



## Copperas-coated zeolite as an efficient adsorbent for cadmium removal from synthetic wastewater

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### ABSTRACT

Water pollution by cadmium is a major global issue as it tends to bioaccumulate and not biodegradable in the environment. Exposure to this heavy metal even at low concentrations can cause many serious health effects to humans. This study aimed to investigate the efficiency of integrated copperas and zeolite as adsorbents for cadmium removal in an aqueous solution. Both materials were integrated by simple immersion and heating methods for 4 h and their properties were each characterized in terms of morphology and functional group analysis via SEM and Fourier-transform infrared spectroscopy, respectively. In the first stage of evaluation, the performance of the adsorbents to remove cadmium was conducted through batch adsorption experiments on natural zeolite and integrated copperas/zeolite. Copperas/zeolite appeared to be a better adsorbent and was selected for further use in batch adsorption experiments at different dosages, initial concentrations, and pH. The highest cadmium removal (99%) was obtained at pH 7, 4.0 g/L dosage, and 0.5 mg/L initial cadmium concentration. The adsorption study was well fitted with the Langmuir and Freundlich isotherm models and indicated both homogenous and heterogeneous adsorption. The findings can provide an essential pathway for developing sustainable and cost-effective adsorbents for cadmium removal in water and wastewater treatment.

*Keywords:* Copperas; Zeolite; Adsorbent; Cadmium; Wastewater

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## 1. Introduction

In recent years, water pollution due to human activities has become a critical problem and represents one of the major environmental concerns worldwide [1]. The presence of heavy metals such as lead, nickel, zinc, cadmium, and copper in wastewater is a major hazard and potentially toxic to surface water, human health and animals. Cadmium is one of the critical pollutants that is abundant in water and soil. The main source of cadmium in the environment stems from untreated effluent discharges from industrial activities such as electroplating, dyeing, metal finishing, chemical processing, mining, and automobile manufacturing [2]. Cadmium is highly toxic and exposure to this heavy metal even at low concentrations can cause many serious effects to human health and the environment. It can enter the human body through the food chain and accumulate in different organs. The most serious disease caused by cadmium poisoning is “Itai-itai” disease which is an action of cadmium toxicity in the human body. In addition, kidney dysfunction, hepatic damage, and hypertension are also other health effects of cadmium.

Various conventional techniques for cadmium removal from water and wastewater, such as ion exchange, membrane separation technique, chemical precipitation, oxidation and reduction, and solvent extraction, have certain disadvantages. Among them are high reagents and energy requirements, generation of toxic sludge or waste, and incomplete metal removal [3]. All of these techniques are often ineffective due to the complexity in the process and are uneconomical when the cadmium concentration is higher (10–100 ppm) than the permitted concentration. Thus, the adsorption technique is one of the most effective techniques and has been proven by many previous researches [4,5]. Renu et al. [6] in their review summarised the cadmium removal from wastewater using adsorbents as shown in Table 1.

Adsorption is a mass transfer process where metal ions are transferred from a solution to the surface of a sorbent and can be bound by physical or chemical interactions. It is one of the most effective techniques due to its simple design, sludge-free environment, suitable for a wide pH range, and low cost. All adsorption mechanisms are dependent

on solid–liquid and mass transfer rates [7]. Recently, efforts have shifted towards the development of methods and materials that have minimal side effects as top priority [8]. Therefore, it is necessary to use low-cost adsorbents for the removal of cadmium from synthetic wastewater. Azmi et al. [9], reported a study on chitosan-coated rice husk as an efficient adsorbent for cadmium removal. This green adsorbent succeeded in achieving a very high cadmium removal of 99% in synthetic wastewater. However, chitosan is an expensive polymer that will result in increased operating costs for industrial-scale treatments.

Zeolite, also known as Permutits, is hydrated aluminosilicate mineral made from the interlinked tetrahedra of alumina ( $Al_2O_3$ ) and silica ( $SiO_2$ ) that can replace other expensive adsorbent materials such as activated carbon. Zeolite can be used as a heavy metal remover due to its high cation exchange capacity, maintaining the structure in high temperature, extraordinary structure, low cost, and abundant distribution in the world [10,11]. To date, numerous studies have confirmed their excellent performance in the removal of metal cations from wastewater. For example, Harun et al. [12], applied zeolite for aquaculture wastewater treatment. This study successfully removed 90.7% of ammonia from crab hatchery wastewater. Metes et al. [13] also reported higher organic removal efficiency of 95% for printing ink wastewater achieved by using zeolite after flocculation.

To enhance the function and performance of natural zeolite, it can be chemically modified by inorganic salts or organic surfactants. The modified zeolite induces the generation of positively charged oxi-hydroxides or surfactants micelles which can adsorb the pollutant, and enable the zeolite to bind anions, such as arsenates or chromates, in stable or less stable complexes [14]. Copperas, or its scientific name ferrous sulphate heptahydrate, is one of the compounds that has the potential to be used as an adsorbent coating agent. Copperas is a commercially available inorganic material, and less expensive as it is a by-product of the manufacture of titanium dioxide ( $TiO_2$ ). It has been applied for various wastewater treatments such as palm oil industry [15], dairy industry [16], olive mill industry [17], petroleum refinery industry [18], and paint/dyeing industry [19,20].

Table 1  
Various types of adsorbents used for cadmium removal from wastewater from previous studies

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best fit model	Contact time (min)	Adsorbent dosage (g/L)	Adsorbent capacity (mg/g)	Percentage removal (%)
Synthetic zeolite A	100–2,000	–	Freundlich	180	1.0	315.65	–
Zeolite	25–100	6	Freundlich	90	25	–	76
Zeolite from fly ash	1,124–3,372	6.6	Langmuir	1,440	10	57–195	95.6
Natural zeolite	9–90	5	Freundlich	1,440	–	9	71
Coffee grounds	10–700	7	Langmuir	120	9	15.65	>80
Activated rice husk	88.9–89	6	Freundlich, Langmuir and Dubinin–Radushkevich	20	4	–	97
Microwaved olive stone activated carbon	20	5	Langmuir	7	0.25–2	11.72	95.32%

This study integrated copperas and zeolite to be used as adsorbents for cadmium removal in synthetic wastewater. The performance of natural and modified zeolites was evaluated and a better adsorbent was selected for batch experiments at different adsorbent dosages, initial concentrations, and initial pH. The characteristics of natural and copperas-coated zeolites were determined by scanning electron microscopy and Fourier-transform infrared spectroscopy (FTIR) analysis.

## 2. Methodology

### 2.1. Material

In this study, copperas or ferrous sulphate heptahydrate was supplied by Venator Asia Sdn. Bhd and natural zeolite was obtained from a local supplier. Cadmium chloride, sodium hydroxide, and hydrochloric acid supplied by Sigma-Aldrich were of analytical grades.

### 2.2. Methods

#### 2.2.1. Adsorbent preparation and characterisation

Natural zeolite with granularity over 3 mm was ground using an analytical mill and passed through a 50-mesh sieve to obtain a uniform size distribution. The given amount of the material was washed with double distilled water five times to remove impurities. The sample was then dried in an electric oven at 200°C for 2 h and then cooled in the desiccator. For coating, 50 g of zeolite was immersed in copperas solution and stirred to make adequate contact. The mixture was kept at 80°C in a water bath, while 50 mL of sodium hydroxide solution was added slowly. It was then placed in a muffle furnace and kept at 500°C for 4 h after reaction. Subsequently, the mixture was cooled to room temperature and washed with distilled water. The copperas/zeolite adsorbent was dried at 110°C and prepared for characterization and batch adsorption methods.

Furthermore, scanning electron microscope (SEM) was used to examine the morphology of the adsorbent. The sample was coated with a thin gold layer before the experiments were conducted to improve the imaging of the coated zeolite samples. Meanwhile, FTIR was used to determine the functional group of the adsorbents. The spectra were measured at room temperature in transmittance mode in the wavenumber range of 4,000–400 cm<sup>-1</sup>.

#### 2.2.2. Batch adsorption

A batch adsorption experiment was conducted to evaluate the performance of natural and coated zeolite for cadmium removal. Better adsorbent was selected for the second-stage of the batch experiment which determined the effects of different adsorbent dosages (0.4–4 g/L), pH (5–9), and initial cadmium concentrations (0.5–1.5 mg/L). The concentrations of cadmium before and after the batch experiment were measured using the atomic absorption spectrometer (AAS), and the cadmium removal was calculated using Eq. (1).

$$\text{Cadmium removal (\%)} = \left[ \frac{(C_i - C_f)}{C_i} \right] \times 100\% \quad (1)$$

where  $C_i$  and  $C_f$  (mg/L) are the initial and final cadmium concentrations, respectively.

### 2.3. Adsorption isotherm

The adsorption process and the interaction between the adsorbents and the cadmium solution can be described by the adsorption isotherm. The adsorption isotherm is an invaluable curve that describes the phenomena governing the retention or mobility of a substance from an aqueous porous media or aquatic environment to a solid phase at a constant temperature and pH. In this study, two important isotherm models were selected to evaluate the adsorption performance of the adsorbents, namely the Langmuir and Freundlich models.

The Langmuir isotherm is based on a homogenous and monolayer adsorbent material with the same energy at all levels of the adsorbents that each molecule has constant enthalpy and sorption activation energy, without transmigration of the adsorbate in the surface plane. The mathematical expression of the Langmuir isotherm models is shown in Eq. (2):

$$\left( \frac{1}{q_e} \right) = \left( \frac{1}{C_e Q_m K_L} \right) + \left( \frac{1}{Q_m} \right) \quad (2)$$

where  $q_e$  is the amount of adsorbed ion on adsorbent at equilibrium (mg/g);  $C_e$  is the equilibrium concentration of adsorbate (mg/L);  $Q_m$  is the maximum adsorption capacity (monolayer coverage) (mg/L);  $K_L$  is the Langmuir constant (L/mg) [21].

Freundlich isotherm, unlike Langmuir, is on the adsorbent based on multilayer adsorption and heterogeneous adsorbent material. The amount adsorbed is the sum of the adsorption on all sites, with the stronger binding sites occupied first until the adsorption energy decreases exponentially upon completion of the adsorption process. The slope range between 0 and 1 is a measure of adsorption intensity or surface heterogeneity; becomes more heterogeneous as its value approaches zero. The mathematical expression of the Freundlich isotherm models is shown in Eq. (3):

$$\ln q_e = \ln K_f + \left( \frac{1}{n} \right) C_e \quad (3)$$

where  $q_e$  is the adsorption capacity at equilibrium (mg/g),  $C_e$  is the concentration at equilibrium (mg/L),  $n$  is the sorption intensity, and  $K_f$  (L/mg) is the Freundlich constant.

## 3. Results and discussion

### 3.1. SEM and FTIR analysis

The morphologies of copperas-coated zeolite, zeolite, and copperas as examined by SEM are shown in Fig. 1. In Fig. 1a, the particle shape resembled a smooth compact gel network structure on the external surface. Previous findings indicated that a cubic-structure was observed on the internal surface of the studied adsorbents [22]. By

comparing the SEM images of Fig. 1a–c, copperas was covered as a thin layer on the surface of the zeolite particles. The morphology of the zeolite completely changed after the modification of the zeolite and copperas.

In addition, Fig. 1b shows the shape of cubic-structured zeolite particles and not in the aggregate form [23]. Fig. 1c, with the scale used in this image being around 10  $\mu\text{m}$ , presents a compact gel network structure and more irregular bulk clusters. Based on previous studies, it was concluded that the compact gel network structure was favorable for coagulating colloidal particles [22].

Table 2 shows the FTIR analysis for zeolite-coated copperas. In the range of 3,200–3,600  $\text{cm}^{-1}$ , there was a broad absorption peak of zeolite coated copperas which was assigned to the O–H stretching. The wavelength of 1,610.56  $\text{cm}^{-1}$  was assigned to either C–H bending or C=C stretching. The absorption that appeared in the region of 900–1,200  $\text{cm}^{-1}$  was the result of the stretching and bending modes of Si–O or Al–O in the zeolite framework. For example, the bands around 1,120  $\text{cm}^{-1}$  were assigned to the asymmetric and symmetric stretching modes of internal tetrahedra, and the bands around 1,017  $\text{cm}^{-1}$  represented the asymmetric and symmetric stretching modes of external linkages [23]. Strong absorption peaks at 1,101.35  $\text{cm}^{-1}$  were assigned to Si–O–C bending. Moreover, no other peaks were found between 2,680 and 2920  $\text{cm}^{-1}$ , indicating no aromatic structures and bands at around 572  $\text{cm}^{-1}$  which were assigned to the C–S stretching group.

### 3.2. Performance of natural and copperas-coated zeolite

Fig. 2 shows the cadmium removal using natural and copperas-coated zeolite. The highest cadmium removal

of 99.52% was demonstrated by copperas-coated zeolite, while the uncoated zeolite adsorbent showed 88.03% cadmium removal. This may be because copperas-coated zeolite has differently charged particles with synthetic wastewater which attracted all the charged particles present in the suspension in removing pollutants. Thus, the copperas-coated zeolite was used in the subsequent batch experiment to investigate the optimum parameters, such as dosage, pH and initial concentration, and the maximum cadmium removal percentage.

### 3.3. Effect of adsorbent dosage

Fig. 3 shows the percentage removal of cadmium at different adsorbent dosages. The adsorbent dosage of 4.0 g/L exhibited the highest cadmium removal of 99%, while the adsorbent dosage of 0.4 g/L showed the lowest cadmium removal of 95%. An increase in the adsorbent dosage from 0.4 to 4.0 g/L resulted in an increase in the adsorption efficiency of cadmium on copperas-coated zeolite. This may be due to the availability of more binding sites as the adsorbent dosage increased, leading to an increase in the total surface area and free bond at the adsorbent level [24]. Furthermore, it is well known that ion exchange between exchangeable cations in the adsorbent structure and cadmium ions is an important mechanism responsible for the cadmium ion adsorption on copperas-coated zeolite.

### 3.4. Effect of initial concentration

A batch equilibrium experiment was performed using 250 mL of cadmium solution with initial concentrations ranging from 0.1 to 1.5 mg/L. The experiment was conducted

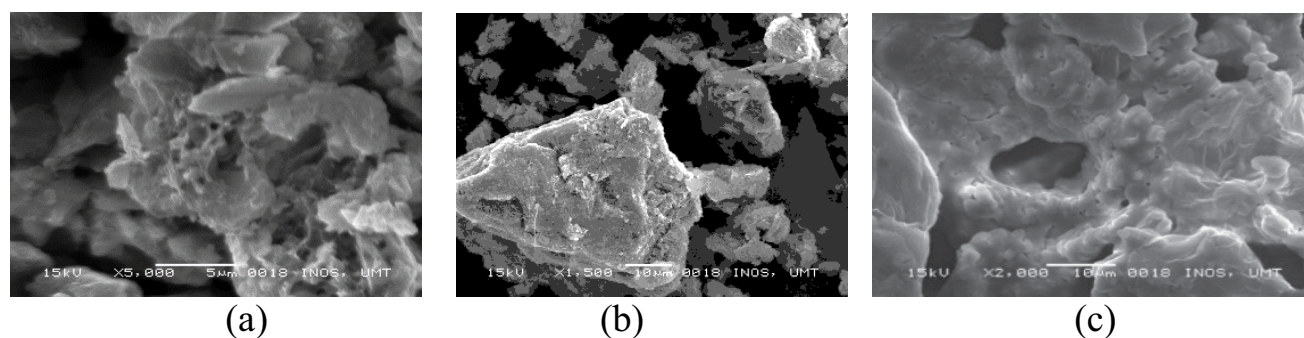


Fig. 1. Morphologies of (a) copperas, (b) natural zeolite and (c) copperas-coated zeolite.

Table 2  
FTIR analysis of copperas-coated zeolite

Absorption ( $\text{cm}^{-1}$ )	Appearance	Group	Compound class
3,396.64; 3,500.80	Broad	O–H stretching	Carboxylic acid
1,610.56	Weak	C–H bending	Aromatic compound
	Medium	C=C stretching	Alkene
1,101	Strong	Si–O–C bending	Organic siloxane
572	Medium	C–S stretching	Polysulfide

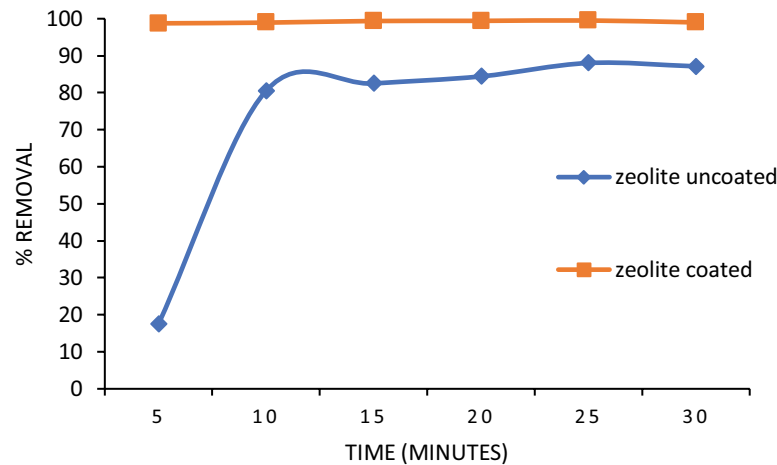


Fig. 2. Cadmium removal using natural and copperas-coated zeolite. Experimental conditions: at room temperature, adsorbent dosage of 4 g/L, initial concentration of 0.5 mg/L, and pH 7.

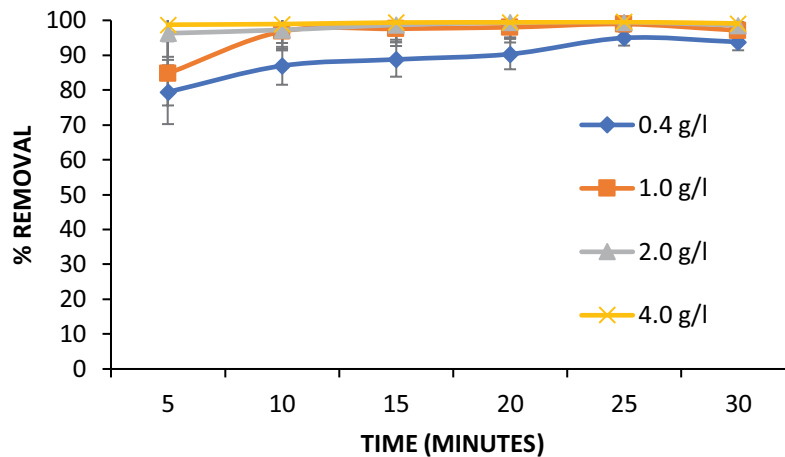


Fig. 3. Cadmium removal by copperas-coated zeolite at different dosages. Experimental conditions: room temperature, initial concentration of 0.5 mg/L, and pH 7.

at an equivalent mass of 1.0 g/L of adsorbent, room temperature, and 200 rpm.

In Fig. 4, it depicted that the initial concentration of 0.5 mg/L has the highest removal percentage of 99%, while the initial concentration of 1.5 mg/L showed the lowest percentage removal of 55.90%. The results indicated that the adsorption of cadmium molecules was dependent on the initial concentration of the solution. At higher initial concentrations, more ions or molecules are available in the cadmium solutions compared to lower initial concentrations of the solution. This can be described by the bulky quantities of Cd(II) ions with inadequate active sites on the adsorbent surface which increase the concentration of Cd(II) ions in the greater part of the aqueous solution, thus decreasing Cd(II) ion removal efficiency [25]. In addition, in low cadmium concentrations, the specific surface and the sites of adsorbent adsorption become numerous so that the adsorbent can attract the cadmium ions on the adsorbent surfaces, resulting in high removal. Moreover, according to Parekh et al., this may also be due to the saturation of the sorption sites on the adsorbent [26].

### 3.5. Effect of pH

In the adsorption process, the pH of the aqueous solutions is one of the important control parameters. The chemical properties of the adsorbate (cadmium solution) and adsorbent have determined the optimum pH value of the adsorption. The determination of the optimum pH of cadmium removal was conducted in the aqueous solution of 1.5 mg/L concentration, 4.0 g/L adsorbent dosage, room temperature, and 200 rpm speed at different pH ranges of 5 to 9.

In Fig. 5, cadmium removal portrayed an increasing and decreasing pattern with increasing pH of aqueous solutions ranging from pH 5 to pH 9. The pH value in this range was chosen considering the electrostatic attraction that occurs between the positively charged surface of the adsorbent mainly due to anionic zeolite. The maximum cadmium removal of 99% was achieved at pH 7. In acidic solution, high concentrations of H<sup>+</sup> ions compete with Cd<sup>2+</sup> for exchangeable cations on the surface of copperas-coated zeolite resulting in suppression of Cd<sup>2+</sup> adsorption. As the

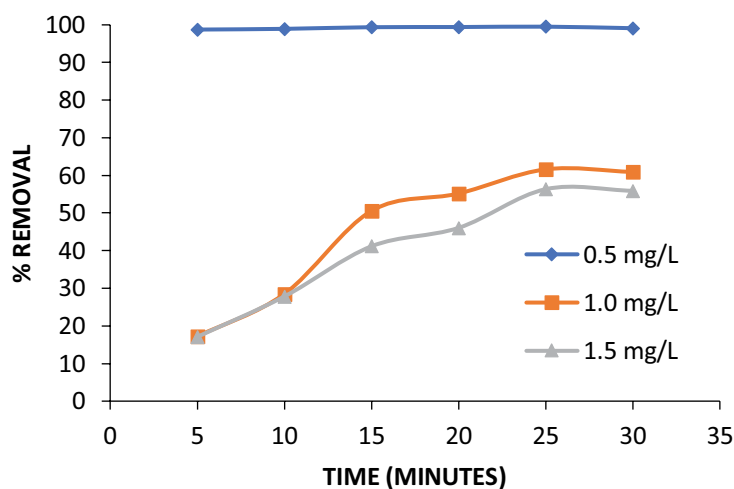


Fig. 4. Effect of initial concentration on cadmium removal. Experimental conditions: at room temperature, copperas-coated zeolite adsorbent, adsorbent dosage of 4 g/L, and pH 7.

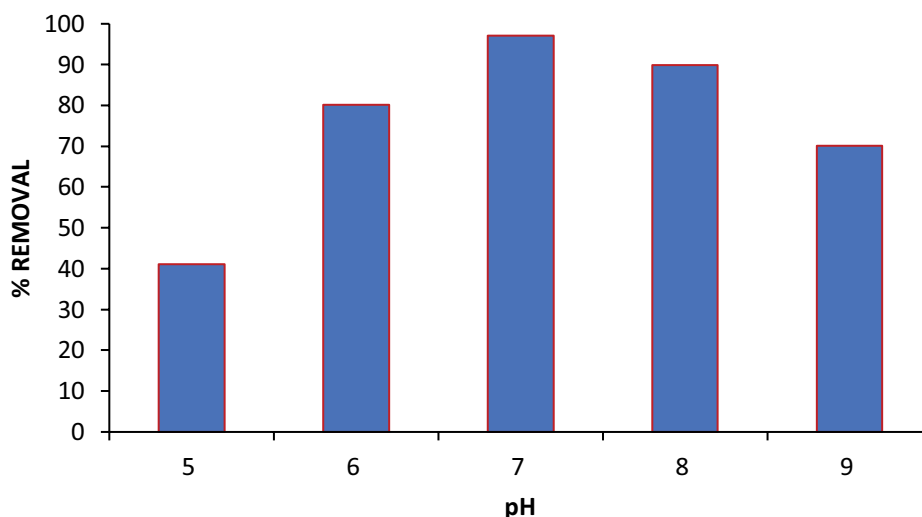


Fig. 5. Effect of initial pH on cadmium removal. Experimental conditions: at room temperature, adsorbent dosage of 4 g/L, and initial concentration of 0.5 mg/L.

pH value increases, the concentration of hydrogen ions as competitors decreases and this causes an increase in the amounts of adsorbed  $\text{Cd}^{2+}$  [27]. This proves that the adsorption capacity of  $\text{Cd}^{2+}$  in a neutral solution is better than in a strongly acidic solution. According to Asrari et al. [7], changes in the pH of the solution can alter the chemical nature of the functional group of the adsorbent and the metal adsorption capacity of the adsorbent. As a result, the absorption efficiency of heavy metals present in cationic form increases with pH. Thus, pH 7 was selected as the optimum condition for subsequent study.

### 3.6. Adsorption isotherm

The adsorption isotherms provide an equilibrium relationship between the amount of adsorbate adsorbed on the surface of the adsorbent and its concentration in the solution at a constant temperature. In this study, the

Langmuir and Freundlich isotherm models were chosen to fit the data. The linear forms of these models were used to evaluate the best fit model to describe the adsorption of cadmium on the copperas-coated zeolite either in a uniform or random distribution layer. Adsorption isotherm models are commonly used to describe the adsorption process and investigate its mechanisms. The suitability of each isotherm model was calculated by the linear regression method by comparing the coefficients of determination ( $R^2$ ) from the experimental data at optimum dosage. The closer the  $R^2$  value to 1.0, the better is the fit. In general, the adsorption strength decreases as the value of  $1/n$  increases and the adsorption capacity decreases as the  $K_f$  value decreases. If the value of  $1/n$  is smaller than 1, it indicates favorable adsorption of  $\text{Cd}^{2+}$  on the surface of the adsorbent. In addition, sun standard error (SSE) value close to 0 indicates that the models have a minor random error component and that the fit will be more useful for

Table 3  
Langmuir and Freundlich isotherm models of cadmium on copperas-coated zeolite

Langmuir isotherm					Freundlich isotherm		
$Q_m$ (mg/g)	$b$ (L/mg)	$R^2$	SSE	$N$	$K_f$ ((mg/g)(L/mg) <sup>1/n</sup> )	$R^2$	SSE
1.43435	0.00045	1.00	9.12332E-08	14.89661	1.87855	0.99018	0.000758167

prediction. Table 3 shows the Langmuir and Freundlich isotherms of cadmium adsorbed on the adsorbent.

Based on Table 3, the copperas-coated zeolite was relatively fitted well with both isotherm models as the  $R^2$  value of the Langmuir model was 1.000 and 0.990 for the Freundlich isotherm model. The  $R^2$  value exceeding 0.9 suggested that the model fitted well with the experimental results. The linearized Langmuir isotherm model was valid for monolayer adsorption on a surface with a finite number of homogenous sites, while the linearized Freundlich isotherm model was valid for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption. The value of  $1/n$  was 0.067 which is less than 1, indicating favorable adsorption of cadmium on copperas-coated zeolite [28].

Fig. S1 shows the equilibrium adsorption of  $R^2$  predicted by Freundlich isotherm and Langmuir isotherm models. Both model plots exhibited good linearity. However, the Freundlich model showed a negative intercept due to the negative values of the isotherm parameter. It showed that the model did not follow the assumptions upon which it was established, thus the adsorption processes cannot be explained by the model.

### 3.7. Analysis of variance

A one-way analysis of variance (ANOVA) test was used in this study to validate the experimental data related to the effects of adsorbent dosage, pH, and initial concentration. The ANOVA evaluated the percentage removal of cadmium at different parameters. The null hypothesis was marked as there were no significant differences between the data. If the observed  $F$ -value is greater than  $F_{critical}$  and the probability ( $P$ -value) is smaller than 0.05, then the null hypothesis is rejected. In other words, the data have a significant difference between the means of groups. Tables S1–S3 summarise the ANOVA of cadmium removal at different dosages, pH, and initial concentrations, respectively.

Except for the effect of initial concentration on cadmium removal, other ANOVA data showed that their  $F$ -values were higher than  $F_{critical}$  and their  $P$ -values were lower than 0.05. These results indicated that the null hypothesis was rejected and there was a significant difference between the data for different dosages and pH used in this study. It is also indicated the statistical significance of the variable at 95% confidence level [29] for the effect of initial concentration on cadmium removal, as shown in Table S3, the  $F$ -value was lower than the  $F_{critical}$  and the  $P$ -value was greater than 0.5, demonstrating that the null hypothesis was accepted and there was no significant difference between the cadmium removal data in this study.

## 4. Conclusion

The overall findings concluded that the optimum condition for the best adsorption capacity was achieved at pH 7 with initial cadmium concentration of 0.5 mg/L and equilibrium mass of 4.0 g/L adsorbent dosage using copperas-coated zeolite. The equilibrium adsorption data fitted well with the Langmuir and Freundlich isotherm models where the  $R^2$  values for both isotherms were in good agreement. Furthermore, the ANOVA showed that there was a significant difference in the effect of adsorbent dosage and pH but no significant difference in the effect of initial concentration. These findings may provide useful information in treating cadmium in an aqueous solution using a low-cost adsorbent. Moreover, the findings revealed the new application of copperas in the titanium dioxide manufacturing process in an environmentally friendly and cost-effective manner and may reduce waste disposal costs. The adsorption techniques provide flexibility and simplicity of design and operation in removing heavy metal; however, the impact reaction parameters including adsorbent dosage, initial concentration, and pH are crucial and must be taken into consideration. The drawback of employing this method is the disposal of the adsorbents. Regeneration is crucial to reduce the need for new adsorbents; consequently, reducing the problem of disposal of used adsorbents.

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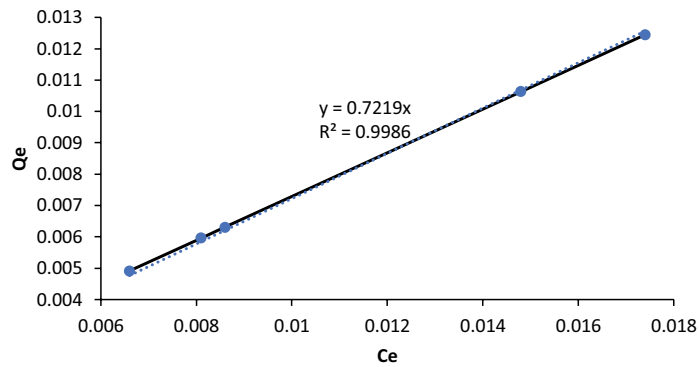
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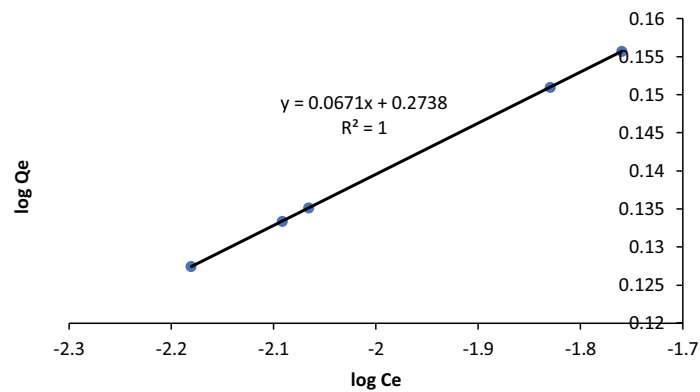
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Supplementary information



(a)



(b)

Fig. S1. Adsorption isotherm of cadmium removal predicted by (a) Langmuir and (b) Freundlich.

Table S1  
ANOVA of cadmium removal at different adsorbent dosage

Source of variation	SS	df	MS	F	P-value	$F_{critical}$
Between groups	1.463	1	1.463	17.8163	0.00555	5.987377
Within groups	0.493	6	0.0821			
Total	1.956	7				

Table S2  
ANOVA of cadmium removal at different pH

Source of variation	SS	df	MS	F	P-value	$F_{critical}$
Between groups	3.460	1	3.460	51.175	0.0000967	5.3176
Within groups	0.541	8	0.068			
Total	4.001	9				

Table S3  
ANOVA of cadmium removal at different initial concentrations

Source of variation	SS	df	MS	F	P-value	$F_{critical}$
Between groups	0.4282	1	0.4282	1.9289	0.2142	5.9873
Within groups	1.332	6	0.222			
Total	1.7603	7				