Adsorption of copper ion from aqueous solutions by well-crystalized nanosized hydroxyapatite

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Abstract
Hydroxyapatite (HAp), the main mineral content of bones and teeth, is one of the most important calcium phosphate-based bio-ceramics. Due to its crystal structure, it has the potential to be used as a low cost and biocompatible adsorbent. In this study, nano-synthesized and well-crystallized HAp was used in adsorption process of copper which causes growth problems. In order to investigate the synthesized nano-HAp crystal structure and functional groups, x-ray diffraction pattern (XRD), Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy analyzes were performed. Nano-HAp concentration, copper concentration and time were selected as variables affecting copper adsorption and Box-Behnken design was applied. According to the results, it was found that at least 33 min and 510 mg l\(^{-1}\) nano-HAp concentration was required to achieve a higher removal rate than 90% removal efficiency. It was determined that all selected independent variables are effective in copper removal. The optimization study was carried out with the findings obtained from the study and 514.0 mg l\(^{-1}\) nano-HAp and 60.4 min were found to be required for optimal removal. Moreover, the lowest selected Cu concentration can be totally removed by 700 mg l\(^{-1}\) nano-HAp and in 60.4 min of reaction time. This study demonstrates that nano-HAp can be used as an environmentally friendly adsorbent for copper removal from aqueous solution.

1. Introduction
Finishing processes and industrial activities carried out to reduce defects such as adhesion, wettability, solubility, corrosion resistance, darkening resistance, chemical resistance, abrasion resistance, hardness, alteration of electrical conductivity on the surfaces create various risks for the ecosystem. Heavy metals, known as water and soil pollutants (Arsenic, Copper, Cadmium, Chromium, Zinc, etc.) are the major risk factors in the ecosystem (Saikia et al 2017, Kumari et al 2018). Copper, which has an insoluble structure, is widely used in industrial fields such as metal plating, mining, nuclear power plants, textile and metallurgy (Jiang et al 2015). Its inability to biologically decompose is an important factor that threatens living health (Mosayebi and Azizian 2016). It is reported that the presence of copper (II) in drinking water causes accumulation in all biological organisms and thus growth problems and liver and eye damage (Bakhtiari et al 2015). According to World Health Organization (WHO) and Environmental Protection Agency (EPA) data, copper above 1.3 mg l\(^{-1}\) causes high toxicity (Kong and Wang 2016).

Today, techniques such as chemical precipitation, adsorption, biosorption, ion exchange, reverse osmosis and filtration are used for copper removal from water and wastewater (Ding et al 2014, Ahmadi et al 2015, Cho et al 2015, Luo et al 2015, Cetinkaya 2018). Due to its economic and effective effect, chemical precipitation is the most commonly used method for removal of copper from water using strong alkalis such as sodium hydroxide and calcium hydroxide (Ye et al 2016). However, as a result of chemical precipitation, the water reaching a value in the range of pH 10–11 must be neutralized using acid (van Hille et al 2005).
using sulfide gives quite rapid results, but the environmental harm of hydrogen sulfide formed is an important disadvantage (Lewis, 2010).

Adsorption process is of great interest in the removal of heavy metals because it is practical (Dias et al 2007, Demirbas, 2008). However, their high cost limits their use. Today, the production and continuous development of lower-cost sorbents gives hope for the adsorption mechanism (Bailey et al 1999, Babel and Kurniawan, 2003). Among the improved solid sorbents, calcium-hydroxyapatite (Ca_{10}(PO_{4})_{6}(OH)_{2}, HAp) is of great interest due to its features such as low cost, high chemical and thermal stability, water insoluble character (Kps $\approx$ 10^{-59} at room temperature) (Recillas et al 2012). HAp can be synthesized at various temperatures but commonly below 100 °C, between pH range of 4–12, and at different Ca/P ratios. Acidic surface is dominant when the Ca/P ratio of HAp samples is 1.50 on average. When the Ca/P ratio is between 1.50 and 1.67, both acidic and basic properties develop (Narasaraju and Phebe, 1996, Webster et al 2004, Kannan et al 2006). In the HAp hexagonal system, in the P63/m space group, the structure crystallizes to include three-dimensional networks of four-sided PO_{4}^{3-} ions packed in hexagons. These ions form the first channel in diameter of 2.5 Å and the first channel form around [Ca (I)] around Ca^{2+} ions. The second channel with a diameter of 3.5 Å is bounded by triangular Ca^{2+} ions [Ca (II)], accommodating OH$^-$ species along the c axis (Dann, 2002). The HAp structure is flexible to cationic and anionic displacements, and by making the structure functional, cations such as Sr^{2+}, Mg^{2+}, Na^{+}, K^{+} can simultaneously replace Ca (I) or Ca (II) ions or both ions. Anions such as F$^-$, Cl$^-$, CO_{3}^{2-} can replace OH$^-$ or PO_{4}^{3-} ions or both (Ferri et al 2019).

HAp has been shown to be a highly effective adsorbent for different types of heavy metals, such as metal cations (Ma et al 1994, Reichert and Binner 1996, Mousa et al 2016, Campisi et al 2018). Multiple metal binding mechanisms have been described, such as ion exchange surface complexation, and dissolution and precipitation of newly formed stable phosphate-containing phases, including the exchange of Ca (I) or Ca (II) ions in the HAp structure (Corami et al 2008, Campisi et al 2018). The predominance of a particular metal retention mechanism depends on the acid—base balance of the HAp sample, along with various parameters such as the properties of the metal species, the pH of the medium and the contact time. From an application-based perspective, the Ca (I) or Ca (II) ion structures of the HAp framework can be replaced completely or in various proportions by one, two, three and higher valued metal ions. But if there are no +2 charged cations suitable for ion exchange, the load balancing mechanism may cause an unequal cation distribution in Ca (I) and Ca (II) regions (Campisi et al 2018). The studies on doping of HAp with elements (such as Fe, Mn, Se, Mg, etc) also attracted attention and showed that the surface electron structure could increase the adsorption capacity. (Jiang et al 2002, Bystrov et al 2015, Zilm et al 2016). 

Recent studies have shown that hydroxyapatite is highly successful in removal of heavy metals (Gupta et al 2012, Hokkanen et al 2016, Yang et al 2016, Long et al 2019). However, the success of hydroxyapatite-based materials in the elimination of other heavy metal types and the competitive effects of other metal types that may exist in the environment with this mechanism should be taken into consideration and studies must be conducted accordingly.

In this study, adsorption of copper ion by hydroxyapatite have been performed based on selected independent variables which are concentration of copper, time and nano-HAp concentration. Box-Behnken design which is a statistical model has been applied to create a model and optimize the adsorption system.

2. Materials and method

2.1. Materials and equipment

In synthesizing nano-HAp, calcium nitrate tetrahydrate (Ca(NO_{3})_{2}.4H_{2}O), diammonium hydrogen phosphate ((NH_{4})_{2}HPO_{4}) and ammonia solution (28%–30%) was used and purchased from Merck (Turkey). In experimental research, CuSO_{4} was used to prepare synthetic samples (Merck, Turkey).

GFL branded orbital shaker used as a mixer during experimental studies was placed into the GallanKamp branded incubator and was operated. Hettich Rotofix branded centrifuge device was used for the recovery of nano-HAp both during nano-HAp synthesis and experimental studies. Copper concentrations of the samples resulting from copper removal were analyzed with Perkin Elmer Atomic Absorption Spectrometer C-400. Hitachi branded HF-200 transmission electron microscopy, Shimadzu branded XRD-6000 x-ray diffraction, Perkin-Elmer branded FTIR-ATR and Quantachrome branded NOVA 2200e Brunauer–Emmett–Teller devices were used in the characterization of nano-HAp.
2.2. Method

2.2.1. Synthesis of hydroxyapatite
The most cost-effective method of wet precipitation was used. Based on this method, a calcium salt and a phosphate are mixed with a Ca/P ratio of 1.67. Stirring of the solutions is continued until HAp formation is observed at a basic pH. For this purpose, in the synthesis of nano-HAp, calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and di-ammonium hydrogen phosphate ((NH₄)₂HPO₄) solutions were prepared separately. Ammonia solution is added to the calcium nitrate tetrahydrate solution (94.64 g in 400 ml deionized water) with a pH above 10.0. Di-ammonium hydrogen phosphate (31.72 g in 400 ml of deionized water) is added dropwise to the solution being stirred in the magnetic stirrer and the pH is maintained above 10.0 by the addition of ammonia. The reaction in this mixture is given in equation (1). After the reaction is complete, the nano-HAp’s are collected by centrifugation at 3000 rpm and washed 3 times with water. It is dried overnight in a drying-oven at 100 °C–120 °C for drying.

\[
10\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} + 6(\text{NH}_4\text{)}_2\text{HPO}_4 + 8\text{NH}_4\text{OH} \rightarrow \text{Ca}_6(\text{PO}_4)_3(\text{OH})_2 + 20 \text{ NH}_4\text{NO}_3 + 20 \text{ H}_2\text{O}
\] (1)

2.2.2. Experimental method
Copper sample were synthetically prepared by using CuSO₄ with ultrapure water. The original pH of the solution was 2.2. Experimental method allows the study of the interactions between the factors affecting a process and the change of the response variable (dependent variable) based on these factors. Therefore, experimental design is an important method for identifying process variables, reducing variability in the process and ensuring process optimization.

Experimental design is one type of experimental design methods and, was first used in 1951 by G. E. Box for optimization in chemical engineering research. For this method, which is used extensively in industrial processes and scientific studies, the inputs are accepted as independent variables and the resulting data are accepted as the response (Ulucan-Altuntas and Debik 2018). Depending on the response surface method, commonly used design methods include central composite design (CCD) and Box–Behnken design (BBD). The Box–Behnken design response surface method is adapted to the full quadratic model. If the BBD model has an optimum point, it is expressed by quadratic polynomial equation (equation (2)).

\[
y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ij} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + e (x_1, x_2, ..., x_k)
\] (2)

In equation (2), \(Y\) = dependent response variable (response), \(X_{ij} = i\) and \(j\) independent variables that affect the dependent variable, \(\beta_0 = \) breakpoint, \(\beta_i = \) coefficients of the linear model, \(\beta_{ij} = \) coefficients of the square model (interaction coefficient between the two factors) interaction coefficient and \(e = \) error are shown. The independent variables were coded via equation (3):

\[
\alpha = \frac{x_i - x_0}{\Delta x}
\] (3)

In equation (3), \(\alpha = \) the coded value of the independent variables, \(x_i = \) the actual value of independent variable, \(x_0 = \) the actual value of independent variable at the midpoint, and \(\Delta x = \) the change in independent variable \(x_i\) are shown.

BBD experimental design for copper removal with hydroxyapatite has been established and given in table 1. Fifteen experiments with 3 repetitions were performed according to the experimental data designed with 3 levels and 3 factors. In this study, \(\alpha\) is chosen as ±1.0. The data of the study is given in table 2. According to the results, ANOVA analysis were applied by excel and the optimum conditions were determine by Mathcad program.
3. Results and discussion

3.1. Characterization

To characterize and observe the phases of synthesized hydroxyapatite powders, TEM imaging (HF-2000, Hitachi), x-ray diffraction (Shimadzu, XRD-6000) were performed. FTIR spectra were analyzed in Perkin-Elmer 2000 FTIR-ATR. X-ray diffraction (XRD) patterns of nano-HAp are shown in figure 1. The crystalline peaks at \(2\theta = 26^\circ\) (002), 31.8\(^\circ\) (211), 39.1\(^\circ\) and 49.5\(^\circ\) are correspond to stoichiometric HAp (JSPDS Card no.09-432) and the sharp peaks confirm that HAp is well crystallized.

TEM images are shown in figure 2 and report the crystallized nano-HAp has a width of 10 nm and a length of 25 nm with nanorod morphology. The nano-HAp particles are also analyzed for their selective area diffraction analysis. These results are compatible with XRD result, which contains (002) and (211) planes.

Fourier transform infrared spectroscopy (FT-IR) was analyzed to determine the functional groups on nano-HAp and given in figure 3. The characteristic bands were detected at 1030, 1423, 1650, 2362 and 3393 cm\(^{-1}\). The strong band observed at 1030 cm\(^{-1}\) indicates P–O and PO\(_4\) stretching. The band at 1423 and 2362 cm\(^{-1}\) are

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**Table 1.** Individual variable matrix used in box-behnken design.

| Independent variable | Levels (\(\alpha\)) |
|----------------------|-------------------|
|                      | \(-1\) | 0 | +1 |
| Nano-HAp concentration (mg/l) | \(X_1\) | 100 | 400 | 700 |
| Time (min) | \(X_2\) | 5 | 35 | 65 |
| Cu concentration (mg/l) | \(X_3\) | 10 | 80 | 150 |

**Table 2.** Copper Adsorption results by nano-HAp.

| No | Nano-HAp Conc. | Time | Cu Cons. | Removal efficiency |
|----|----------------|------|----------|-------------------|
| 1  | -1             | -1   | 0        | 81.69             |
| 2  | 1              | -1   | 0        | 91.53             |
| 3  | -1             | 1    | 0        | 96.58             |
| 4  | 1              | 1    | 0        | 98.78             |
| 5  | -1             | 0    | -1       | 78.50             |
| 6  | 1              | 0    | -1       | 95.30             |
| 7  | -1             | 0    | 1        | 95.12             |
| 8  | 1              | 0    | 1        | 99.30             |
| 9  | 0              | -1   | -1       | 81.30             |
| 10 | 0              | 1    | -1       | 95.88             |
| 11 | 0              | -1   | 1        | 92.95             |
| 12 | 0              | 1    | 1        | 99.05             |
| 13 | 0              | 0    | 0        | 98.69             |
| 14 | 0              | 0    | 0        | 98.70             |
| 15 | 0              | 0    | 0        | 98.64             |

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corresponding CO$_3^{2-}$ and C–H stretching, respectively. The strong band at 3393 cm$^{-1}$ points the O–H stretching.

In addition, Brunauer–Emmett–Teller (BET, Quantachrome-NOVA 2200e) was used to determine specific surface areas of the synthesized nano-HAp and, the specific surface area was obtained as 81.48 m$^2$ g$^{-1}$. The specific surface area of the adsorbent material plays an important role in the adsorption of heavy metal ions in the wastewater. Since larger specific surface area of the synthesized nano-HAp, might perform better absorption performance than coarse crystalline HAp.

### 3.2. Heavy metal adsorption

HAp concentration, time and Cu concentration were determined as independent variables having effect and the study matrix is given in table 1. Experimental design and removal efficiencies generated according to Box–Behnken design are shown in table 2.

The significance of the variables used in the model after the model is created is important for checking the suitability of the model. For this purpose, variance analysis (ANOVA) was used. In variance analysis, meaningful terms for the model and the significance of the model are determined according to the Probe $>$ F value. If the
90% can be obtained even in low nano-HAp concentrations than 1.0 g l\(^{-1}\). The probe developed by StatSoft. The graphs can be seen in figure 4. Cu was removed by 99.81\% of nano-HAp concentration and time, are determined as significant effective parameters. The coefficient of parameters gives opinion about their effect. While individual effect of nano-HAp concentration (x\(_1\)), time (x\(_2\)) and Cu concentration (x\(_3\)) have positive in removal efficiency, their quadratic effects (x\(_1^2\), x\(_2^2\), x\(_3^2\)) have negative effect.

The equation generated from ANOVA result is given in the following equation (4):

\[
y = 98.675 + 4.152x_1 + 5.356x_2 + 4.403x_3 - 3.205x_1x_2 - 3.365x_2^2 - 3.170x_3^2 - 3.205x_2^2
\]

Response surface graphs were generated via Statistica program which is an advanced analytics software package developed by StatSoft. The graphs can be seen in figure 4.

The effect of nano-HAp concentration (x\(_1\)) and time (x\(_2\)) can be seen in figure 4(a). As determined in ANOVA results, the removal efficiency is increasing with the increment on nano-HAp concentration (x\(_1\)) and time (x\(_2\)). To remove copper with higher efficiency than 90%, the required nano-HAp concentration and time is approximately 510 mg l\(^{-1}\) and 33 min, respectively. Gandhi \textit{et al} (2011) observed copper removal by nano-hydroxyapatite and, showed that at least 30 min of reaction time is required for adsorption equilibrium. In addition, Yang \textit{et al} (2016) synthesized poorly crystallized nano-HAp and applied in copper removal and, reported that copper was removed by 80% with 1.0 g l\(^{-1}\) nano-HAp when the copper concentration is 100 mg l\(^{-1}\). In this study, the synthesized nano-HAp is well crystallized and higher removal efficiencies than 90% can be obtained even in low nano-HAp concentrations than 1.0 g l\(^{-1}\).

The effect of Cu concentration (x\(_3\)) on copper removal efficiency can be seen in figure 4(b) and the effect of Cu concentration (x\(_3\)) and time (x\(_2\)) can be seen in figure 4(c). In both graphs, the removal efficiency can be higher than 90% if Cu concentration (x\(_3\)) is between 45–150 mg l\(^{-1}\) when the nano-HAp is higher than 280 mg l\(^{-1}\) and reaction time is higher than 20 min Long \textit{et al} (2019) studied lead removal by hydroxyapatite carbon composite and observed that total removal can be obtained for the Pb concentration lower than 2 mmol l\(^{-1}\) (414 mg l\(^{-1}\)). In this study, the Cu concentration higher than 60 mg l\(^{-1}\) is determined that it can be totally removed when time is high as 65 min. The increment in all selected variables affect positively in removal efficiency, as determined in ANOVA results.

In order to find the optimum points belonging to each independent variable of the study, maximize function in Mathcad (14.0) program was used. Equation (4) obtained by ANOVA results was maximized. Accordingly, to achieve maximum removal efficiency, when Cu concentration is 115 mg l\(^{-1}\), the nano-HAp concentration and time to be used should be 514.0 mg l\(^{-1}\) nano-HAp and 60.4 min, respectively. To remove the lowest selected Cu concentration of 10 mg/l, 60.4 min of reaction time and nano-HAp concentration of 700 mg l\(^{-1}\) is required. To evaluate the accuracy of the model, the optimum points, which are 115 mg l\(^{-1}\) of Cu concentration, 514.0 mg l\(^{-1}\) of nano-HAp concentration and 60.4 min of reaction time, were investigated experimentally three times. Cu was removed by 99.81 ± 0.9\%, while the removal rate can be calculated as 100% in model.

| Table 3. ANOVA results of copper adsorption by nano-HAp. |
|---------------------------------------------------------|
| Intersection | Coefficients | Std. Error | t Stat | P-value | Significant |
| x\(_1\) | 98.675 | 0.989 | 99.832 | 1.9 E-09 | — |
| x\(_2\) | 4.152 | 0.605 | 6.860 | 0.0010 | Very Significant |
| x\(_3\) | 5.356 | 0.605 | 8.848 | 0.0003 | Very Significant |
| x\(_1\).x\(_2\) | 4.403 | 0.605 | 7.274 | 0.0007 | Very Significant |
| x\(_1\).x\(_3\) | −1.909 | 0.856 | −2.231 | 0.0761 | — |
| x\(_1\).x\(_2\).x\(_3\) | −3.205 | 0.856 | −3.744 | 0.0133 | Significant |
| x\(_1\).x\(_2\).x\(_3\) | −2.123 | 0.856 | −2.480 | 0.0558 | — |
| x\(_1\) | −3.365 | 0.891 | −3.777 | 0.0129 | Significant |
| x\(_1\) | −3.170 | 0.891 | −3.557 | 0.0162 | Significant |
| x\(_1\) | −3.205 | 0.891 | −3.597 | 0.0155 | Significant |
Figure 4. Surface graphs of Cu adsorption by nano-HA.
4. Conclusion

Well-crystalized hydroxyapatite nanoparticles have been effectively used in copper removal. The study was designed with the help of Box-Behnken design and ANOVA analysis was used to investigate the significance of the model. According to obtained results, the effective independent variables are determined as nano-HAP concentration and time. Optimization was carried out and 514 mg l\(^{-1}\) nano-HAP concentration and 60.4 min were determined required for maximum removal efficiency. The lowest selected Cu concentration of 10 mg l\(^{-1}\) can also be removed totally when nano-HAP concentration is 700 mg l\(^{-1}\) and time is 60.4 min. It is shown that nano-HAP can be used as a promising adsorbent in environmental applications. Although it has been shown to be effective in the removal of heavy metal copper, it needs to be investigated in the presence of different pollutants. Also, we expect that the addition of hydroxyapatite with elements such as Fe, Mg may increase the adsorption efficiency and/or reduce the required reaction time.

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