




# Synthesis of hydroxyapatite nanoparticles using dolomite powder

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## ABSTRACT

This study has been developed for the synthesis of hydroxyapatite using low-cost dolomite material. We investigated the influence of calcination temperature and feed gases on the decomposition of raw dolomite, and the relation between the calcination temperature and the phosphorus affinity. Also, the influence of calcination temperature on the porosity of the novel dolomite-based adsorbent with phosphorus was considered. Characteristics of the new adsorbent were evaluated by N<sub>2</sub>-BET and XRD apparatuses. The synthesized adsorbent is composed of magnesium oxide (MgO) and hydroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH or Hap), which has high ion-exchange properties and displays efficient adsorption of heavy metals in the wastewater.

**Keywords:** Dolomite, Synthesis, Phosphorus, Hydroxyapatite, Nanoparticle

## 1. INTRODUCTION

Heavy metals contamination of water is caused by human activity such as mining, manufacturing, and waste discharge, which are released into the air, soil, and water are having a significant influence on the health of many individuals and the environment [1]. Industrialized nations in Europe and North America, where heavy metal concentrations in water were lower, reversely, more heavy metals were found in developing countries in Africa, Asia, and South America with concentrations over the permissible levels for both WHO and USEPA standards. For the management of heavy metal contamination in water, strict controls on emissions and recycling are also essential [2][3].

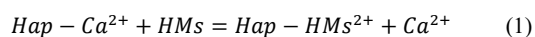
Due to industrial growth over the past few decades, a variety of environmental issues, including air and water pollution and soil contamination, have become increasingly widespread in Mongolia. Three principal industrial regions are Ulaanbaatar, Darkhan, and Erdenet

in Mongolia. Ulaanbaatar which is the capital of Mongolia has a wide range of industries and is home to half of the country's population. Heavy metal contamination, particularly in the water environment, is a problem in Mongolia in several places with significant population densities and businesses. According to data, concentrations of heavy metals decreased in the following order based on their geochemical characteristics; As>Cr>Ni>Pb>Zn for the big cities [4].

The largest sources of heavy metal pollution, which is harmful to both human health and the environment, are concentrated in Ulaanbaatar, where there are 60 tanning companies, 135000 traditional dwellings, over 100,000 cars, and coal-fired thermal power plants. This issue is becoming a concerned issue in Mongolia. Additionally, Ulaanbaatar receives all its water from the sewage center, water consumption is expected to increase to 510700m<sup>3</sup>/day by 2030 [5] due to the city's expanding population, which may cause leaks in water supplies and wastewater treatment.

On the other hand, adsorption has been shown to be an efficient method for the removal of heavy metal contaminants in the aqueous medium, and it is essential that developing nations use easily obtainable, affordable adsorbents for the treatment of water [6]. Adsorbents based on the carbonate mineral of dolomite have been the target of a lot of research for the removal of heavy metals in an aqueous medium due to low-cost and simple removal technologies. The application of dolomite adsorbent for the removal of fluoride and heavy metals is increasing due to this natural mineral being economical as well as non-toxic and abundant around the world. Some researchers have used raw dolomite for removing Cd, Zn, Pb [7,8], Sr (II) and Ba (II) [3], and Ur(VI)[10], As(V) [11] ions in wastewater. Likewise, Yousef Salameh et. al has described the removal of As (III) and As(V) [12] from aqueous solution using thermally modified dolomites. Moreover, there is reported that the synthesized materials, such as modified silicate dolomite [13], and modified phosphate dolomites [14,15] used for the removal of Cu (II), multi-cations of heavy metals, and bi-valent cations of heavy metals, respectively.

Furthermore, there is some research on hydroxyapatite used for the removal of bivalent cations such as  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  [16,17], and  $Pb^{2+}$  [18]. Authors suggested that the reaction mechanism between Hap and bi-valent heavy metals could be a dissolution-precipitation process that leads to ion-exchange mechanism and the reaction could be described as the following;



It has been found that dolomite and modified dolomite adsorbents have an affinity for bi-valent cations, and thermally modified dolomite has increased the removal amount. The affinity of heavy metals has usually been processed in an acidic aqueous medium for all the research. However, the adsorption amounts are generally not high, and few research works have been reported to remove As(III) using dolomite-based material.

This research work aims to obtain a novel adsorbent of hydroxyapatite ( $Ca_5(PO_4)_3OH$ ) to remove heavy metals from an aqueous solution by using dolomite as raw material. We assessed the influence of calcination temperature and input gases on the decomposition of raw dolomite, and the relation between the calcination temperature and the phosphorus affinity. Also, the influence of calcination temperature on the porosity of the novel synthesized adsorbent was investigated.

## 2. EXPERIMENTAL

### 2.1. Materials

A sample of dolomite analysed in this research originates from the Sano area (Japan), which was sieved

(75–150  $\mu m$ ) and dried in a horizontal drying oven at 105°C for 24 h. Then dolomite samples (approximate mass of 0.5 g) were calcined (decomposed) in the vertical fixed-bed reactor at 300–900°C temperatures under air,  $N_2$ , and  $CO_2$  atmosphere, and calcined dolomites were used for adsorption of phosphorus.

### 2.2. Methodology

By using TG-DTA, thermal analysis of raw dolomite and synthesized adsorbent was performed in the condition of continuous heating from room temperature to 1000°C at a heating rate of 20°C/min, under air atmosphere, and TG and DTA curves were obtained. The chemical compositions of raw dolomite, calcined dolomites, and synthesized adsorbents were determined by XRD analysis. The specific surface areas and pore volumes of synthesized adsorbents were measured by  $N_2$  adsorption/desorption using a surface area and pore size analyzer (TriStar II 3020, Micromeritics, Instrument, Corporation).

### 2.3. Adsorption experiment of phosphorus onto calcined dolomite

Calcined dolomite (calcined at 800°C in air atmosphere) was stirred with phosphorus solution 1000 ml (20.0 w.t %). Previously, the phosphorus solution was adjusted at pH12 by drop-wise of 5M NaOH. Then the solution was stirred at room temperature for 24h and separated into liquid and solid. The synthesized adsorbent was dried at 80°C for 24 hours and re-calcined or re-heated at 360°C for 40 minutes. A re-calcined novel adsorbent was used in further experiments of heavy metal removal.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of the calcination process of raw dolomite

Fig. 1a, 1b shows TG and XRD curves of dolomite in air atmosphere, which is followed by a one-stage decomposition due to one endothermic peak, and the maximum of the DTA peak was at 732.3°C. The TG analysis showed that a weight loss occurred between 450 and 800°C due to the loss of  $CO_2$ , and the total weight loss was 47wt.% above 650°C heating temperature. The crystallinity of raw dolomite both before and after calcination was investigated using XRD analysis. As shown in Fig. 1b, raw dolomite has an impurity of calcite. Dolomite disappeared after calcination at 800°C and was replaced by lime and periclase [19]. Additionally, calcite was not formed during the calcination process, it was evident that a one-stage decomposition mechanism was adequate to produce a mixed oxide phase (CaO/MgO) as the following reaction [20]:



Thermal decomposition or calcination of raw dolomite was studied at 450–800°C under different input gases of air, N<sub>2</sub>, and CO<sub>2</sub> by using the vertical fixed bed reactor. Data about the decomposition of raw dolomite in different input gas was recapped in reference [19]. The obtained products after calcination of raw dolomite or calcined dolomites were used for the adsorption of phosphorus.

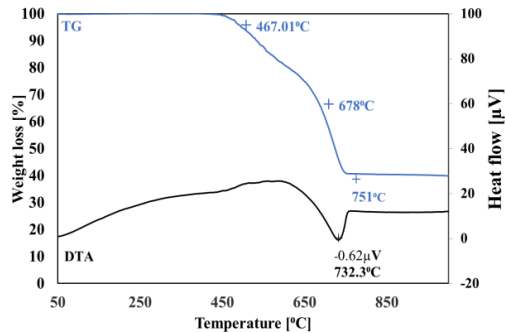


Figure 1a. TG-DTA of raw dolomite

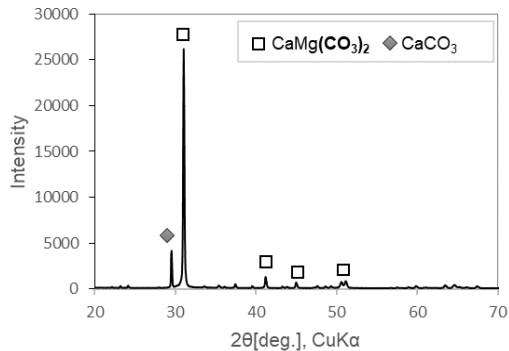


Figure 1b. XRD profile of raw dolomite

### 3. 2. Adsorption of phosphorus onto calcined dolomite

Adsorption experiments of phosphorus were conducted using calcined dolomites which were calcined at different temperatures of 450–800°C in an air atmosphere. As can be seen from Fig. 2, calcined dolomites prepared at 650 and 700°C have a high affinity of phosphorus compared to other calcined dolomites (>650°C). Then, there is a negligible increased adsorption amount of phosphorus above 700°C. We assumed that the main role of phosphorus affinity was the CaO component which is obtained by the full decomposition of CaCO<sub>3</sub> (<650°C). In further experiments, calcined dolomite at 800°C was chosen for the adsorption of phosphorus experiments, and obtained or synthesized hydroxyapatite adsorbents were used for the

recalcination process at different temperatures and different input gases to improve the porosity.

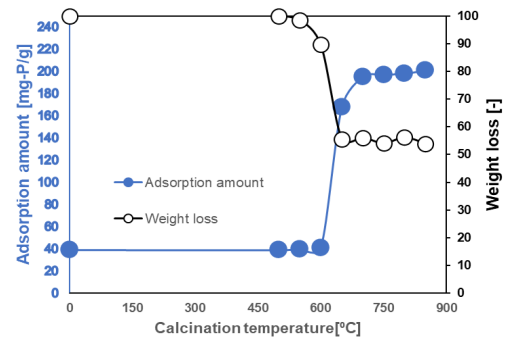


Figure 2. Adsorption of phosphorus onto the dolomites calcined in different temperatures

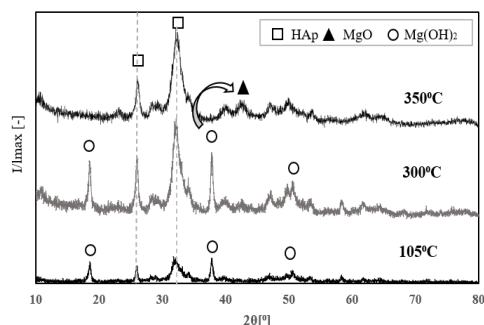
### 3. 3. Characterization of synthesized hydroxyapatite adsorbent

We re-calcined the synthesized hydroxyapatite adsorbent for 30 min at 340–800 °C under air, N<sub>2</sub>, and CO<sub>2</sub> atmosphere. Then, re-calcined adsorbents were analyzed for porosity. Table 1. shows the BET surface area of the different re-calcined adsorbents. Thermal modification reveals that the surface area was the highest data at a re-calcination temperature of 360 °C in each input gas. However, these parameters decreased at high temperatures. According to the viewpoint of Stefaniak et al [21] the high temperature leads to the increased density of the solid, so the pore volume and the specific surface area decrease due to the growth of grain size. Also, it was found that the atmosphere of re-calcination affected porosity. Re-calcination under an N<sub>2</sub> atmosphere leads to the highest BET surface area in each temperature compared to Air and CO<sub>2</sub> atmospheres.

Table 1. BET surface area (m<sup>2</sup>/g) of the synthesized adsorbent in different feed gases and different recalcination temperatures (°C)

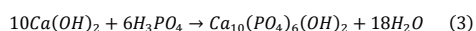
Re-calcination temperature, (°C)	N <sub>2</sub>	Air	CO <sub>2</sub>
360	125.6686	72.1016	40.8077
650	39.3388	30.4040	19.2047
800	26.5322	23.0791	9.9950

On the other hand, as can be seen from the XRD results (Fig. 3) reveal dried synthesized adsorbent confirmed that added phosphorus reacted with Calcium part formed into Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, and Mg part remained unreacted with phosphorus. Also, we can see MgO formation occurred at 360°C due to the dehydration reaction of Mg(OH)<sub>2</sub> in Fig. 3.

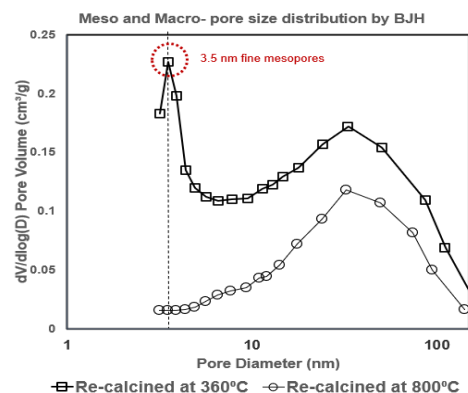


**Figure 3.** XRD results of synthesized adsorbent with phosphorus in different re-calcination temperatures

According to the speciation of orthophosphates,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  species are in the acidic or slightly base medium, and  $\text{PO}_4^{3-}$  species become significant and exceed that of  $\text{HPO}_4^{2-}$  in the basic medium and act as a source of anions [22]. The effective adsorption sites of phosphate were coincident with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Due to the presence of various species of anions and cations in the aqueous solution, some new phosphate compounds can be formed on the surface of the adsorbent material [23]. In previous studies, Miculescu et al [24] synthesized Hap derived from Marble and Shell by adding  $\text{H}_3\text{PO}_4$ . Experimental results confirmed the following reaction (3);



As result, the adsorption of phosphate onto calcined dolomite may involve chemisorption, and  $\text{Ca}^{2+}$  is the main role in the adsorption of phosphate anions in an alkalic medium and the adsorption amount of phosphate depends on the amount of CaO in calcined dolomite. Furthermore, Fig. 4 shows pore volume distribution calculated by the BJH method of two different adsorbents re-calcined at 360°C and 800°C temperatures. BET surface area increased sharply for the sample re-calcined at 360°C. We assume the fine mesoporous MgO formed at this temperature which leads to increasing the BET surface area, however increasing the re-calcination temperature fine mesoporous disappeared due to the growth of crystallization of MgO. Analysis of curves of the pore diameter distributions by the BJH method reveals the mesoporous structure with a pore diameter of 3.5 nm for adsorbent re-calcined 360°C, and a wide curve at the interval 10-100 nm, but disappeared fine mesoporous peak for adsorbent re-calcined at 800°C. The basis of the findings of the re-calcination experiments, in subsequent heavy metals adsorption experiments, we employed a synthesized adsorbent recalcined at 360 °C.



**Figure 4.** BET surface areas in different re-calcination temperatures and BJH pore distribution in different temperatures

Our developed new adsorbent revealed that it can be an efficient adsorbent material for the removal of As(III) in an aqueous solution [19].

#### 4. CONCLUSION

We developed a new hydroxyapatite adsorbent using low-cost dolomite for heavy metal removal in an aqueous solution. The following could be drawn;

1. The composition of calcined dolomite is controlled by calcination reaction time and input gas.
2. Phosphate was adsorbed by precipitation of hydroxyapatite onto the surface of calcined dolomite in the alkalic medium.
3. Equilibrium isotherm adsorption data revealed Langmuir isotherms and dominated chemisorption.
4. Synthesized adsorbent consists of Hydroxyapatite and Magnesium oxide, which has high porosity and good at ion exchange process for the removal of cations in wastewater.

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