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RESEARCH ARTICLE – CHEMICAL ENGINEERING

Optimization of the Adsorption of Cadmium and Copper Ions from an Aqueous Solution by Alum Sludge

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Abstract

This work aims to reuse waste from drinking water treatment plants that use alum, called alum sludge (AS). By calcining alum sludge (CAS) at 550 °C for two hours, then using it to adsorb the heavy metals copper and cadmium from their aqueous solutions with the batch adsorption method. The ability of CAS to remove Cd (II) and Cu (II) was studied under the influence of several factors (i.e., initial concentration of metal ions, contact time and CAS dosage) by using Box-Behnken experimental designs (BBD) for the response surface methodology (RSM) and with statistical analysis (ANOVA). Then, identify the optimal conditions that produce the maximum removal. The AS, which has been dried and ground was characterized by chemical method analysis (SEM, XRD, and EDX). At optimum conditions, the maximum removal percentages of Cu and Cd reached 92.5% and 98.8%, respectively. The adsorption isotherms for Cu data followed the Langmuir model, while the Cd data fitted well with the Freundlich and the Langmuir models. For each Cd (II) and Cu (II), the maximum monolayer adsorption capacity was 29.101 and12.45 mg/g, respectively. The pseudo-second-order kinetic model provided a good match to the kinetic data. It was found that water treatment sludge is a good source from which to create an inexpensive adsorbent to remove heavy metal ions from wastewater.

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1. Introduction

Geological processes, such as erosion, naturally release heavy metals into the aquatic environment. These minerals originate in rocks and sediments, which are the natural sources of heavy metals [1, 2]. Another natural source of contamination for the aquatic environment is volcanic activity. It may pass through acid rain that is tainted with heavy metals and other contaminants. The soil may erode, and heavy metals may be released into the water by these rains [2, 3]. Heavy metal contamination in the environment is mostly caused by industrial activities, which include petroleum, oil refineries, iron and steel, copper, glass, aluminium, tanning, fertiliser, pesticides, fuel, and other industries [2].

As a result, pollution of heavy metals is a serious environmental problem that poses a threat to both animal and human life, because it is toxic even in low concentrations [4], this is why unsafe drinking water remains a problem for about 15% of the world population [5]. Therefore, chemical concentrations in water in industrial discharges and wastewater should be strictly controlled [6]. Several techniques of heavy metal removal, including coagulation-flocculation, chemical precipitation, , adsorption, ion exchange, floating and membrane filtration, have been developed and thoroughly studied in the previous several decades. Nevertheless, the majority of these methods are expensive, energy-intensive, and frequently result in the production of hazardous byproducts [7]. The sorption process is a promising and extremely effective technology to remove heavy metals from wastewater effluents. High removal of heavy metals in wastewater is achieved by using both commercial and bioadsorbents. The adsorption method is frequently employed instead of more traditional techniques because of its accessibility, low cost and environmental friendliness [7, 8]. To remove heavy metals, different methods of adsorption are used, including: Activated carbon [9], Nanomaterial [10], rice husk silica [11], Egg shell [12], Bentonite Clay [13], agricultural wastes, peat moss and chitin [14], TiO2, synthetic resins, zeolites and clay [15].

Adsorption is regarded as an all-inclusive method of treating water. It may also be used to remove 99% of organic, inorganic and biological contaminants. Due to its metal selectivity, cheap cost, ease of metal recovery, reuse of heavy metal and increased adsorption, the method has drawn interest for the treatment of industrial effluent [16]. The term alum sludge (AS) describes the residue left after drinking water is treated in water treatment facilities using aluminum sulfate, most used as a coagulant to reduce water turbidity. Dewatered AS is then dumped as garbage at waste disposal sites, and this occurs in many parts of the world. Since alum contains a high percentage of aluminium, it is considered toxic to aquatic life [17]. A literature review reveals an evolving movement away from the recycling and reuse of raw AS and towards the synthesis of value-added AS-based adsorbents. AS has been studied as an adsorbent both untreated and after chemical and physical processing

Nomenclature & Symbols

AS	Alum Sludge	EDX	Energy Dispersive X-Ray Analysis
CAS	Calcining Alum Sludge	$Cd(NO^3)_2.4H_2O$	Cadmium Salt
BBD	Box-Behnken Experimental Designs	$CaCO_3$	Calcium Carbonate
RSM	Response Surface Methodology	Ce	Equilibrium Metal Ion Concentration (mg/L)
$Al2\ (SO_4)^3$	Aluminum Sulphate	q_e,q_t	Adsorption Capacity At Equilibrium Time
SEM	Scanning Electron Microscope	T	Denotes Time (min)
XRD	X-Ray Diffraction	q_{max}	The Maximum Adsorption Capacity (mg/g)

to enhance the material's adsorption capacity. And has been used in several investigations, including dye removal [18, 19], phosphorus removal (P) [20], and heavy metals removal from wastewater streams such as: V, As, Mo, Se, Zn, Cd, Pb, Cu, Co, Hg, Cr [21, 22].

Zeolite is a group of crystalline, microporous aluminosilicate minerals utilized as industrial catalysts and adsorbents. They are mostly composed of silicon, aluminum, and oxygen. Their general formula is [(AlO2) a (SiO2) y] Ma/b. cH2O, where a and y stand for the total number of [SiO4]-4 and [AlO4]-5 tetrahedra in a unit cell of the zeolite, M for either an alkali metal or an alkaline earth metal cation, b for the valency of the earth metal cation, and c for the amount of water of crystallization per unit cell of the zeolite. Although the ratio y/a typically has a value between 1 and 5, it can have values between 10 and 100 in the case of silica-based zeolites [23]. Based on their Si/Al ratio, zeolites have been divided into many varieties. Zeolites are distinctive adsorbents due to their enormous specific surface areas, distinctive structure, strong ion-exchange capacity, and above all low cost [19]. Water treatment plant AS is a plentiful byproduct with high Si and Al levels. It is the perfect precursor for zeolite synthesis because of these properties [24, 25, 19].

Copper and cadmium are highly toxic heavy metals, and there are many sources of water pollution with their ions. When their levels exceed the permissible limits, they can cause health effects [26, 27]. The adsorption of Cd and Cu elements by AS has been addressed by several research studies using either AS directly without treatment [28, 29] or AS modified by calcination and accompanied by chemical and physical treatment [30]. In this study, aluminum sludge (AS), a by-product of drinking water treatment, was calcined at 550 °C for 2 hours without any additional treatments. This study evaluates the feasibility of this thermally treated waste as a low-cost adsorbent for the removal of copper and cadmium in polluted water. The adsorption performance was assessed under varying conditions, including metal ion concentration, contact time, and CAS dosage. This approach not only proposes a sustainable solution for managing industrial waste but also offers an environmentally and economically viable method for heavy metal removal from wastewater.

2. Materials and Methods

2.1. Preparation of alum sludge and characterization

The AS was collected from an Iraqi water treatment facility in Baghdad. Samples were taken of the clay collected at the bottom of the secondary sedimentation tank, by draining the tank of water during the cleaning process. AS refers to the by-product generated in the production of drinking water, where used aluminum sulphate $Al_2\ (SO4)^3$ as a coagulant in water treatment processes to remove turbidity.

The sludge was collected and dried at ambient temperature for seven days, and then manually ground with a hammer to produce alum sludge powder. The powder was dried at 120 °C in an oven for three hours then reground for 10 minutes in a small electric mill. After that, the particle size of the sludge powder was measured at or below 250 µm using the dry technique of sieving. Lastly to ensure that all moisture was removed; Dried AS powder in the oven for one hour at 110°C. The raw sludge powder is then calcined for two hours at 10 ± °C/min to 550 °C in an electrical furnace. These temperatures and durations were selected based on preliminary experimental results. The resulting calcined alum sludge (AS) is referred to as CAS, which is ready for adsorption experiments.

A scanning electron microscope (SEM) and X-ray diffraction (XRD-6000, Shimadzu, Japan) were used to analyze the AS powder. By using an Energy Dispersive X-ray (EDX-Vega III TESCAN, Czech), the chemical composition was examined.

2.2. Preparing the solution of a heavy metal

(1000 mg/L) A stock solution of each Cd (II) and Cu (II) was made by dissolving copper salt Cu (NO3)2 .3H2O (≥ 95% pure) from HiMedia Co. and cadmium salt $Cd\ (NO_3)^2\ .4H2O$ (99% pure) from CDH Co. separately in 1000 ml of deionised water. The stock solutions were diluted with deionised water to obtain standard solutions containing 20–120 mg/l of Cd (II) and 50–200 mg/l of Cu (II). A solution with a pH value of 6.0 was used for both metals, since several studies have demonstrated that it is appropriate for the adsorption process and to avoid precipitation when the pH increases. [31], 0.1M NaOH or 0.1M HCl was used to adjust the pH.

2.3. Batch adsorption studies

At room temperature (24 ºC±1), batch experiments of adsorption were carried out to ascertain the adsorption degree of each heavy metal ion. The effects of several factors, including: contact time, CAS dose (adsorbent) and initial metals concentration, were investigated.

A set of 250 mL conical flasks was used, each flask containing 50 mL of a known concentration of Cd and Cu, adsorption isotherms and the impact of initial concentration was examined. Different amounts of CAS (0.05–0.35) g were added for Cd removal and (0.1–0.7) g for Cu. The effect of contact time on adsorption was determined at different times between 10 and 90 minutes for each Cd and Cu adsorption. All samples were shaken, and the agitation speed was kept constant at 160 r.p.m. At the end of each experiment, filter paper was used to filter the sample solution (removal of the residual of CAS), and determine the concentration of the remaining Cd (II) and Cu (II) by Agilent 280FS AA Atomic Adsorption Spectrometer. Adsorption capacity and Percentage removal of heavy metal ions were calculated using Eq. 1, 2 and 3 [19, 32].

$$\text{Metal removal: (R)\%} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \qquad (1)$$

$$q_t = (C_0 - C_t) \cdot \frac{V}{m} \tag{2}$$

$$q_e = (C_0 - C_e) \cdot \frac{V}{m} \tag{3}$$

The concentrations of metal ions before and after adsorption (mg/L) at different times are denoted by C_0 and C_t, respectively. Where V is volume (L), m is the adsorbent dose (g), and qt is the adsorption capacity (mg/g) at any given time. C_e is the equilibrium metal ion concentration (mg/L), and q_e is the adsorption capacity at equilibrium time.

2.4. Experiments design

A method known as experimental design has been used to identify the key variables influencing experiment results as well as potential interactions that may be significant. Box-Behnken designs (BBD) were used in this study, which is one sort of response surface methodology (RSM). Response surface methodology is a mathematical collection and methods of statistics that focus on fitting a polynomial equation to experimental data, which must depict the behavior of a data set to produce statistical predictions [33]. Only three levels of each parameter are used by the BBD denoted by the codes (-1, 0, 1) to fit a second-order regression model (quadratic model). The three independent variables or parameters (CAS amount, time, and concentration of each metal) were examined as shown by Table 1. The Box-Behnken design includes 15 experiments in the three-parameter case, as shown in Table 2.

Table 1. Codes and the actual experimental values of the box-behnken design parameters

Codes Level	**Cu II adsorption**			**Cd II adsorption**		
	CAS (g)	**Conc. (mg/L)**	**Time (min)**	**CAS (g)**	**Conc. (mg/L)**	**Time (min)**
	X_1	**X_2**	**X_3**	**X_1**	**X_2**	**X_3**
-1	0.1	50	10	0.05	20	10
0	0.4	125	50	0.2	70	50
1	0.7	200	90	0.35	120	90

Table 2. The (BBD) matrix with experimental and predicted values for Cu adsorbed by CAS

Run	**Parameters**			**Experimental Cu Removal%**	**Predicted Removal%**
	CAS(g) X_1	**Conc.(mg/l) X_2**	**Time(min) X_3**		
1	0.1	50	50	65.193	62.579
2	0.7	50	50	90.820	92.843
3	0.1	200	50	18.793	16.770
4	0.7	200	50	91.968	94.583
5	0.1	125	10	26.586	28.231
6	0.7	125	10	84.509	81.517
7	0.1	125	90	35.867	38.859
8	0.7	125	90	95.296	93.650
9	0.4	50	10	88.169	89.137
10	0.4	200	10	51.170	51.547
11	0.4	50	90	85.338	84.961
12	0.4	200	90	79.452	78.483
13	0.4	125	50	70.065	70.529
14	0.4	125	50	70.092	70.529
15	0.4	125	50	71.429	70.529

The response and independent variables are related mathematically (using a second-order polynomial model), as follows:

$$\mathbf{Y} = \mathbf{b}_0 + \boldsymbol{b_1X_1} + \boldsymbol{b_2X_2} + \boldsymbol{b_3X_3} + \boldsymbol{b_{12}X_1X_2} + \boldsymbol{b_{13}X_1X_3} + \boldsymbol{b_{23}X_2X_3} + \boldsymbol{b_{11}X_1}^2 + \boldsymbol{b_{22}X_2}^2 + \boldsymbol{b_{33}X_3}^2 \tag{4}$$

Where, (Y) is the response, (% metal removal), (X1, X2 and X3) are the independent variables' coded levels., and (b0, b1, b2, b12, b11, …etc.) are coefficients of regression.

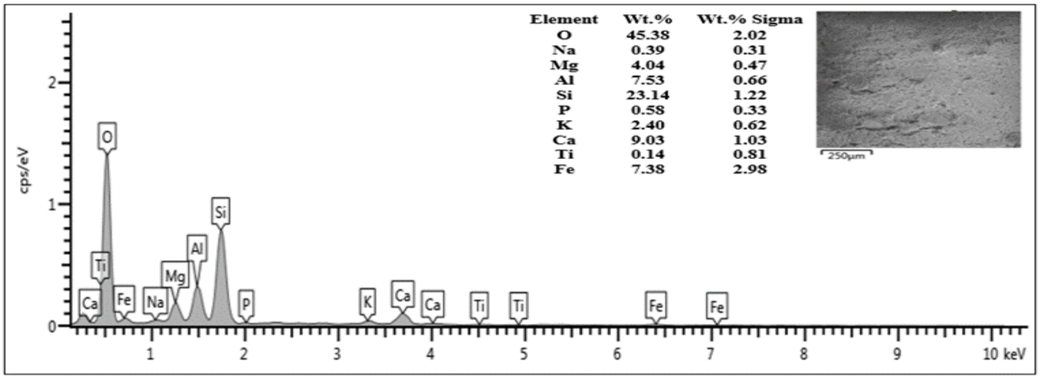
3. Results and Discussion

3.1. Characterization of raw material

Fig. 1 illustrates the Energy Dispersive X-ray Analysis (EDX) analysis for the elemental composition of AS, showing that AS has some Si and Al in it, which is suitable for use as a raw material for the zeolite synthesis.

Fig. 2 displays the AS's X-ray diffraction (XRD) spectrum. It demonstrates that AS is made up of calcite and quartz. The mineral calcite is mostly made up of calcium carbonate ($CaCO_3$). It is the second most common mineral on Earth after quartz. Geological calcium carbonate is not very effective in adsorbing heavy metals; instead, the exchange process that results in the creation of poorly soluble metal compounds is the main removal mechanism. Consequently, carbonates of biological origin are used in most research [34, 35]. Moreover, certain conditions and treatments are required for the utilisation of quartz in the adsorption of heavy metals [36].

The AS sample has an Si/Al molar ratio of 3, Zeolites type Y, P, RHO and L can be formed with this ratio [37, 38]. In Fig. 3, two types of Zeolites (Y and RHO) were formed after the fusion step of the AS.



Element	Wt.%	Wt.% Sigma
O	45.38	2.02
Na	0.39	0.31
Mg	4.04	0.47
Al	7.53	0.66
Si	23.14	1.22
P	0.58	0.33
K	2.40	0.62
Ca	9.03	1.03
Ti	0.14	0.81
Fe	7.38	2.98

Fig. 1. (EXD) Spectrum of alum sludge powder

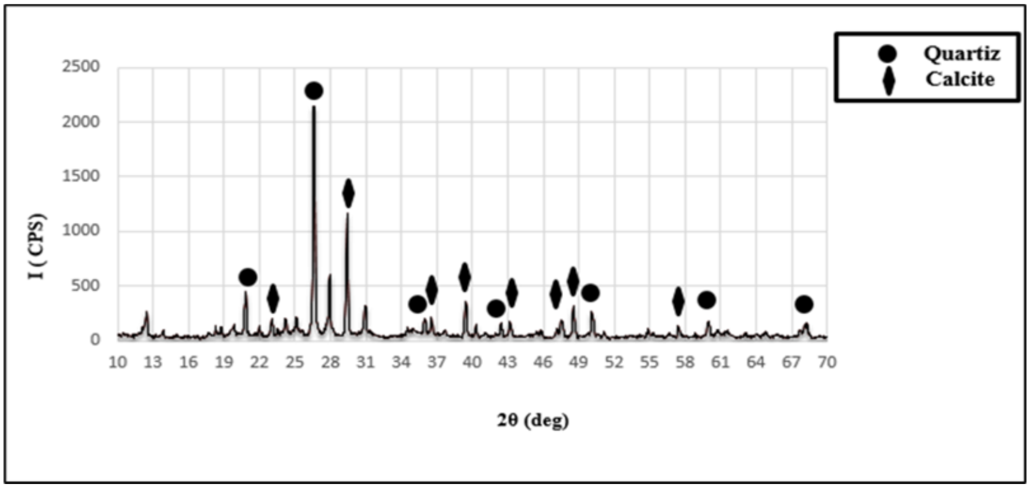


Fig. 2. XRD of AS powder

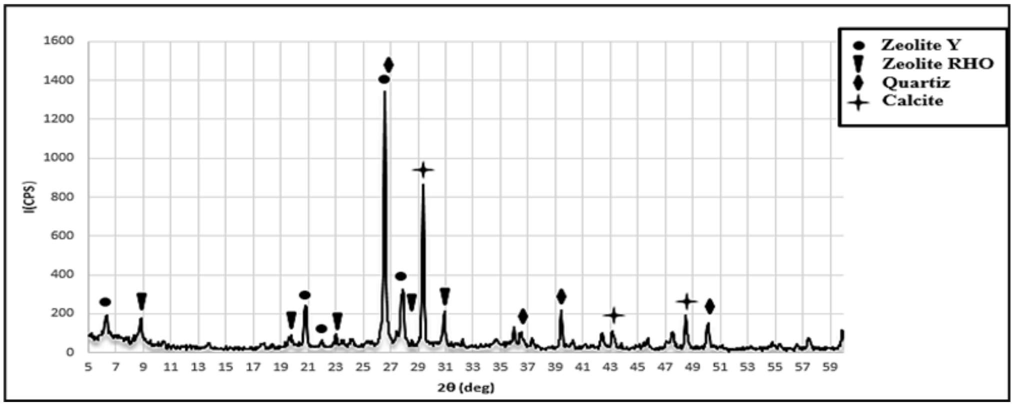
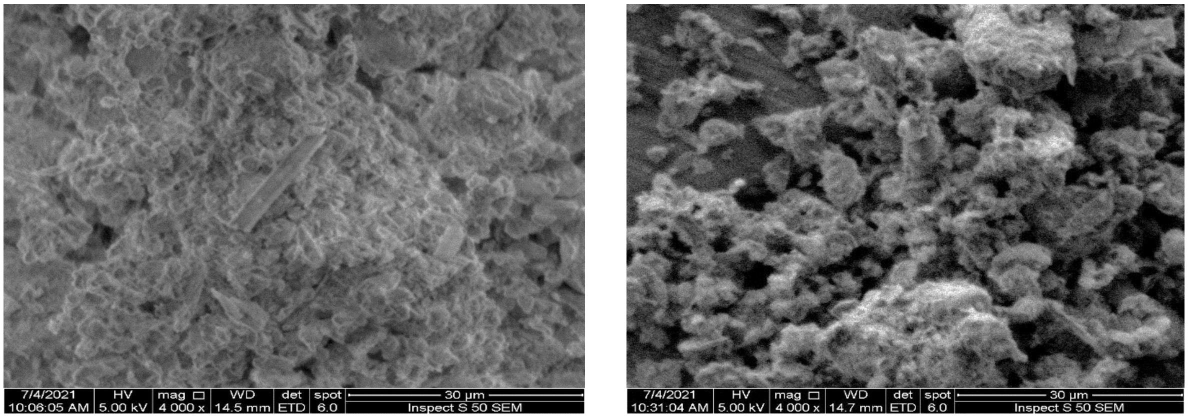


Fig. 3. XRD of (AS) after fusion at 550 °C for 2 hours

The scanning electron microscopy (SEM) in Fig. 4(a) displays the AS powder. It demonstrates that AS has a plate-like microstructure that gives it a clay-like appearance.

In the diffraction diagram in Fig. 3, zeolites (Y and RHO) were modified. This was confirmed by scanning electron microscopy (SEM) Fig. 4(b), which showed that the sludge calcined at 550 °C included a crystalline zeolite group.

The CAS's porous structure is heterogeneous in nature, with a heterogeneous variety of porous forms, as shown in Fig. 4(b). As a result, the sludge's structure is irregular [39].



(a) (b)

Fig. 4. SEM images; (a) AS powder, (b) fusion AS at 550 °C for two hours

3.2. Statistical analysis of experimental results

The RSM is used to determine the optimal factors that yield maximum removal by establishing a polynomial Equation between the metal removal percentage (as the response) and the factors under study. A statistical technique for examining and contrasting the means of two or more groups or treatments is the analysis of variance (ANOVA). It was employed to ascertain the variables of the generated model's statistical significance [40]. Minitab (17software) was used for statistical analysis of all the results. According to the design of Box-Behnken, Tables 2 and 3 show the parameters of the process and the (anticipated and experimental) Removal % for each metal (Cu, Cd).

Table 3. The (BBD) matrix with experimental and predicted values for Cd adsorbed by CAS

Run	Parameters			Experimental Cd Removal%	Predicted Removal%
	CAS(g) X_1	Conc.(ppm) X_2	Time(min) X_3		
1	0.05	20	50	77.569	76.759
2	0.35	20	50	95.5	101.180
3	0.05	120	50	12.256	9.554
4	0.35	120	50	56.493	60.281
5	0.05	70	10	21.55	29.564
6	0.35	70	10	67.181	67.138
7	0.05	70	90	35.891	38.439
8	0.35	70	90	78.388	76.013
9	0.2	20	10	89.3	84.532
10	0.2	120	10	32.589	30.480
11	0.2	20	90	93.51	93.407
12	0.2	120	90	38.331	39.355
13	0.2	70	50	54.99	52.789
14	0.2	70	50	56.036	52.789
15	0.2	70	50	55.485	52.789

The analysis of variance (ANOVA) to ascertain the impact of independent factors on the dependent variable is shown in Tables 4 and 5.

Table 4. Presents the analysis of variance (ANOVA) for Cu removal

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	8381.83	931.31	95.92	0
Linear	3	7070.35	2356.78	242.73	0
X_1-AS(g)	1	5840.32	5840.32	601.51	0
X_2-Conc.(mg/L)	1	971.02	971.02	100.01	0
X_3-Time(min)	1	259.01	259.01	26.68	0.004
Square	3	503.72	167.91	17.29	0.005
X_1X_1	1	343.94	343.94	35.42	0.002
X_2X_2	1	124.91	124.91	12.87	0.016
X_3X_3	1	0.36	0.36	0.04	0.855
2-Way Interaction	3	807.76	269.25	27.73	0.002
X_1X_2	1	565.21	565.21	58.21	0.001
X_1X_3	1	0.57	0.57	0.06	0.819
X_2X_3	1	241.98	241.98	24.92	0.004
Error	5	48.55	9.71		
Lack-of-Fit	3	47.33	15.78	25.95	0.037
Pure Error	2	1.22	0.61		
Total	14	8430.37			
S = 3.11599 R-sq = 99.42% R-sq(adj)= 98.39% R-sq(pred)=90.98%					

Table 5. Presents the analysis of variance (ANOVA) for Cd removal

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	9369.86	1041.1	42.54	0
Linear	3	8824.49	2941.5	120.2	0
X_1-AS(g)	1	2823.61	2823.61	115.39	0
X_2-Conc.(mg/L)	1	5843.35	5843.35	238.79	0
X_3-Time(min)	1	157.53	157.53	6.44	0.052
Square	3	369.33	123.11	5.03	0.057
X_1X_1	1	55.14	55.14	2.25	0.194
X_2X_2	1	286.94	286.94	11.73	0.019
X_3X_3	1	2.9	2.9	0.12	0.745
2-Way Interaction	3	176.04	58.68	2.4	0.184
X_1X_2	1	173	173	7.07	0.045
X_1X_3	1	2.46	2.46	0.1	0.764
X_2X_3	1	0.59	0.59	0.02	0.883
Error	5	122.36	24.47		
Lack-of-Fit	3	121.81	40.6	148.3	0.007
Pure Error	2	0.55	0.27		
Total	14	9492.2			

S = 4.94682 R-sq = 98.71% R-sq(adj)= 96.39% R-sq(pred)= 79.46%

In Tables 4 and 5, the ANOVA analysis was used to identify the significant parameters, also obtaining a model with second-order polynomials. The empirical models were represented in uncoded units in Equations (5, 6) for Cu and Cd removal%, respectively.

$$Cu\ R\,\% = 87.51+108.2\ X_1-0.7464\ X_2-0.175\ X_3-107.2\ X_1^2+0.001034\ X_2^2-0.00020\ X_3^2+0.5283\ X_1X_2+0.031X_1X_3+0.002593\ X_2X_3 \qquad (5)$$

$$Cd\ R\% = 83.4+139.1\ X_1-1.219\ X_2+0.179\ X_3-172\ X_1^2+0.00353\ X_2^2-0.00055\ X_3^2+0.877\ X_1X_2-0.131\ X_1X_3+0.00019\ X_2X_3 \qquad (6)$$

Where Cu R% and Cd R% are Cu and Cd removal percentages.

The probability, or P-value, was used to evaluate the model terms with a confidence level of 95%. Each coefficient's importance was assessed, and the F-value's ability to demonstrate statistical significance was gauged. The parameters are more significant when the F-values are higher and the P-values are lower than 0.05 [33]. Table 4 shows all factors ($P < 0.05$) indicated that the model terms were statistically significant, except for X32 and X1 X3, so Equation (5) is reduced after removing these terms, presented by Equation (7).

$$Cu\ R\,\% = 87.29+109.6\ X_1-0.7474\ X_2-0.1818\ X_3-107.0\ X_1^2+0.001038\ X_2^2+0.5283\ X_1X_2+0.002593\ X_2X_3 \qquad (7)$$

The model's high fit is demonstrated by the values of R-sq, R-sq adjusted, and R-sq predicted, which were all extremely close to 100% and to one another. This indicates that the values of practical obtained for the efficiency of Cu removal and the projected values correspond.

Also, for Cd removal as in Table 5, the non-significant terms that have ($p>0.05$) are X12, X32, X1 X3 and X2 X3 Then the Equation 6 becomes:

$$Cd\ R\,\% = 90.25+63.9\ X_1-1.229\ X_2+0.1109\ X_3+0.003662\ X_2^2+0.877\ X_1X_2 \qquad (8)$$

According to the statistical data in Tables 4 and 5, the amount of the adsorbent and the concentration of each of the two minerals have the most impact on the adsorption process. Regarding time, it has the least impact on the two minerals' adsorption process. As a result, the R-sq values for the efficiency adsorption of the Cu and Cd models in Equations 7 and 8 improve, as shown in Table 6. This indicates how well the model fits the data.

Table 6. Values of R-square for the metal removal% equation for each Cu and Cd

Metal	R-sq	R-sq(adj)	R-sq(pred)
Cu R% Eq.	99.41%	98.83%	96.03%
Cd R% Eq.	98.08%	97.02%	92.64%

Equations 7 and 8 were used, along with Minitab 17, to determine the optimum variables condition that gives the highest removal percentage for each metal. Table 7 shows the obtained results for the values of the three variables: dose, concentration, and time, at the optimal conditions. To ensure the accuracy of the results, an experiment was conducted using these ideal conditions to compare the expected result with the experimental result, as shown in Table 7. The results are close.

3.3. Assess the variables' effect on metal removal

The link between the factors (time, metal concentration, and CAS dosage) and the response (Cd (II) and Cu (II) removal %) is made clearer in Figs. 5 and 6 respectively. Plotting of these associations was done at the 0-code level for every parameter.

- Effects of the adsorbent dose

An important factor in determining an adsorbent's capacity for a particular initial concentration of the adsorbate is its mass. Figs. 5 and 6 show response surface plots of metal ion removal (%) versus the variables. The correlation between the adsorbent dose and the removal percentages of Cd^{+2} and Cu^{+2} shows a strong positive correlation. This is because there was a greater rate of adsorption when the molecules of adsorbate were transferred to the wide surface of the material's adsorbent. So, the two metals are removed to a greater extent when the adsorbent dose is increased; this indicates that the higher content of the adsorbent sites led to an increase in the removal percentage as shown in Figs. 5(a and b) and 6 (a and b).

Table 7. Metal removal percentage at optimal variable settings, both experimentally and predictably

Variables	**Optimum value**		**Cu(II) removal%**		**Cd(II) removal%**	
	Cu(II)	**Cd(II)**	**Predictive**	**Experimental**	**Predictive**	**Experimental**
CAS (g) X_1	0.627	0.35	94.78	92.5	100	98.8
Conc.(mg/L)X_2	50	20				
Time (min)X_3	10	90				

- Effects of the initial concentrations

Figs. 5(a, c) and 6(a, c) illustrate the effects of the initial concentrations of metal ions on removal%. There was a substantial inverse association between the percentages of Cu^{+2} and Cd^{+2} removal and their initial concentrations. This is because nearly all of the lower concentrations of the ions were extremely quickly adsorbed. But as the metal ion concentration increased, the CAS surface became saturated at equilibrium, and the number of vacant sites dropped. After that, the removal percentage decreased with respect to the extra ions.

- Effect of time

Figs. 5(b) and 6(b) illustrate how time and the amount of adsorbed material at a particular solution concentration affect the removal of metals. Removing copper and cadmium is not strongly impacted by increasing time when increasing the amount of adsorbed material. Figs. 5(c) and 6(c) illustrate the effect of time in relation to concentration at a specific amount of adsorbent. Good metal removal takes longer with increasing concentration, and this is more noticeable with copper than with cadmium.

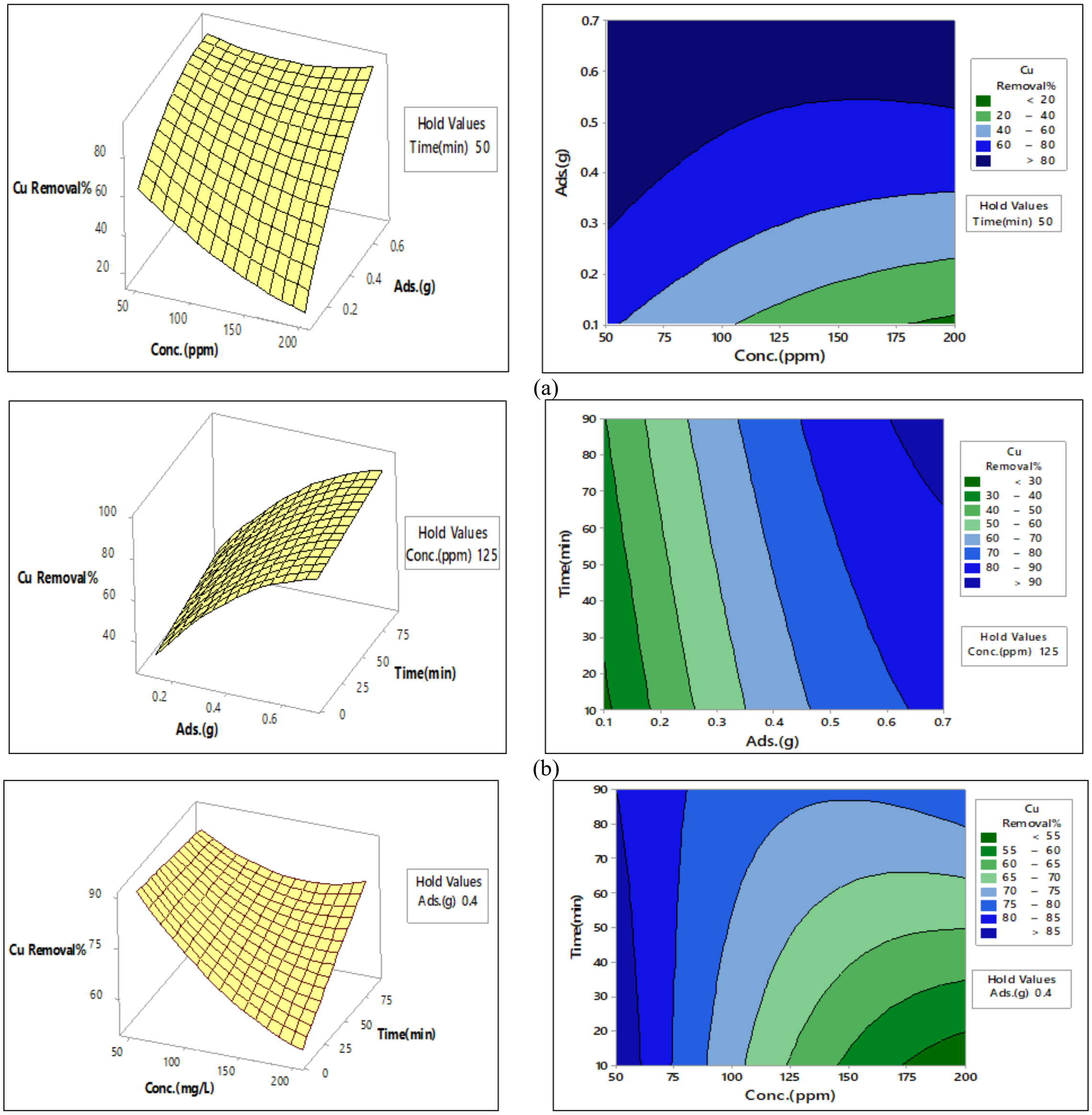
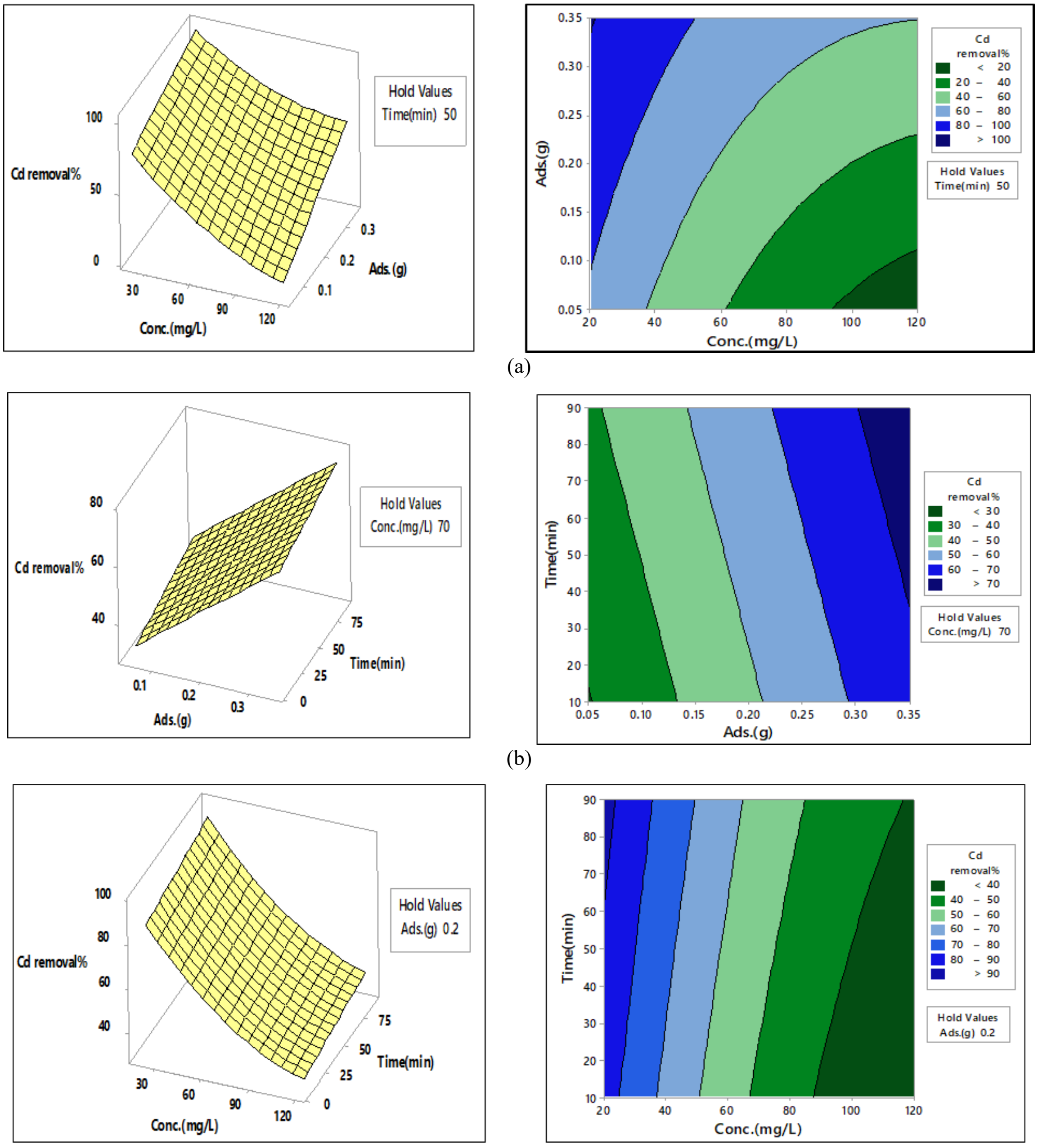


Fig. 5. Three-dimensional response surface and contour plots of Cu removal the function; (a) conc and dosage, (b) dosage and time, and (c) conc and time



(a)

(b)

(c)

Fig. 6. Three-dimensional response surface and contour plots of Cd removal as a function; (a) conc. and dosage, (b) dosage and time, and (c) conc and time

3.4. Adsorption isotherms

adsorption isotherms are essential to study to forecast how the amount of adsorbate and the adsorbent surface would interact at equilibrium at a specific temperature. Three types of isotherm models were used: the Freundlich, Langmuir, and Temkin isotherm models. These models are useful for examining the adsorption efficiencies and capacities of the adsorbent. Equations (9, 10, and 11) express these models [32].

Langmuir: $$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_l\, q_{\max}} \quad (9)$$

Freundlich: $$\ln(qe) = \left(\frac{1}{n}\right)\ln(C_e) + \ln(Kf) \quad (10)$$

Temkin: $$\frac{RT}{Bt}\ln(K_t\ C_e) \quad (11)$$

Where K$_l$ is the Langmuir equilibrium constant, Kf and n are the Freundlich constants, R is the ideal gas constant (8.314 J/mol K), K$_t$ is the Temkin isotherm constant (L/g), T is the temperature (K), and Bt is a constant related to the adsorption heat (J/mol). Where q$_e$ is the adsorption capacity at equilibrium (mg/g), amount of metal adsorbed per unit of adsorbent, q$_{max}$ is the maximum adsorption capacity (mg/g), and c$_e$ is the concentration of metal ion in the solution at adsorption equilibrium (mg/L).

The Langmuir adsorption isotherm is predicated on the monolayer adsorption of metal ions on the sorbent surface, and the adsorption system's energy is taken to be constant. For heterogeneous systems, the Freundlich adsorption isotherm was created, which provides insight into the notion of multilayer adsorption on the sorbent surface. The uniform distribution of energy over the surface adsorption sites is assumed by the Temkin isotherm model [41, 42].

3.5. Equilibrium time for metal adsorption

The kinetic properties of adsorption are determined by contact time, which is a crucial component to consider when examining the equilibrium state of the adsorption process. Cd (II) and Cu (II) metal ion adsorption is influenced by contact time, as Fig. 7 illustrates. As the contact duration for both metal ions increases, there is a slight rise in specific adsorption. There are enough adsorption sites on the adsorbent surface during the initial stage of adsorption to adsorb a significant amount of heavy metal ions. As a result, diffusion resistance is produced by the adsorption sites becoming more saturated and the removal efficiency decreasing and reaching equilibrium [43].

According to the curves in Fig. 7, it takes 90 minutes for Cu (II) and 105 minutes for Cd (II) to reach equilibrium. Cu (II) has a higher adsorption than Cd (II), nevertheless. This indicates that adsorbent CAS has a greater affinity for Cd than for Cu.

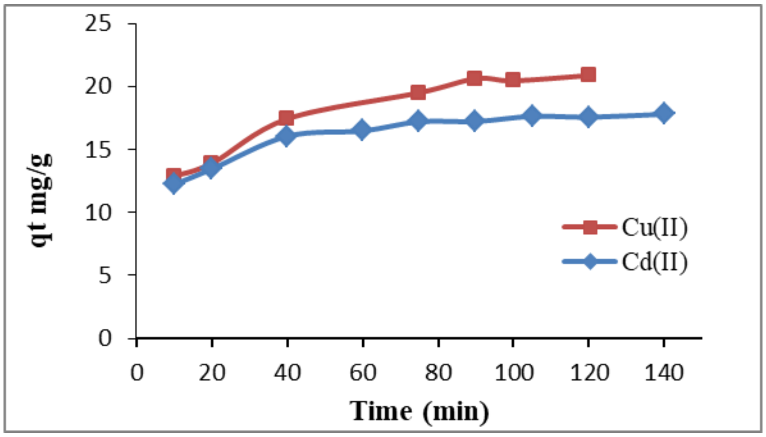


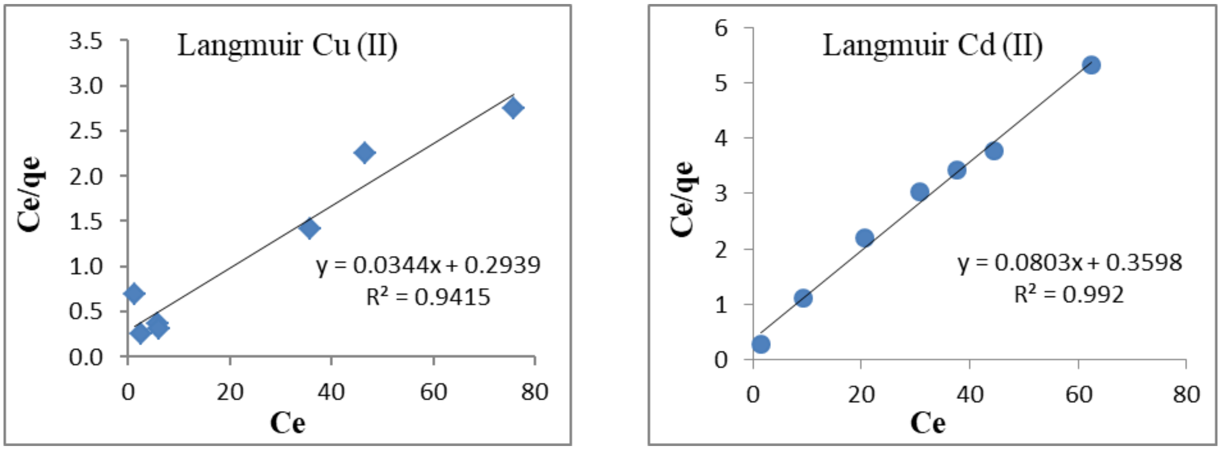
Fig. 7. The effect of contact time on the adsorption of Cu (II) and Cd (II) ions onto alum sludge(CAS) at pH =6 and 0.2 g of alum sludge, 50 ml solution containing 120 mg/L and 125 mg/L of Cd (II) and Cu (II), respectively

The results of the Freundlich, Langmuir and Temkin isotherms are displayed in Fig. 8. In the meantime, Table 8 displays their fitting parameters.

Table 8 presents the equilibrium data analysis for the three models. In comparison, the R^2 values for Cd (II) in the Freundlich, Langmuir, and Temkin models showed 0.992, 0.9886, and 0.976, respectively, indicating a satisfactory fit for the experimental data. Additionally, well-fitting curves with R2 = 0.9415 and 0.918 in the Temkin and Langmuir models were obtained, respectively, for the Cu(II), but the Freundlich model, on the other hand, gave poor-fit curves with R2 = 0.6512. Thus, CAS is a monolayer adsorbent of these metal ions [29].

Table 8. The correlation coefficients (R2) and isotherm model parameters for the adsorption of Cd (II) and Cu (II) onto alum sludge (CAS)

Metal ions	**Langmuir**			**Freundlich**			**Temkin**		
	q_{max} (mg/g)	**K_l (L/mg)**	**R^2**	**K_f (L/g)**	**n**	**R^2**	**B_t J/mol**	**K_t(L/mol)**	**R^2**
Cu(II)	29.101	0.1169	0.9415	4.2924	2.0491	0.6512	5.485	1.891	0.918
Cd(II)	12.456	0.2231	0.992	4.9351	4.5827	0.9886	1.7816	11.993	0.976



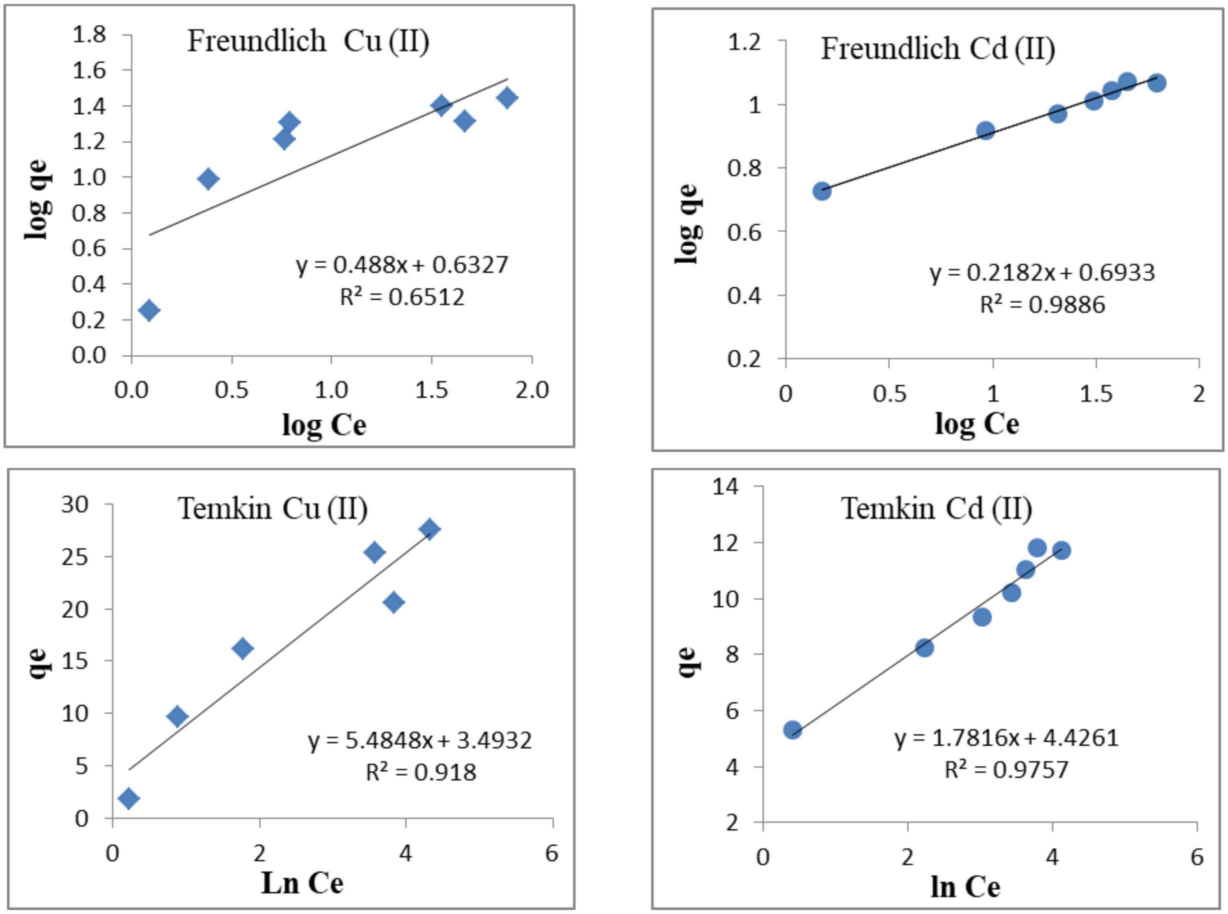


Fig. 8. Adsorption isotherm models for each metal Cu and Cd

The disparity in the applicability of the Freundlich equation is likely attributable to the differing interactions of copper and cadmium ions with the CAS surface, as well as their distinct chemical and physical properties, including size and charge differences, water interactions, and adsorption capacity [26, 44]. The nonlinearity degree between adsorption and solution concentration is indicated by the value of the constant n. An adsorption is considered linear if the value of n is 1. When n is less than one, the process of adsorption is considered to be chemical; but, when n is more than one, as demonstrated for the two metals in Table 8, the process of adsorption is considered to be physical. Physical adsorption is when an adsorbent sticks to an adsorbate surface due to the nonspecific force of van der Waals, which doesn't depend on the type of material. Physical adsorption is a reversible process [42].

Table 8 notes that copper's qmax is greater than cadmium's, indicating that copper has a higher adsorbance. This may be due to the properties of heavy metals. Heavy metal adsorption is often influenced by the metals' hydration energies, hydrated radii, solubility, and electronegativity in the aqueous phase. Both Cd(II) and Cu(II) have hydrated radii of 4.26 and 4.19 Å, hydration energies of -1807 and -2100 kJ/mol, and electronegativity of 1.69 and 2.00, respectively. Heavy metals adsorb onto the CAS surface more quickly and quantitatively when their hydrated radius is smaller. Heavy metal cation interacts easily with the surface of CAS during adsorption as reflected in the hydration energy, which allows water molecules to separate from the cation in the aqueous phase. Consequently, a heavy metal cation's hydration energy increases with its level of hydration, reducing its ability to interact with the adsorbent. Furthermore, the greater the heavy metal's electronegativity, the greater its propensity to quantitatively adsorb [44].

3.6. Adsorption kinetic

The mechanism of sorption can be learned through the study of kinetic adsorption. In this work, the experimental data of two metals adsorption from an aqueous solution were explained by means of three kinetic models. Equations (12-15) give these models [45].

Pseudo-first-order model: $$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (12)$$

Pseudo-second-order model: $$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{qe} \quad (13)$$

The initial sorption rate, h (mg/g.min), is computed using the second-order rate constants.

$$h = k_2 {q_e}^2 \quad (14)$$

Intraparticle diffusion model: $$q_t = k_I\, t^{0.5} + C \quad (15)$$

Where t denotes time (min), qe and qt (mg/g) represent the adsorption capacity at equilibrium and any time, respectively, and k1 and k2 denote the pseudo-first- and pseudo-second-order adsorption rate constants (1/min and g/mg.min), respectively.

Where C is the constant, denoting the boundary layer's thickness, and kI is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) [45].

In Fig.9, the kinetic fitting lines are evaluated, and in Table 9, the parameters for each Equation are listed for Cu (II) and Cd (II). The results of the kinetic modelling indicated that pseudo-second-order kinetics provided the best fit to the experimental data. With (R2 = 0.9981, 0.9996) for each Cu (II) and Cd (II), respectively, and the values of qe exp. and qe cal. are convergent for each metal.

Table 10 shows the Maximum adsorption capacities of several adsorbents towards Cu (II) and Cd (II) ions.

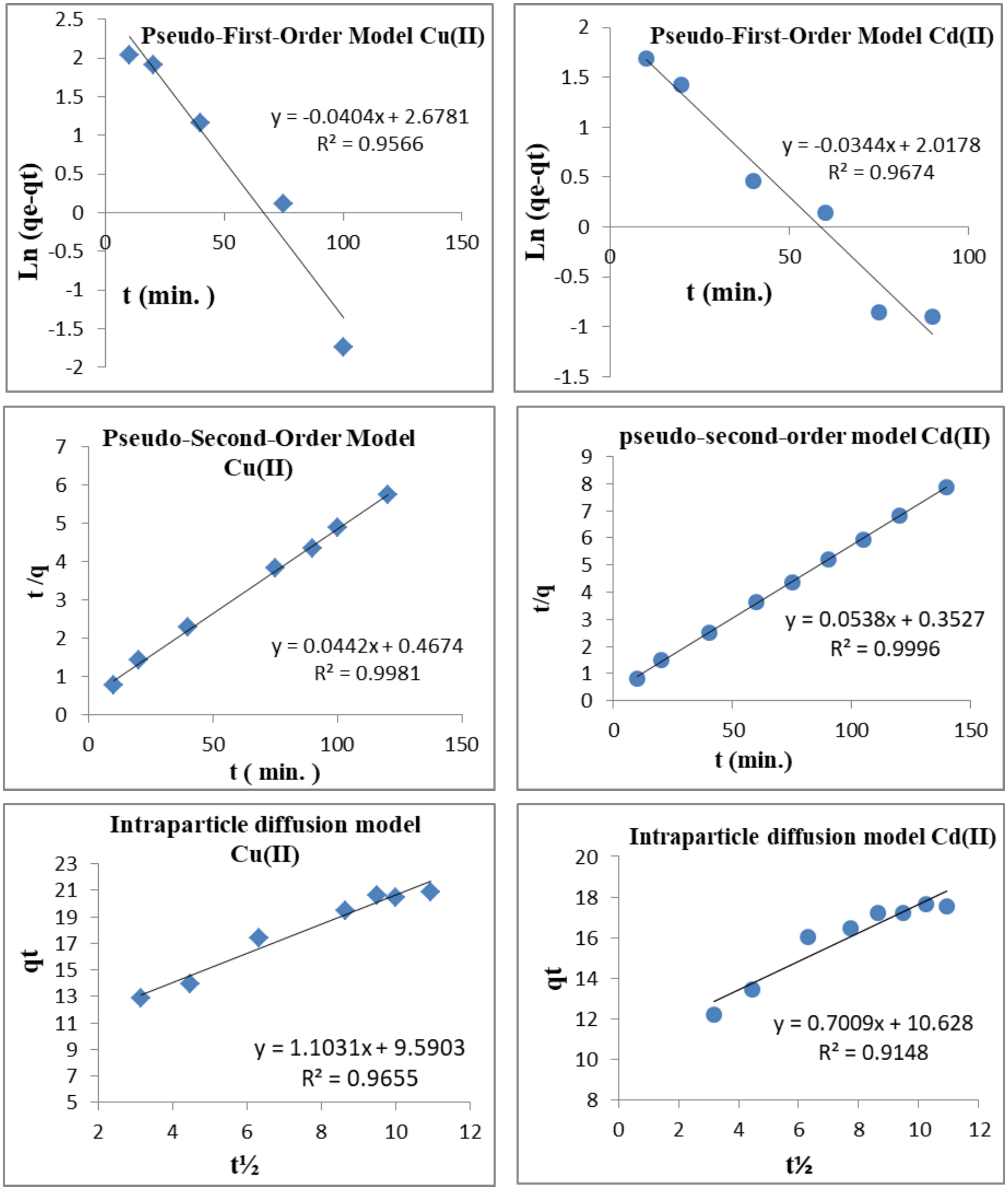


Fig. 9. Kinetic models of Cu (II) and Cd (II) adsorption onto alum sludge CAS

Table 9. The parameters obtained from kinetic models for Cd (II) and Cu (II) adsorption onto alum sludge CAS

Kinetic models		Cu(II)	Cd(II)
Pseudo-First-Order Model	q_e exp. (mg/g)	20.625	17.629
	q_e cal. (mg/g)	14.557	7.522
	K_1(min^{-1})	-0.0404	-0.0344
	R^2	0.9566	0.967
Pseudo-Second-Order Model	q_e cal. (mg/g)	22.624	18.587
	K_2 (g/min mg)	0.0042	0.0082
	R^2	0.9981	0.9996
Intraparticle diffusion model	K_I mg/g.$m^{0.5}$	1.1031	0.701
	C	9.5903	10.628
	R^2	0.9655	0.9148

Table 10. Comparing the capacities of adsorption of several adsorbents for Cd (II) and Cu (II) ions [7]

Metal adsorbed	Adsorbents type	qmax (mg/g)	Removal (%)	References
Cu (II)	Nano-bentonite	19.92	97.4	[46]
	Phosphogypsum	9.615	-	[47]
	Modified diatomaceous ceramic	91.912	121.803	[48]
	Red Mud	5.3		[49]
	Ceramic pottery waste	2.747	-	[50]
	Siderite and Kaolin	19.80	39.8	[51]
	Na-montmorillonite	84, 89, 95	90	[52]
	Alum sludge	29.101	-	This study
Cd (II)	Zeolite from fly ash	7–195	-	[53]
	Natural zeolite	9	71	[54]
	Nano-hydroxyapatite Chitosan composite	92, 122	92	[55]
	Microwaved olive stone Activated carbon	11.72	95.32	[56]
	Fly Ash, Bottom Ash	142.9, 23.3	-	[57]
	Montmorillonite, Kaolinite	30.70, 6.80	-	[58]
	Alum sludge	12.456		This study

4. Conclusion

Alum sludge has been calcined at 550°C for 2 hours. Then they were used as low-cost adsorbents to remove ions of heavy metal (Cd (II), Cu (II)) from their aqueous solutions. And investigate the parameters that influence the adsorption (i.e., CAS dosage, time, and concentration of metal ion). The maximum Cu and Cd removal percentages have reached 92.5% and 98.8%, respectively, at the optimum conditions of the three parameters. Adsorption isotherm data suited the Freundlich, Langmuir, and Temkin models for Cd (II), while Cu (II) data followed the Temkin and Langmuir models. According to the results of the kinetic modelling, pseudo-second-order kinetics best explained the experimental data for both metals. The results show that the thermally treated alum sludge is a promising adsorbent for copper and cadmium ions removal from wastewater. However, these results were obtained under laboratory conditions. Therefore, future studies recommend testing alum sludge in real wastewater samples and in realistic continuous flow systems to evaluate its long-term efficiency and stability under varying operating conditions. The potential for regeneration and reuse should also be investigated to determine its environmental and economic feasibility in practical applications.

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