kinetic model constants and correlation coefficients

	First Order			Second Order		
Adsorbate	k_1 (min^{-1})	q_e	R^2	k_2 (min^{-1})	q_e	R^2
Pb	0.0259	1.38828	0.9388	0.04595	10.0482	0.99998
Cu	0.0268	1.96998	0.9286	0.0340	10.036	0.99996
Zn	0.0254	4.26144	0.9402	0.0153	10.0009	0.9997

4. Conclusion

I-Optimal design approach was selected to design and analysis the experimental data of Pb^{2+}, Cu^{2+} and Zn^{2+} adsorption on activated carbon prepared from pomegranate peels activated by sulfuric acid microwave technique. The raw material and activated carbon where characterized FESEM with EDX, BET, FTIR and XRD techniques. The effect of contact time, metals concentration, pH, and adsorbent dosage on the simultaneous removal efficiencies. The results elaborated that the pomegranate activated carbon can be used as efficient adsorbent for pb, Cu, and Zn with order of removal efficiencies of 99.373 % for Pb^{2+}, 98.88 % for Cu^{2+} and 97.89% for Zn^{2+} at optimum conditions of adsorption time = 3 hr, pH = 6, metal ions concentration = 30 mg/L, adsorbent dose = 0.3 g/100ml. Langmuir and Freundlich isotherm models were used to analyzed the equilibrium adsorption data, and results showed that the Langmuir model provided a more accurate description as compared with Freundlich model. In addition, the pseudo-second-order model was found as more accurate model for adsorption kinetics representation.

Acknowledgments

The authors express their gratitude to University of Baghdad / Al-Khwarizmi College of Engineering - Department of Biochemical Engineering for their acceptance to use materials and laboratory facilities that necessary to complete this work.

Declaration of conflicting interests

All authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

All authors received no financial support for the research, authorship, and/or publication of this article.

References

[1] N. Emmanuel C, "LACK OF ACCESS TO POTABLE WATER SUPPLY AND ITS IMPACT ON THE NIGERIAN RURAL COMMUNITIES," 10/19 2018.

[2] S. Bolan *et al.*, "Impacts of climate change on the fate of contaminants through extreme weather events," *Sci. Total Environ.,* vol. 909, p. 168388, 2024/01/20/ 2024, doi: https://doi.org/10.1016/j.scitotenv.2023.168388.

[3] Y. Wang, T. Rume, S. M. D. Islam, W. Fan, J. Wu, and X. Li, "Water Quality Criteria and Ecological Risk Assessment of Typical Transition Metals in South Asia," (in eng), *Int. J. Environ. Res. Public Health,* vol. 19, no. 23, Dec 2 2022, doi: 10.3390/ijerph192316125.

[4] D. Witkowska, J. Słowik, and K. Chilicka, "Heavy Metals and Human Health: Possible Exposure Pathways and the Competition for Protein Binding Sites," (in eng), *Molecules,* vol. 26, no. 19, Oct 7 2021, doi: 10.3390/molecules26196060.

[5] N. Muhammad, L. Lao, A. Intisar, H. Cui, and Y. Zhu, "Simultaneous Determination of Fluoride and Chloride in Iron Ore by Steam Distillation Followed by Ion Chromatography," *Chromatographia,* vol. 82, no. 12, pp. 1839-1844, 2019/12/01 2019, doi: 10.1007/s10337-019-03798-7.

[6] N. Muhammad *et al.*, "Ion chromatography: A comprehensive review of sample preparation methods for analysis of halogens and allied nonmetals in critically challenging inorganic matrices," *Journal of Chromatography A,* vol. 1734, p. 465311, 2024/10/11/ 2024, doi: https://doi.org/10.1016/j.chroma.2024.465311.

[7] M. R. Slobodian, J. D. Petahtegoose, A. L. Wallis, D. C. Levesque, and T. J. S. Merritt, "The Effects of Essential and Non-Essential Metal Toxicity in the Drosophila melanogaster Insect Model: A Review," (in eng), *Toxics,* vol. 9, no. 10, Oct 16 2021, doi: 10.3390/toxics9100269.

[8] Z. Rengel, "Heavy Metals as Essential Nutrients," 1999, pp. 231-251.

[9] K. Jomova *et al.*, "Essential metals in health and disease," *Chemico-Biological Interactions,* vol. 367, p. 110173, 2022/11/01/ 2022, doi: https://doi.org/10.1016/j.cbi.2022.110173.

[10] R. Singh, N. Gautam, A. Mishra, and R. Gupta, "Heavy metals and living systems: An overview," (in eng), *Indian J. Pharmacol.,* vol. 43, no. 3, pp. 246-53, May 2011, doi: 10.4103/0253-7613.81505.

[11] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, and D. J. Sutton, "Heavy metal toxicity and the environment," (in eng), *Exp Suppl,* vol. 101, pp. 133-64, 2012, doi: 10.1007/978-3-7643-8340-4_6.

[12] A. Saad, A. El--Sikaily, and H. Kassem, "Essential, non-essential metals and human health," 2016, pp. 87-135.

[13] M. Balali-Mood, K. Naseri, Z. Tahergorabi, M. R. Khazdair, and M. Sadeghi, "Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic," (in eng), *Front. Pharmacol.,* vol. 12, p. 643972, 2021, doi: 10.3389/fphar.2021.643972.

[14] J. Vizuete Zorita, M. Pérez-López, M. Miguez, and D. Hernandez-Moreno, "Mercury (Hg), Lead (Pb), Cadmium (Cd), Selenium (Se), and Arsenic (As) in Liver, Kidney, and Feathers of Gulls: A Review: Continuation of Residue Reviews," *Rev. Environ. Contam. Toxicol.,* vol. 247, pp. 85-146, 11/10 2018, doi: 10.1007/398_2018_16.

[15] E. Álvarez-Ayuso, A. García-Sánchez, and X. Querol, "Purification of metal electroplating waste waters using zeolites," *Water Res.,* vol. 37, no. 20, pp. 4855-4862, 2003/12/01/ 2003, doi: https://doi.org/10.1016/j.watres.2003.08.009.

[16] V. J. Inglezakis, M. M. Loizidou, and H. P. Grigoropoulou, "Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility," *Journal of Colloid and Interface Science,* vol. 275, no. 2, pp. 570-576, 2004/07/15/ 2004, doi: https://doi.org/10.1016/j.jcis.2004.02.070.

[17] "EFFICIENCY ASSESSMENT OF ARABIC GUM FOR HEAVY METAL REMOVAL FROM POLLUTED WASTEWATER," *IRAQI JOURNAL OF AGRICULTURAL SCIENCES,* vol. 53, no. 3, pp. 570- 577, 06/29 2022, doi: 10.36103/ijas.v53i3.1565.

[18] "Adsorption of Cd(II) and Pb(II) Ions from Aqueous Solution by Activated Carbon," *Al-Khwarizmi Engineering Journal,* vol. 5, no. 4, pp. 13-17, 12/01 2009. [Online]. Available: https://alkej.uobaghdad.edu.iq/index.php/alkej/article/view/578.

[19] "Thermodynamic and Kinetic Study of the Adsorption of Pb (II) from Aqueous Solution Using Bentonite and Activated Carbon," *Al-Khwarizmi Engineering Journal,* vol. 9, no. 2, pp. 48-56, 06/30 2013. [Online]. Available: https://alkej.uobaghdad.edu.iq/index.php/alkej/article/view/167.

[20] M. A. Alkhadra *et al.*, "Electrochemical Methods for Water Purification, Ion Separations, and Energy Conversion," *Chem. Rev.,* vol. 122, no. 16, pp. 13547-13635, 2022/08/24 2022, doi: 10.1021/acs.chemrev.1c00396.

[21] J. A. Garrido-Cardenas, B. Esteban-García, A. Agüera, J. A. Sánchez-Pérez, and F. Manzano-Agugliaro, "Wastewater Treatment by Advanced Oxidation Process and Their Worldwide Research Trends," (in eng), *Int. J. Environ. Res. Public Health,* vol. 17, no. 1, Dec 25 2019, doi: 10.3390/ijerph17010170.

[22] S. Al-Asheh and Z. Duvnjak, "Sorption of cadmium and other heavy metals by pine bark," *J. Hazard. Mater.,* vol. 56, no. 1, pp. 35-51, 1997/09/01/ 1997, doi: https://doi.org/10.1016/S0304-3894(97)00040-X.

[23] W. T. Mohammed, H. F. Farhood, and A. H. B. Al-Mas'udi, "Removal of Dyes from Wastewater of Textile Industries Using Activated Carbon and Activated Alumina," *Iraqi Journal of Chemical and Petroleum Engineering,* vol. 10, no. 1, pp. 43-52, 03/30 2009, doi: 10.31699/IJCPE.2009.1.7.

[24] S. H. Ammar and S. A. Jaafar, "Adsorption Kinetic and Isotherms Studies of Thiophene Removal from Model Fuel on Activated Carbon Supported Copper Oxide," *Iraqi Journal of Chemical and Petroleum Engineering,* vol. 18, no. 2, pp. 83-93, 06/30 2017, doi: 10.31699/IJCPE.2017.2.7.

[25] R. Salim, M. Al-Subu, and E. Dawod, "Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency," *J. Environ. Manage.,* vol. 87, no. 3, pp. 521-532, 2008/05/01/ 2008, doi: https://doi.org/10.1016/j.jenvman.2007.01.028.

[26] "COMPARATIVE STUDY OF REMOVAL POLLUTANTS (HEAVY METALS) BY AGRICULTURAL WASTES AND OTHER CHEMICAL FROM THE AQUEOUS SOLUTIONS," *IRAQI JOURNAL OF AGRICULTURAL SCIENCES,* vol. 52, no. 2, pp. 392-402, 04/19 2021, doi: 10.36103/ijas.v52i2.1300.

[27] S. Hanafiah *et al.*, "Efficiency of Coconut Husk as Agricultural Adsorbent in Removal of Chromium and Nickel Ions from Aqueous Solution," *IOP Conference Series: Earth and Environmental Science,* vol. 596, p. 012048, 12/29 2020, doi: 10.1088/1755-1315/596/1/012048.

[28] S. Ayob *et al.*, "A Review on Adsorption of Heavy Metals from Wood-Industrial Wastewater by Oil Palm Waste," *Journal of Ecological Engineering,* vol. 22, no. 3, pp. 249-265, 2021 2021, doi: 10.12911/22998993/132854.

[29] M. Abbas, S. Turky, and R. Abass, "RICE HUSKS AS A BIOSORBENT AGENT FOR PB 2+ IONS FROM CONTAMINATED AQUEOUS SOLUTIONS : A REVIEW," *Biochemical and Cellular Archives,* vol. 20, pp. 1813-1820, 07/01 2020, doi: 10.35124/bca.2020.20.1.1813.

[30] Y. Bulut and Z. Tez, "Removal of heavy metals from aqueous solution by sawdust adsorption," *Journal of Environmental Sciences,* vol. 19, no. 2, pp. 160-166, 2007/02/01/ 2007, doi: https://doi.org/10.1016/S1001-0742(07)60026-6.

[31] M. W. Khalid and S. D. Salman, "Adsorption of Heavy Metals from Aqueous Solution onto Sawdust Activated Carbon," 2019, https://alkej.uobaghdad.edu.iq/index.php/alkej/article/view/650.

[32] T. W. Tee and A. R. M. Khan, "Removal of lead, cadmium and zinc by waste tea leaves," *Environmental Technology Letters,* vol. 9, no. 11, pp. 1223-1232, 1988/11/01 1988, doi: 10.1080/09593338809384685.

[33] Y. A. B. Neolaka *et al.*, "Potential of activated carbon from various sources as a low-cost adsorbent to remove heavy metals and synthetic dyes," *Results in Chemistry,* vol. 5, p. 100711, 2023/01/01/ 2023, doi: https://doi.org/10.1016/j.rechem.2022.100711.

[34] M. Momčilović, M. Purenović, A. Bojić, A. Zarubica, and M. Ranđelović, "Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon," *Desalination,* vol. 276, no. 1, pp. 53-59, 2011/08/02/ 2011, doi: https://doi.org/10.1016/j.desal.2011.03.013.

[35] B. Dash, "Competitive Adsorption of dyes (congo red, methylene blue, malachite green) on Activated Carbon," 2010.

[36] T. Velempini and K. Pillay, "Sulphur functionalized materials for Hg(II) adsorption: A review," *Journal of Environmental Chemical Engineering,* vol. 7, no. 5, p. 103350, 2019/10/01/ 2019, doi: https://doi.org/10.1016/j.jece.2019.103350.

[37] M. K. B. Gratuito, T. Panyathanmaporn, R. A. Chumnanklang, N. Sirinuntawittaya, and A. Dutta, "Production of activated carbon from coconut shell: Optimization using response surface methodology," *Bioresour. Technol.,* vol. 99, no. 11, pp. 4887-4895, 2008/07/01/ 2008, doi: https://doi.org/10.1016/j.biortech.2007.09.042.

[38] N. M. Jabbar, S. D. Salman, I. M. Rashid, and Y. S. Mahdi, "Removal of an anionic Eosin dye from aqueous solution using modified activated carbon prepared from date palm fronds," *Chemical Data Collections,* vol. 42, p. 100965, 2022/12/01/ 2022, doi: https://doi.org/10.1016/j.cdc.2022.100965.

[39] S. D. Salman, I. M. Rasheed, and M. M. Ismaeel, "Removal of diclofenac removal from aqueous solution on apricot seeds activated carbon synthesized by pyro carbonic acid microwave," *Chemical Data Collections,* p. 100982, 2022/12/28/ 2022, doi: https://doi.org/10.1016/j.cdc.2022.100982.

[40] G. M. A.-H. S. D. Salman, "Adsorption of Para Nitro-phenol by Activated Carbon produced from Alhagi " *Sains Malaysiana* vol. 49, no. 1, pp. 57-67, 2020, doi: DOI: 10.17576/jsm-2020-4901-07.

[41] N. Kannan and T. Veemaraj, "Removal of Lead(II) Ions by Adsorption ontoBamboo Dust and Commercial Activated Carbons -A Comparative Study," *E-Journal of Chemistry,* vol. 6, p. 515178, 1900/01/01 2009, doi: 10.1155/2009/515178.

[42] Z. Z. Chowdhury, S. M. Zain, R. A. Khan, and M. S. Islam, "Preparation and characterizations of activated carbon from kenaf fiber for equilibrium adsorption studies of copper from wastewater," *Korean Journal of Chemical Engineering,* vol. 29, no. 9, pp. 1187-1195, 2012/09/01 2012, doi: 10.1007/s11814-011-0297-9.

[43] O. S. Amuda, A. A. Giwa, and I. A. Bello, "Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon," *Biochem. Eng. J.,* vol. 36, no. 2, pp. 174-181, 2007, doi: 10.1016/j.bej.2007.02.013.

[44] K. Y. Foo and B. H. Hameed, "Preparation of oil palm (Elaeis) empty fruit bunch activated carbon by microwave-assisted KOH activation for the adsorption of methylene blue," *Desalination,* vol. 275, no. 1, pp. 302-305, 2011/07/15/ 2011, doi: https://doi.org/10.1016/j.desal.2011.03.024.

[45] A. E. Nemr, "Potential of pomegranate husk carbon for Cr(VI) removal from wastewater: Kinetic and isotherm studies," *J. Hazard. Mater.,* vol. 161, no. 1, pp. 132-141, 2009/01/15/ 2009, doi: https://doi.org/10.1016/j.jhazmat.2008.03.093.

[46] C. A. Toles, W. E. Marshall, and M. M. Johns, "Granular activated carbons from nutshells for the uptake of metals and organic compounds," *Carbon,* vol. 35, no. 9, pp. 1407-1414, 1997/01/01/ 1997, doi: https://doi.org/10.1016/S0008-6223(97)00073-0.

[47] C. Ng, W. Marshall, R. Rao, R. Bansode, and J. Losso, "Activated carbon from pecan shell: Process description and economic analysis," *Industrial Crops and Products,* vol. 17, pp. 209-217, 05/01 2003, doi: 10.1016/S0926-6690(03)00002-5.

[48] M. A. Ferro-García, J. Rivera-Utrilla, J. Rodríguez-Gordillo, and I. Bautista-Toledo, "Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products," *Carbon,* vol. 26, no. 3, pp. 363-373, 1988/01/01/ 1988, doi: https://doi.org/10.1016/0008-6223(88)90228-X.

[49] U. Khalil *et al.*, "Selective Removal of Hexavalent Chromium from Wastewater by Rice Husk: Kinetic, Isotherm and Spectroscopic Investigation," *Water,* vol. 13, no. 3, p. 263, 2021. [Online]. Available: https://www.mdpi.com/2073-4441/13/3/263.

[50] M. M. Johns, W. E. Marshall, and C. A. Toles, "Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics," *J. Chem. Technol. Biotechnol.,* vol. 71, no. 2, pp. 131-140, 1998, doi: https://doi.org/10.1002/(SICI)1097-4660(199802)71:2<131::AID-JCTB821>3.0.CO;2-K.

[51] M. W. Khalid and S. D. Salman, "Adsorption of Heavy Metals from Aqueous Solution onto Sawdust Activated Carbon," *Al-Khwarizmi Engineering Journal,* vol. 15, no. 3, pp. 60- 69, 09/01 2019. [Online]. Available: https://alkej.uobaghdad.edu.iq/index.php/alkej/article/view/650.

[52] I. K. Shakir, "Kinetic and Isotherm Modeling of Adsorption of Dyes onto Sawdust," *Iraqi j. chem. pet. eng.,* vol. 11, no. 2, pp. 15-27, 06/30 2010. [Online]. Available: https://ijcpe.uobaghdad.edu.iq/index.php/ijcpe/article/view/373.

[53] M. J. Ahmed and S. K. Theydan, "Microwave assisted preparation of microporous activated carbon from Siris seed pods for adsorption of metronidazole antibiotic," *Chem. Eng. J.,* vol. 214, pp. 310-318, 2013/01/01/ 2013, doi: https://doi.org/10.1016/j.cej.2012.10.101.

[54] M. J. Ahmed and S. K. Theydan, "Microporous activated carbon from Siris seed pods by microwave-induced KOH activation for metronidazole adsorption," *J. Anal. Appl. Pyrolysis,* vol. 99, pp. 101-109, 2013/01/01/ 2013, doi: https://doi.org/10.1016/j.jaap.2012.10.019.

[55] S. D. Salman, I. M. Rasheed, and A. K. Mohammed, "Adsorption of heavy metal ions using activated carbon derived from Eichhornia (water hyacinth)," *IOP Conference Series: Earth and Environmental Science,* vol. 779, no. 1, p. 012074, 2021/06/01 2021, doi: 10.1088/1755-1315/779/1/012074.

[56] "Optimization of Activated Carbon Preparation from Date Stones by Microwave Assisted K2CO3 Activation," *Iraqi Journal of Chemical and Petroleum Engineering,* vol. 15, no. 1, pp. 33-42, 03/30 2014, doi: 10.31699/IJCPE.2014.1.4.

[57] D. S. Sami and K. E. Talib, "Removal of Malachite Green from Aqueous Solution using Ficus Benjamina Activated Carbon-Nonmetal Oxide synthesized by pyro Carbonic Acid Microwave " *Al-Khwarizmi Engineering Journal* vol. 19, no. 2, pp. 26-38, 2023.

[58] Khatab E. Talib and S. D. Salman, "Removal of Malachite Green from Aqueous Solution using Ficus Benjamina Activated Carbon-Metal Oxide synthesized by pyro carbonic acid microwave," *Desalination and Water Treatment,* vol. 302, no. August 2023, pp. 105-209, 2023, doi: https://doi.org/10.5004/dwt.2023.29949.

[59] S. D. Salman, I. M. Rashid, and Y. D. Abdulwahab, "Adsorption of bimetal from aqueous solution on plum seed activated carbon synthesized by pyrocarbonic acid microwave method," *J. Chem. Technol. Biotechnol.,* vol. 99, no. 9, pp. 2057-2068, 2024, doi: https://doi.org/10.1002/jctb.7708.

[60] R. Hoseinzadeh Hesas, W. M. A. Wan Daud, J. N. Sahu, and A. Arami-Niya, "The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review," *J. Anal. Appl. Pyrolysis,* vol. 100, pp. 1-11, 2013/03/01/ 2013, doi: https://doi.org/10.1016/j.jaap.2012.12.019.

[61] D. Seo, K. Yu, and R. Delaune, "Comparison of monometal and multimetal adsorption in Mississippi River alluvial wetland sediment: Batch and column experiments," *Chemosphere,* vol. 73, pp. 1757-1764, 12/01 2008, doi: 10.1016/j.chemosphere.2008.09.003.

[62] B. Xiao and K. M. Thomas, "Competitive Adsorption of Aqueous Metal Ions on an Oxidized Nanoporous Activated Carbon," *Langmuir,* vol. 20, no. 11, pp. 4566-4578, 2004/05/01 2004, doi: 10.1021/la049712j.

[63] K. Srinivasan and E. Sathiya, "Bimetal Adsorption by Cottonseed Carbon: Equlibrium and Kinetic Studies " *Journal of Chemistry,* vol. 6, no. Article ID 106127, p. 9 pages, 2009, doi: https://doi.org/10.1155/2009/106127.

[64] M. Waleed Khalid and S. D. Salman, "Adsorption of Chromium Ions on Activated Carbon Produced from Cow Bones," *Iraqi Journal of Chemical and Petroleum Engineering,* vol. 20, no. 2, pp. 23-32, 06/30 2019, doi: 10.31699/IJCPE.2019.2.4.

[65] E. A. Taki and S. D. Salman, "Removal of Diesel Oil from Aqueous Solution Using Agro-Waste Activated Carbon Synthesized by Chemical and Microwave Activation," *Journal of Ecological Engineering,* journal article vol. 25, no. 5, pp. 10-28, 2024, doi: 10.12911/22998993/185321.

[66] S. Kasaoka, Y. Sakata, E. Tanaka, and R. Naitoh, "Preparation of activated fibrous carbon from phenolic fabric and its molecular-sieve properties," *Int. Chem. Eng.,* vol. 29, no. 1, pp. 101-114, 1989.

[67] V. Amaral *et al.*, "Phenolic Compounds from Psidium guajava (Linn.) Leaves: Effect of the Extraction-Assisted Method Upon Total Phenolics Content and Antioxidant Activity," *Biointerface Research in Applied Chemistry,* vol. 11, pp. 9346-9357, 09/11 2020, doi: 10.33263/BRIAC112.93469357.

[68] R. Nunes Oliveira *et al.*, "FTIR analysis and quantification of phenols and flavonoids of five commercially available plants extracts used in wound healing," *Revista Materia,* vol. 21, pp. 767-779, 09/01 2016, doi: 10.1590/S1517-707620160003.0072.

[69] S. Sharma, V. Sharma, and A. Kuila, "Cellulase production using natural medium and its application on enzymatic hydrolysis of thermo chemically pretreated biomass," *3Biotech,* vol. 6, 06/01 2016, doi: 10.1007/s13205-016-0465-z.

[70] P. Khare and B. P. Baruah, "Structural Parameters of Perhydrous Indian Coals," *International Journal of Coal Preparation and Utilization,* vol. 30, no. 1, pp. 44-67, 2010/05/26 2010, doi: 10.1080/19392691003781616.

[71] Ş. Taşar, F. Kaya, and A. Özer, "Biosorption of lead(II) ions from aqueous solution by peanut shells: Equilibrium, thermodynamic and kinetic studies," *Journal of Environmental Chemical Engineering,* vol. 2, no. 2, pp. 1018-1026, 2014/06/01/ 2014, doi: https://doi.org/10.1016/j.jece.2014.03.015.

[72] E. Yagmur, M. Ozmak, and Z. Aktas, "A novel method for production of activated carbon from waste tea by chemical activation with microwave energy," *Fuel,* vol. 87, no. 15-16, pp. 3278-3285, 2008.

[73] T. Benzaoui, A. Selatnia, and D. Djabali, "Adsorption of copper (II) ions from aqueous solution using bottom ash of expired drugs incineration," *Adsorption Science & Technology,* vol. 36, no. 1-2, pp. 114-129, 2018.

[74] N. M. Jabbar, S. D. Salman, I. M. Rashid, and Y. S. Mahdi, "Removal of an anionic Eosin dye from aqueous solution using modified activated carbon prepared from date palm fronds," *Chem. Data Collect.,* vol. 42, p. 100965, 2022/12/01/ 2022, doi: https://doi.org/10.1016/j.cdc.2022.100965.

[75] *DESIGN EXPERT 13*. Stat-Ease Inc.

[76] S. Saini, J. Chawla, R. Kumar, and I. Kaur, "Response surface methodology (RSM) for optimization of cadmium ions adsorption using C16-6-16 incorporated mesoporous MCM-41," *SN Applied Sciences,* vol. 1, 08/01 2019, doi: 10.1007/s42452-019-0922-5.

[77] S. Bouazizi, B. Jamoussi, and D. Bousta, "Application of Response Surface Methodology for Optimization of Heavy Metals Biosorption on Natural Gum of Acacia Nilotica," *International Journal of Engineering Research & Technology,* vol. 5, 05/05 2016.

[78] K. K. Hummadi, "Optimal Operating Conditions for Adsorption of Heavy Metals from an Aqueous Solution by an Agriculture Waste," *Iraqi Journal of Chemical and Petroleum Engineering,* vol. 22, no. 2, pp. 27-35, 06/30 2021, doi: 10.31699/IJCPE.2021.2.4.

[79] C. Gabaldón, P. Marzal, A. Seco, and J. Gonzalez, "Cadmium and Copper Removal by a Granular Activated Carbon in Laboratory Column Systems," *Sep. Sci. Technol.,* vol. 35(7), pp. 1039-1053, 01/07 2000, doi: 10.1081/SS-100100209.

[80] M. Kobya, E. Demirbas, E. Senturk, and M. Ince, "Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone," *Bioresour. Technol.,* vol. 96, no. 13, pp. 1518-1521, 2005/09/01/ 2005, doi: https://doi.org/10.1016/j.biortech.2004.12.005.

[81] J. C. Moreno-Piraján, V. S. Garcia-Cuello, and L. Giraldo, "The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells," *Adsorption,* vol. 17, no. 3, pp. 505-514, 2011/06/01 2011, doi: 10.1007/s10450-010-9311-5.

[82] V. C. Taty-Costodes, H. Fauduet, C. Porte, and A. Delacroix, "Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris," *J. Hazard. Mater.,* vol. 105, no. 1, pp. 121-142, 2003/12/12/ 2003, doi: https://doi.org/10.1016/j.jhazmat.2003.07.009.

[83] M. Kavand, P. Eslami, and L. Razeh, "The adsorption of cadmium and lead ions from the synthesis wastewater with the activated carbon: Optimization of the single and binary systems," *Journal of Water Process Engineering,* vol. 34, p. 101151, 2020/04/01/ 2020, doi: https://doi.org/10.1016/j.jwpe.2020.101151.

[84] S. Z. Mohammadi, M. A. Karimi, D. Afzali, and F. Mansouri, "Removal of Pb(II) from aqueous solutions using activated carbon from Sea-buckthorn stones by chemical activation," *Desalination,* vol. 262, no. 1, pp. 86-93, 2010/11/15/ 2010, doi: https://doi.org/10.1016/j.desal.2010.05.048.

[85] Y. Huang, S. Li, J. Chen, X. Zhang, and Y. Chen, "Adsorption of Pb(II) on mesoporous activated carbons fabricated from water hyacinth using H3PO4 activation: Adsorption capacity, kinetic and isotherm studies," *Appl. Surf. Sci.,* vol. 293, pp. 160-168, 2014/02/28/ 2014, doi: https://doi.org/10.1016/j.apsusc.2013.12.123.

[86] M. Imamoglu and O. Tekir, "Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks," *Desalination,* vol. 228, no. 1, pp. 108-113, 2008/08/15/ 2008, doi: https://doi.org/10.1016/j.desal.2007.08.011.

[87] E. I. Ugwu *et al.*, "Adsorption mechanisms for heavy metal removal using low cost adsorbents: A review," *IOP Conference Series: Earth and Environmental Science,* vol. 614, no. 1, p. 012166, 2020/12/01 2020, doi: 10.1088/1755-1315/614/1/012166.

[88] M. I. Bnar, "Heavy metal ions removal from wastewater using various low-cost agricultural wastes as adsorbents: a survey," *Zanco Journal of Pure and Applied Sciences,* vol. 33, no. 2, pp. 76-91, 04/15 2021, doi: 10.21271/ZJPAS.33.2.8.

[89] N. Abdel-Ghani and G. Elchaghaby, "Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption," *Int. J. Environ. Sci. Technol. (Tehran),* vol. 4, pp. 451-456, 2007.

[90] L. Mouni, D. Merabet, A. Bouzaza, and L. Belkhiri, "Removal of Pb2+ and Zn2+ from the aqueous solutions by activated carbon prepared from Dates stone," *Desalination and Water Treatment,* vol. 16, pp. 66-73, 08/03 2012, doi: 10.5004/dwt.2010.1106.

[91] M. Jiménez-Reyes and M. Solache, "Adsorption of U(IV) by several geomaterials: kinetic, adsorbent dosage and thermodynamic," *J. Radioanal. Nucl. Chem.,* vol. 317, 04/03 2018, doi: 10.1007/s10967-018-5847-8.

[92] I. Langmuir, "THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM," *Journal of the American Chemical Society,* vol. 40, no. 9, pp. 1361-1403, 1918/09/01 1918, doi: 10.1021/ja02242a004.

[93] T. A. Saleh, "Isotherm, kinetic, and thermodynamic studies on Hg(II) adsorption from aqueous solution by silica- multiwall carbon nanotubes," (in eng), *Environ. Sci. Pollut. Res. Int.,* vol. 22, no. 21, pp. 16721-16731, 2015/11// 2015, doi: 10.1007/s11356-015-4866-z.

[94] "Permeable Reactive Barrier of Coated Sand by Iron Oxide for Treatment of Groundwater Contaminated with Cadmium and Copper Ions," *Al-Khwarizmi Engineering Journal,* vol. 16, no. 2, pp. 47- 55, 06/01 2020, doi: 10.22153/kej.2020.05.002.

[95] N. Jawad and T. M. Naife, "Mathematical Modeling and Kinetics of Removing Metal Ions from Industrial Wastewater," *Iraqi Journal of Chemical and Petroleum Engineering,* vol. 23, no. 4, pp. 59-69, 12/30 2022, doi: 10.31699/IJCPE.2022.4.8.

[96] B. Liu *et al.*, "Temperature-induced adsorption and desorption of phosphate on poly(acrylic acid-co-N-[3-(dimethylamino)propyl]acrylamide) hydrogels in aqueous solutions," *DESALINATION AND WATER TREATMENT,* vol. 160, pp. 260-267, 08/01 2019, doi: 10.5004/dwt.2019.24351.

[97] E. D. Revellame, D. L. Fortela, W. Sharp, R. Hernandez, and M. E. Zappi, "Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review," *Cleaner Engineering and Technology,* vol. 1, p. 100032, 2020/12/01/ 2020, doi: https://doi.org/10.1016/j.clet.2020.100032.

[98] G. Crini and P.-M. Badot, "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature," *Progress in Polymer Science,* vol. 33, no. 4, pp. 399-447, 2008/04/01/ 2008, doi: https://doi.org/10.1016/j.progpolymsci.2007.11.001.

[99] M. S. Chiou and H. Y. Li, "Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads," *Chemosphere,* vol. 50, no. 8, pp. 1095-1105, 2003/03/01/ 2003, doi: https://doi.org/10.1016/S0045-6535(02)00636-7.

[100] Q. Lin, K. Wang, M. Gao, Y. Bai, L. Chen, and H. Ma, "Effectively removal of cationic and anionic dyes by pH-sensitive amphoteric adsorbent derived from agricultural waste-wheat straw," *Journal of the Taiwan Institute of Chemical Engineers,* vol. 76, pp. 65-72, 2017/07/01/ 2017, doi: https://doi.org/10.1016/j.jtice.2017.04.010.