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Synthesis and application of hydroxyapatite (HA) for removal of heavy metal ions from water

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Abstract
Hydroxyapatite $Ca_{10} (PO_4)_6 (OH)_2$ (HA) is a calcium phosphate biomaterial, commonly used as an artificial bone replacement material in orthopedic surgery. Besides, HA is also a very potential material to remove heavy metal ions in wastewater. HA has been shown to be an effective adsorbent and ion exchanger. This manuscript briefly presents some selective methods to synthesize HA material as well as its application in treatment of heavy metal ions, with a typical example being ion removal of Pb^{2+} in wastewater.

Keywords: Hydroxyapatite, heavy metal ions, environment, HA synthesis method, adsorption

Introduction

Hydroxyapatite (HA) has the full molecular formula of $Ca_{10} (PO_4)_6 (OH)_2$ or can be abbreviated as $Ca_5 (PO_4)_3$ OH, the molecular mass of 1004.60 (g/molar mass). Hydroxyapatite has a hexagonal lattice structure with the lattice constants listed as a = 9.42 Å, b = 1.89 Å, c = 6.88 Å, $\alpha = \beta = 90^o$, and $\gamma = 120^o$ [1]. The HA crystal structure is described as a spatial ensemble composed of ions such as Ca^{2+}; PO_4^{3-}; OH^-, wherein the PO_4 tetrahedral group the P^{5+} ions are located in the center of the tetrahedron. The individual Ca^{2+} ions are ionically connected to each PO_4 tetrahedron and OH^- groups [2].

HA has been and is being studied for use as an artificial bone material because of its interesting properties such as biocompatibility and bioactivity [3-4]. HA material is highly biocompatible with the human body because the Ca/P ratio in the HA molecule is similar to that of Ca/P in human bones. The bioactivity of HA is shown in that after being used to implant missing or damaged bones, HA will dissolve due to the interaction with body's environment, then Ca^{2+}, PO_4^{3-}, and OH^- ions in the environment will precipitate on the surface of the material to form a new layer of HA mineral which takes the role as a bridge for the attachment of bone grafts and natural bone. Due to the above special properties, HA material is widely applied in medicine for bone orthopedic surgery, making dentures, and implanting broken bones - missing bones.

Regarding the chemical properties, HA does not react with alkalis but reacts with acids to form salts of calcium and water:

$$Ca_{10}(PO_4)_6(OH)_2 + 2HCl \rightarrow 3Ca_3(PO_4)_2 + CaCl_2 + 2H_2O \quad (1)$$

HA is not heating stable, easily decomposed in the temperature range of 800-1200 °C according to the following reaction:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x + xH_2O \ (0 \leq x \leq 1) \quad (2)$$

HA may be decomposed into other substances in the calcium phosphate compounds depending on the temperature condition according to the reaction equations below:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 2\beta\text{-TCP} + Ca_4P_2O_9 + H_2O \quad (3)$$

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3\beta\text{-TCP} + CaO + H_2O \quad (4)$$

In particular, HA material also exhibits efficient ion exchange with many divalent metals such as Zn, Pd, Cd, Cu, Co. The ion exchange process is represented by the following equation

$$Ca_{10}(PO_4)_6(OH)_2 + xM^{2+} \leftrightarrow Ca_{10-x}M_x(PO_4)_6(OH)_2 + xCa^{2+} \quad (5)$$

Based on the above properties, HA has been widely used to successfully remove heavy metals from polluted wastewater. In recent years, many scientific works have been published on the use of HA materials for environmental treatment [5-6].

In this paper, the author emphasizes on methods of synthesizing HA materials and its application in removing heavy metal ions.

Methods for synthesizing HA material

HA material has been synthesized with different structures and morphologies based on two main ways: chemical synthesis and separation from natural bones of animals. Here are a few typical synthesis methods.

Solid-state method

The solid state reaction is considered to be the interaction of precursors at high temperature to produce a new substance. This is a simple method derived from calcining chemical precursors containing calcium and phosphate to obtain HA material [7-9].

$$3Ca_3(PO_4)_2 + Ca(OH)_2 \leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (6)$$

For above reaction, the molar ratio of tri-calcium phosphate and calcium hydroxide is 1/1 or 3/2, pure HA material has been successfully prepared at 1000 ^oC. Although this is a simple method, the production of pure HA requires rigorous investigation and adjustment of reaction parameters because the final product can be contained different calcium phosphate phases.

Precipitation method

Precipitation method is commonly used to prepare HA materials. This is a method used to precipitate HA in powder or film form from solutions containing precursors of calcium and phosphorus. The advantage of the precipitation method is that it is possible to adjust the size of HA particles as desired. However, parameters such as pH, ratio of precursors, reaction temperature must be controlled strictly [10-11]. The principle of this synthesis is the precipitation of Ca^{2+} and PO_4^{3-} ions in water solution in one of the following ways:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O \quad (7)$$

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (8)$$

In the previous study [12], the author successfully synthesized HA material by precipitation method. The crystallinity and purity of the material were confirmed by XRD technique with sharp lines characteristic for HA (Fig. 1). Observation by SEM method showed that the porous structure of synthetic material consists of fairly uniformly interwoven rod-shaped crystals (Fig. 2).

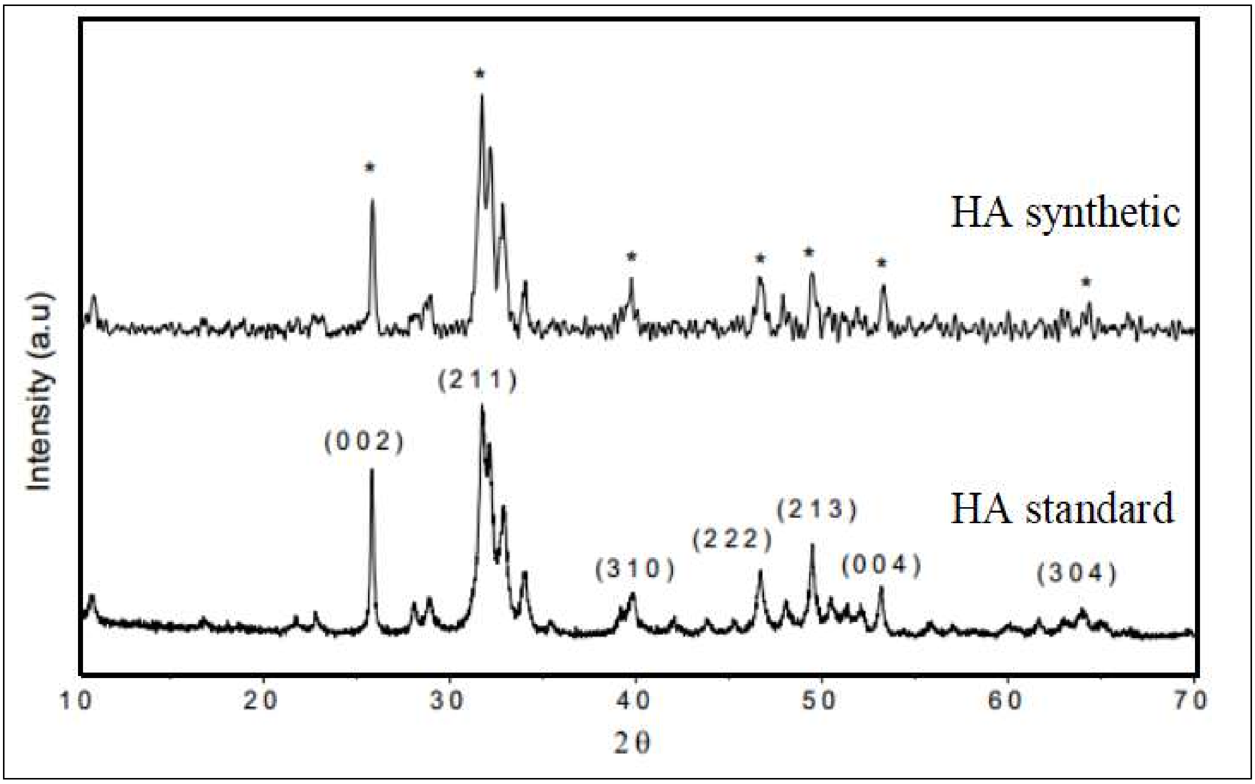

Fig 1: XRD diagram of synthetic HA [12]

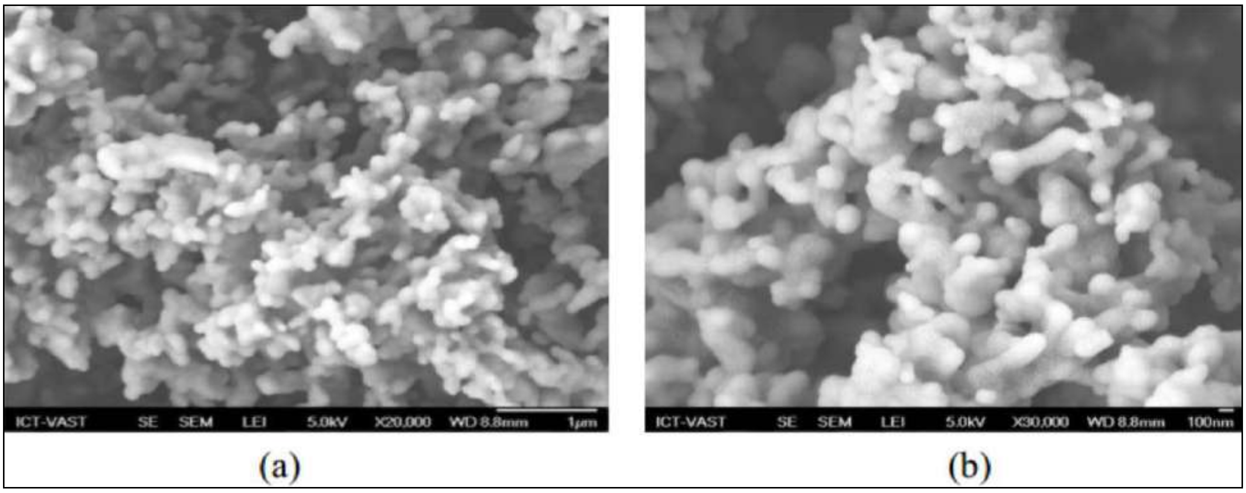

Fig 2: SEM images of synthetic HA with different magnifications a) X. 20.000 and b) X. 30.000 [12]

Hydrothermal method

The hydrothermal method performs the synthesis reaction at high temperature and pressure conditions. For example, a mixture of calcium chloride ($CaCl_2$) and phosphoric acid (H_3PO_4) precursors is placed in a hydrothermal vessel, and heated at about 200 ºC with spontaneous pressure [13-14]. This method has the advantage of fast synthesis, and no need to undergo processing of the resulting product. However, the amount of synthetic product is usually small because the reaction is carried out in a closed system with a small volume.

Thermal treatment method

Thermal process can be used to synthesize the HA material from the natural bones. In the research paper [15], the authors have synthesized HA from animal bones such as bovine, caprine and galline bones. Raw bones were thermally heated in the range of temperatures from 600 to 1000 ºC. The research shows that bovine bone can produce pure HA while caprine and galline bones yielded HA material in the presence of tri-calcium phosphate TCP at processing temperature above 700 °C. In our research [16], thermal treatment method was used to extract HA from porcine bone. The powder of raw bone was heated at several temperature without using the chemical agents. The survey results show that the optimal condition for HA synthesis was selected as heating teperature of 750 ºC and heating time of 6 hours. XRD investigation showed that the raw bone is an amorphous

calcium phosphate phase (ACP). However, the XRD of heated bone at 750 ºC present the narrow and sharp peaks, confirming the crystalline state of obtained HA material (Fig 3). All crystalline peaks fit fully to the ones of pure hydroxyapatite [17]. Fig. 4 shows the SEM images of synthetic HA with different magnifications. At lower magnifications (X 5000 and X 10.000), the agglomerated particles including small spheres, scales, and rods are observed. These different particles are interconnected to form the porous structure of synthetic HA. The SEM images at higher magnifications (X 20.000 and X 50.000) clearly confirms the spheres, scales, rods, and pores in the 3D structure of material (Fig 4).

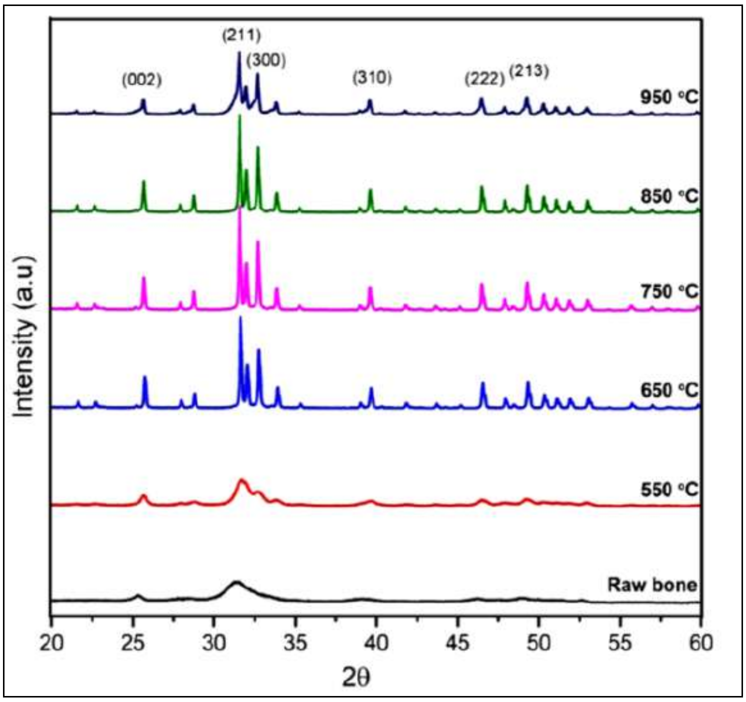

Fig 3: XRD diagram of HA synthesized at different temperatures during 3 hours [16]

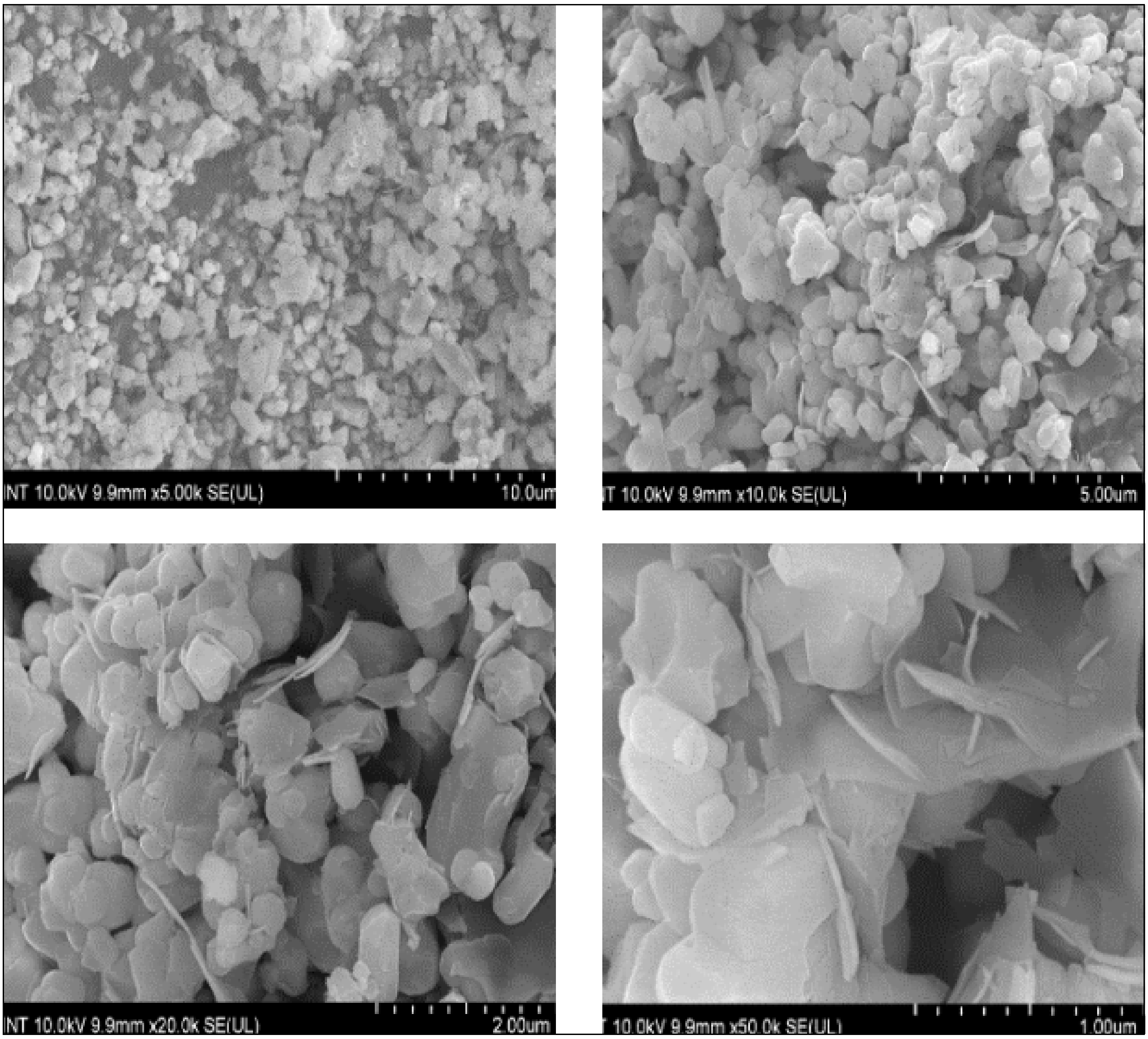

Fig 4: SEM images of HA extracted at 750 °C at different magnifications [16]

Application of HA for removal of heavy metal ions

Heavy metals are discharged into the aquatic environment due to industrial activities such as battery production, electroplating, metallurgy. Heavy metal pollution is a serious threat to human health, animal and plant life. Heavy metals cause mass accumulation over time and are harmful to living organisms. Furthermore, they are not biodegradable and exhibit toxicity even at low concentrations [18]. At present, many methods have been developed to remove the pollution of heavy metal ions from water environment, such as chemical reduction, precipitation, adsorption, electrochemical deposition, membrane technology, ion exchange and ultrafiltration. Among the above methods, absorption is an effective, economical and easy to implement method. Hydroxyapatite (HA) material is considered to be a potential mineral with good properties for use as absorbent materials to remove heavy metal ions in aqueous media. The superior characteristics of HA materials can be mentioned as non-toxic, cheap and can be exploited in mineral deposits, high absorption capacity, and stability in the aquatic environment [18]. HA material exhibits the ability to remove heavy metal ions through physical adsorption and ion exchange. Physical adsorption ability is thanks to the porous structure of HA material, through which heavy metal ions are trapped in the pores of HA material. Ion exchange capacity is shown through the exchange of Ca^{2+} cations with heavy metal ions such as Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} [19]. The mecanism of ion exchange is described as the following equation:

In our previous study, mineral HA was modified with the simulated body fluid (SBF) for 3 days to improve the porous structure (Fig 5). Then, the modified HA was used for removal of Pb^{2+} ions in aqueous solution [20]. The adsorption experiment proved that the surface-modified HA can remove almost 100% of Pb^{2+} ions. The mechanism of Pb^{2+} adsorption on the surface-modified HA are fully fitted to both Langmuir and Freundlich models.

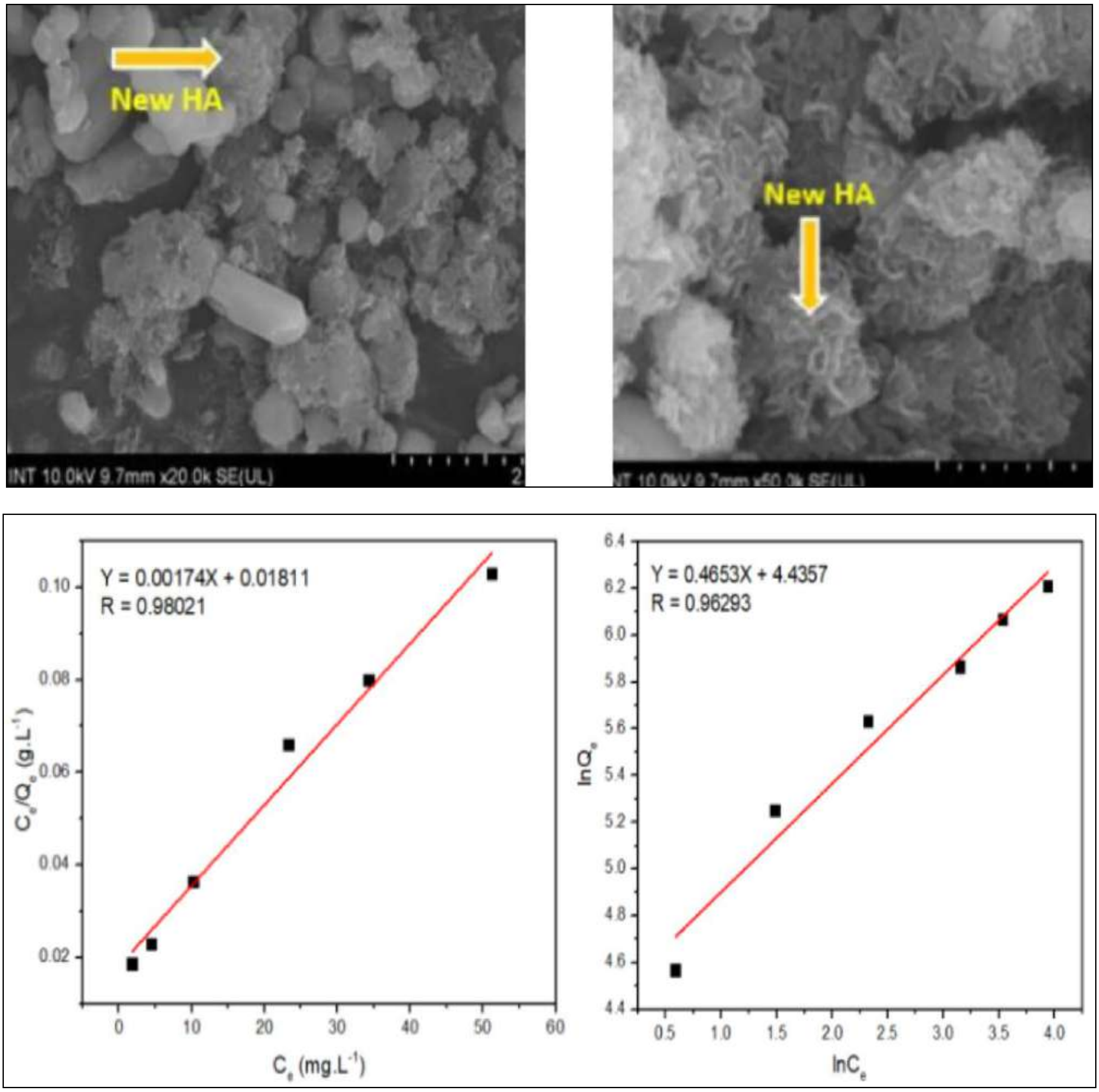

Fig 5: SEM images of surface-modified HA and Langmuir, Freundlich models of Pb^{2+} adsorption [20].

Conclusion

This paper introduces the synthesis of HA material and its application in the treatment of heavy metal ions in water. Regarding the synthesis of HA, several important synthesis methods have been introduced including our selected results. The application of HA material in the treatment of heavy metal ions is generalized, together with the introduction of research result demonstrating the effectiveness of HA in removing Pb^{2+} metal ions in aqueous media. Through this article, readers can find interesting information about HA material applied in wastewater treatment contaminated with heavy metal ions.

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