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Optimization of Copper Adsorption Process on Synthesized Porous Hydroxyapatite

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Abstract

Water pollution is a critical global issue that poses significant threats to ecosystems and human health. The contamination of water sources by various pollutants, such as heavy metals, chemicals, and organic compounds, has adverse impacts on the environment and public well-being. To address this challenge, adsorption has emerged as a promising solution. Utilizing adsorbent materials like hydroxyapatite (HAp), contaminants can be effectively removed from water through the adsorption process. HAp, derived from sustainable sources, serves as an eco-friendly adsorbent. Porous hydroxyapatite (p-HAp) was prepared using the neutralization method of calcium hydroxide ($Ca(OH)_2$) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$). p-HAp was characterized by using different methods such as BET (Brunauer-Emmett-Teller), FTIR (Fourier transform infrared spectroscopy), and XRD (X-ray diffraction). The characterization of p-HAp by FTIR and XRD showed that the synthetic HAp has an apatite phase which is essential for the adsorption of heavy metals. The BET method is used for measuring the specific surface area of p-HAp. The adsorption process was studied using optimization by Design-Expert 11 software, with a quadratic model.

Keywords

Hydroxyapatite, Full factorial design, Optimization, Desirability, Adsorption

Introduction

Heavy metals are natural elements and are present in all ecosystems at different concentrations. In recent times, the presence of heavy metals at concentrations above natural loads has become a problem of increasing concern, they can cause serious damage to humans, wildlife, and plants [1]. Heavy metals are one of the most important groups of water pollutants related to rapid population growth, expansion of industrial activities, technological development, as well as the lack of environmental regulation [2-4].

Copper is a metal widely used in the manufacture of pesticides, paper, electronics, automotive parts, fertilizers, and coatings. Copper (Cu^{2+}) ions are commonly present in vital industries and commercial products and have resulted in the continuous release of a large amount of Cu^{2+} into the environment from industrial effluents, this leads to its frequent detection in a wide range of aquatic environments such as surface water, drinking water and groundwater [5, 6].

Many methods have been used for the removal of toxic heavy metals, such as coagulation [7-10], membrane filtration [11], ion exchange, filtration, precipitation, reduction, and photocatalytic degradation of organic pollutants [12-14]. However, some of these methods have several drawbacks including inefficiency and relatively high operating costs [15].

Adsorption is considered one of the most effective methods, widely used to treat water contaminated with heavy metals, due to its simplicity of use, low energy consumption, and lack of secondary pollution, which is compatible with the circular economy and sustainable development [16]. Research is already being conducted on a wide variety of adsorbents such as carbon nanotubes, activated carbon, clays, zeolites, and apatites [17].

In this context, a synthesis of HAp was performed to be used as an adsorbent of Cu^{2+} present in the aqueous medium. A factorial design technique was applied to reduce the number of experiments, time, and overall cost of the process. This technique is also used to develop adsorption in various applications and obtain a better response.

Materials and Method

Materials

p-HAp) is prepared by the neutralization method of $Ca(OH)_2$ and $NH_4H_2PO_4$ at room temperature and in aqueous medium [18]. The obtained precipitate was filtered under vacuum and dried in an oven at a temperature of 100 °C. overnight. The chemical composition and structure of the prepared materials were characterized by XRD, FTIR, and BET analysis. All used materials are nanoscale materials.

Characterization of adsorbent

The surface area of synthesized HAp was calculated according to the BET method using adsorption data in the relative range of 0.05 to 0.25, and the distribution was determined using the approximation of Barret-Joyner-Halenda in the mesoporous range. The XRD pattern of the HAp composite was recorded on a Philips PW131 diffractometer, equipped with a copper anticathode (λ = 1.5454 Å), and computer-controlled for data storage and processing. The sample was measured at room temperature in powder form, and an analysis of the infrared spectra recorded on a spectrophotometer, (Bruker counter, IFS 66v FT-IR) with a resolution of 2 cm^{-1} was carried out [19].

Batch adsorption experiments

The operating protocol involves the dispersion of an amount of 0.2 g of HAp in a volume of 100 ml. 20 mmol/L of Cu^{2+} was added to the solution, then the pH was adjusted at pH = 5, using solutions 0.1 N of HCl and 0.1 N of NaOH. The mixture was stirred for a period of 30 min to reach equilibrium. The resulting solution was filtered to remove adsorbents, then analyzed by inductively coupled plasma atomic emission spectrometry using the VISTA AX instrument from Varian, we analyzed samples for quantification. All samples to be analyzed were acidified to a 2% concentration using ICP-grade HNO_3 (TraceSelect 69.5%, Fluka). The experimental instrument used for this analysis was calibrated using four commercial standard solutions. The limit of detection for the acidified aqueous solutions was 2 µg/L.

Results and Discussion

Characterization

The specific surface area of the synthesized HAp, the pore size, and the adsorption-desorption isotherms was calculated using the BET analysis. The obtained results show that the variation of the reaction temperature influences the specific surface area of HAp. The specific surface area of HAp is equal to 235 m^2/g at T = 25 °C, and at a temperature of 70 °C and 90 °C, the specific surface area is equal to 151 m^2/g and 108 m^2/g, respectively. Thus, the specific surface area of synthesized HAp decreases by increasing the reaction temperature [20].

XRD analysis shows that HAp is weakly crystallized. This analysis shows that the synthesized HAp consists of an apatitic phase and that the lines are indexes in the hexagonal system of the $P6_3/m$ space group [21].

An FTIR analysis of the synthesized samples was performed to, identify the characteristic bands of the synthesized HAp. FTIR spectroscopy analysis reveals several bands. The absorption bands of PO_4^{3-} ions are characterized by 2 absorption regions located between 1100 and 900 cm^{-1} and between 500 and 600 cm^{-1}. The first region corresponds to the symmetrical and antisymmetrical vibrations of P-O (ν1 + ν3), while the second region corresponds to the vibrations of O-P-O deformation (ν2 + ν4). We also identified the characteristic absorption bands of the presence of CO_3^{2-} located around 1000 cm^{-1} and the characteristic absorption bands of hydroxyl ions located around 3500 cm^{-1} [20].

Design of experiments by full factorial design

The levels and ranges of the process parameters studied (A - pH of the solution, B - initial copper concentration, C - adsorbent dose, and D - contact time) affecting Cu^{2+} removal employed in the experiment are shown in table 1.

The design of experiments needs a set of experiments in different operating conditions (Table 2) to be able to find an optimal condition model.

Table 1: Experimental ranges and levels of the factors used in the factorial design.

Independent variable	Coded symbol	Range and level	
		-1	+1
pH	A	3	6
Initial concentration of Cu^{2+} (mmol/L)	B	5	35
Mass of HAp (g)	C	0.1	0.4
Contact time (min)	D	60	360

Final equation in terms of coded factors

The equation in terms of real factors can be used to make predictions about the response for given levels of each factor. The coded mathematical model is represented by the following expression.

$\%R = X_0 - X_1$ x pH – X2 x Initial concentration of Cu^{2+} + X_3 x Mass of HAP + X_4 x Contact time

Where R (%) is the percentage removal of Cu^{2+}, X_0 is the global mean, X_i represents the other regression coefficients. By substituting the coefficients X_i in the equation by their values, we get [22]:

%R = 23.43078 – 0.429444 x pH – 0.574278 x Initial concentration of Cu^{2+} + 45.47778 x Mass of HAp + 0,065428 x

Table 2: Plan matrix used in the pesent study.

Run	Factor 1 A: pH of the solution	Factor 2 B: Initial copper concentration, mmol/l	Factor 3 C: Mass of HAp, g	Factor 4 D: Contact time, min	Response 1 %R (Percentage removal of Cu^{2+})
1	4.5	50	0.25	210	20
2	4.5	20	0.25	210	50.7
3	6	5	0.1	360	30.5
4	6	35	0.4	360	40.2
5	4.5	20	0.25	210	58.7
6	3	5	0.4	360	60
7	3	5	0.1	60	5.2
8	6	5	0.4	60	30.9
9	6	35	0.4	60	6.12
10	3	35	0.1	360	20
11	4.5	20	0.25	510	58.35
12	3	5	0.1	360	30.9
13	3	35	0.4	60	7.3
14	4.5	20	0.25	210	58.5
15	4.5	20	0.25	-	42.67
16	3	5	0.4	60	31.05
17	1.5	20	0.25	210	58.05
18	4.5	-	0.25	210	68.8
19	4.5	20	0.25	210	58.7
20	6	5	0.4	360	62.12
21	4.5	20	-	210	49.1
22	4.5	20	0.25	210	58.7
23	6	5	0.1	60	8.72
24	3	35	0.4	360	39.09
25	3	35	0.1	60	5.5
26	6	35	0.1	360	24.1
27	4.5	20	0.25	210	58.7
28	4.5	20	0.55	210	59
29	6	35	0.1	60	7.94
30	7.5	20	0.25	210	60

Contact time

Analysis of variance (ANOVA)

ANOVA is a statistical technique used to analyze and compare the means of two or more groups to determine if there are any statistically significant differences between them. It accomplishes this by partitioning the total variation observed in a dataset into different sources of variation, namely the variation between groups and the variation within groups. By calculating the F-statistic, which is the ratio of between-group variation to within-group variation, ANOVA helps determine whether the observed differences between groups are likely due to true differences in the population means or simply random chance. ANOVA is widely utilized in various fields of research to assess the effects of different factors or treatments on a dependent variable. After estimating the main effects, the interaction factors influencing Cu^{2+} removal were determined by performing an ANOVA. The F value of the model of 4.15 implies that the model is significant. There is only a 1.03% chance that such a high F value is due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, initial concentration, and contact time are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 36.90 implies the Lack of Fit is significant. There is only a 0.04% chance that a Lack of Fit F-value this large could occur due to noise [23] (Table 3).

Fit statistics

The Predicted R^2 of 0.1395 is in reasonable agreement with the Adjusted R^2 of 0.3032; i.e., the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio

Table 3: Results of variance analysis (ANOVA).

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	5219.32	4	1304.83	4.15	0.0103	Significant
A-pH	9.96	1	9.96	0.0317	0.8601	
B-Initial concentration	1780.89	1	1780.89	5.67	0.0252	
C-Mass of HAP	1116.84	1	1116.84	3.56	0.071	
D-Contact time	2311.63	1	2311.63	7.36	0.0119	
Residual	7851.96	25	314.08			
Lack of fit	7799.12	20	389.96	36.9	0.0004	Significant
Pure error	52.83	5	10.57			
Cor total	13071.28	29				

Table 4: Fit statistics.

Std Dev	17.72	R^2	0.3993
Mean	38.99	Adjusted R^2	0.3032
C.V. %	45.46	Predicted R^2	0.1395
		Adeq Precision	7.1579

greater than 4 is desirable. The ratio of 7.158 indicates an adequate signal (Table 4). This model can be used to navigate the design space [24].

Optimization

To obtain a percentage of Cu^{2+} removal equal to 38.99% the pH should be set at 4.5, and the contact time at 210 min, while the initial concentration of Cu^{2+} and the dose of adsorbent should be set at 20 mmol/L and 0.25g, respectively. Figure 1 shows the optimized response.

Conclusion

In this research, synthesized p-HAp was used to remove Cu^{2+}, from aqueous solutions. Results analysis performed by Design-Expert 11 software using a two-level full factorial design to avoid traditional one-factor experiments at a time, improve response, reduce experiments, and optimize time. ANOVA and F-test were used to define the most important process variables influencing Cu^{2+} adsorption efficiency. The use of a full factorial design with two levels of 2k identified the most significant parameters under the conditions tested. Main effects such as pH (A), initial Cu^{2+} concentration (B), HAp adsorbent mass (C), and contact time (D) played a significant role. The results of adsorption Cu^{2+} by the porous apatites that we have synthesized allow us to think that these apatitic materials could be advantageously used in the fields of catalysis of certain chemical reactions, de-pollution wastewater, and industrial effluents.

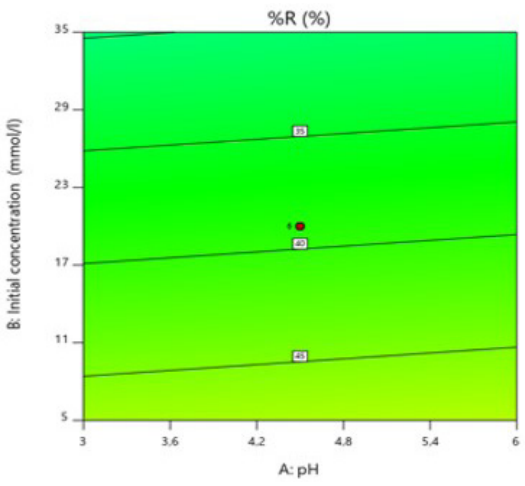


Figure 1: Optimized response.

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None.

Conflict of Interest

The authors declare that they have no competing interests.

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