Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 8, No. 3, 2023

Application of Hydroxyapatite for the Adsorption of Heavy Metals in Water Treatment

Binyi Xiong[1, a]

[1]Oregon State University, Corvallis, 97333, US
[a]xiongbinyify@yeah.net

Abstract: In recent years, the increasingly severe environmental problems, especially those related to aquatic organisms and chemical pollution, have become a significant threat to the ecosystem and human health. Many new composite materials are used to control pollution because of their environmentally friendly properties. Hydroxyapatite is a kind of phosphate biomaterial. Compared with the original ore, it has improved the adsorption of heavy metals. Because of its eco-friendliness, good dispersibility, outstanding stability, and rich surface functional groups, it has a good prospect in treating water, air, and soil pollution. It is expected to inhibit toxic pollutants for a long time. Against this background, this paper introduces the adsorption of dyes and heavy metals by hydroxyapatite and its composites, and the influence of technological factors. For instance: contact solute concentration, time, temperature, pH of the solution, etc. on adsorption.

Keywords: Metals ions; Limitations; adsorption materials; synthetic hydroxyapatite; water de-pollution and treatment.

1. Introduction

Mining, electroplating, steeling and nonferrous metallurgy, and other human activities have significantly increased the incidence of different types of pollutants in water. The heavy metals mentioned in environmental pollution mainly refer to cadmium, chromium, lead, mercury, and metalloid arsenic. Pollutants are usually divided into several categories, such as nutrients (such as nitrate, phosphate, etc.), inorganic metal ions, synthetic organic compounds (such as pesticides, dyes, polycyclic aromatic hydrocarbons, drugs, petroleum by-products, etc. Once these harmful substances enter the human body through breathing, eating, drinking, or other direct contact, they will significantly damage the normal function of the body. Because, unlike other toxins, heavy metals can be excreted after liver catabolism, on the contrary, they are quickly accumulated in organs such as the brain and kidney, ranging from mild skin allergy to serious organ disorder, and even cause gene mutation, affect cell inheritance, produce teratoma or induce cancer. In recent years, clay nano-materials and synthetic environmental mineral materials have shown their development potential and advantages. Compared with inorganic adsorbents such as zeolite and metal oxides, hydroxyapatite (HAP), a kind of apatite with a clear crystal structure, shows good adsorption potential [1]. This paper reviews the latest research results of hydroxyapatite in removing metal ions from wastewater.

2. Removal of Heavy Metal Ions from Water by Nano-hydroxyapatite

Although the traditional HAP NPs have many excellent characteristics, HAP has high brittleness and poor flexibility. However, nano-cellulose has the advantages of corresponding defects, such as good physical and mechanical properties (tensile strength, high surface area, etc.); Renewable, biodegradable, and non-toxic. Many researchers have used different experimental methods to prepare nano-hydroxyapatite in the past ten years. For example, (1) Biomineralization. It is a kind of physiological environment mirror that simulates the human body with simulated body fluid which is specifically temperature 37℃ and pH 7.4, and inorganic ions such as Ca2+, Na+, K+, PO43−, etc.). Under the action of static electricity, negatively charged sites first form nucleation sites, and HAP composites with different shapes and structures are finally formed after continuously absorbing inorganic ions in the solution [2, 3]. (2) Physical mixing method. It refers to the method of combining HAP and nano-cellulose through electrostatic adsorption. Zhang et al. [4] first successfully prepared monodisperse, biocompatible, single-crystal HA nanotubes by a simple one-step solvothermal method. At room temperature, the acetic acid solution containing chitosan was mixed with HAP nano-microtubules by a simple physical mixing method and mechanically stirred into a slurry. HAP aerogels with excellent air permeability and ultra-low thermal conductivity were successfully prepared by high-temperature burning and freeze-drying without adding additives. This method has many advantages, such as high HAP crystallinity, simple operation, uniform, dispersed structure, and excellent performance, and it has broad application prospects in various fields. (3) In-situ synthesis method. It is to combine HAP precursors with groups on the molecular chain of modified nano-cellulose. Because of the high energy of this chemical bond, it is difficult for HAP NPs to fall off from the modified nano-cellulose under mechanical action. For example, Sarkar et al. [5] used an in-situ synthesis method to take calcium nitrate and ammonium dihydrogen phosphate as precursors and carboxymethyl cellulose as substrate, which was alkalized by mechanical stirring under the regulation of ammonia water, and finally formed carboxymethyl cellulose (CMC)/HAP with conjugated carbon points after refluxing at 140℃ for 8 hours.

Literature research shows that nano-hydroxyapatite particles have good excellent ability for heavy metal ions in water. 0.6 g/L HAP nanoparticles can remove about 88% arsenate from the polluted drinking water within one hour [6]. Synthesized nano-hydroxyapatite for the removal of Cd2+ from water with using 0.5 g/L hydroxyapatite nano-powder [7]. Nano-hydroxyapatite shows an excellent binding affinity for Cu^{2+}, and its rate kinetics conforms to the pseudo-second-order model [8]. In addition, the maximum adsorption capacity of nano-hydroxyapatite particles is related to pH value, temperature, and water environment. For example, low molecular weight organic acids reduced the adsorption capacity of HAP for Cu^{2+}. In addition to the synthetic materials used to synthesize HAP, HAP derived from chicken bone showed considerable Pb^{2+} removal potential (105.26 mg/g, equivalent to a 93.75% removal rate) . The Langmuir adsorption capacity of HAP derived from eggshell (1 g/L) for Pb^{2+} is 500 mg/g (equivalent to 99.78%), the initial adsorbate concentration is 200 mg/L, and the pH value is 3.

The efficiency of hydroxyapatite on multi-metal solutions is also valued. As mentioned above, the novel porous hydroxyapatite nanofibers synthesized in the laboratory have excellent removal efficiency for Pb^{2+}, Cu2, and Cd^{2+}. The research shows that about 89.8% of Pb^{2+} is removed within two hours, which is higher than that of Cd^{2+} and Cu^{2+}. In addition, the existence of other divalent cations, such as Pb^{2+}, Zn^{2+}, and Fe^{2+}, reduces the ability of hydroxyapatite to adsorb Cu^{2+}. The adsorption mechanism is usually divided into two steps: rapid surface complexation accompanied by partial dissolution of hydroxyapatite, and to exchange with calcium ions and then precipitate. Table 1 summarizes the adsorption of hydroxyapatite nanoparticles for heavy metal ions.

Table 1. Adsorption of hydroxyapatite nanoparticles for heavy metal ions

HAP	Ions	Binding mechanism
Synthetic from wet precipitation method	Cd2+	Ion exchange
Synthetic from wet precipitation method	Cu2+	Ion exchange and surface complexation
Synthetic from microwave assisted mesoporous	Pb2+	Physical and chemical mechanism operative; ion exchange binding confirmed by XRD
Mussel shell sourced HAP; synthesis from wet precipitation method	Cd2+	Rapid ion exchange followed by partial dissolution of HAP and precipitation of Cd2+ containing HAP
Egg shell sourced HAP; wet precipitation method	Pb2+	low concentration: dissolution and precipitation high concentration: adsorption and ion exchange
Synthetic from wet precipitation method	Cd2+, Pb2+, Zn2+ and Sr2+	Cd2+, Zn2+, Sr2+: ion exchange and specific cation sorption Pb2+: dissolution and precipitation
Commercial synthetic	Cd2+ (single metal system /in presence of Cd2+, Pb2+ Zn2+, Cu2+)	Partial dissolution of HAP and ion exchange
Synthetic from hydrothermal method	Pb2+, Cu2+, Co2+, Ni2+, Zn2+, Hg2+, Cd2+	Ion exchange and adsorption

3. Conclusions

HAP is considered a promising advanced adsorption material, and its inherent physical and chemical characteristics can effectively remove toxic metal ions from wastewater through ion exchange and dissolution-precipitation mechanisms. The simple conversion of biological waste sources for extracting hydroxyapatite and the easy manufacturing method by wet chemical precipitation ensures that even cheap hydroxyapatite can be used for water remediation. By adopting different manufacturing methods, its structural characteristics have great room for improvement, such as increased porosity, better surface function, and reduced crystallinity. The main focus is to design HAP porous nano-adsorbent with better stability. HAP composed of a single material has high brittleness and poor mechanical properties, and it is difficult to be molded into specific shapes required by materials in biomedical, papermaking, adsorption catalysis, and other fields, which will greatly limit its application scope. The excellent mechanical properties of cellulose and nano-cellulose improve the stability and mechanical properties of HAP NPs to some extent. The synthesis of HAP NPs/ cellulose-based composites has made great progress and has broad research and application prospects in the fields of adsorption, biomedicine, and papermaking. We should also consider the regeneration of the adsorbent. In order to meet the growing demand for HAP and its composites in production and life, the preparation and properties of HAP are studied deeply and perfectly.

References

[1] Mehta, D., Mondal, P., Saharan, V.K., et al. (2018) In-vitro synthesis of marble apatite as a novel adsorbent for removal of fluoride ions from groundwater: An ultrasonic approach. Ultrason Sonochem, 40: 664–674.

[2] Zhai Y. (2010) Preparation and Characterization of Hydroxyapatite/Nano-cellulose Composites. Tianjin University.

[3] Zhai Y. (2010) Preparation and characterization of hydroxyapatite/nano-cellulose composites. Tianjin University.

[4] Guo W., Wang X., Zhang P., et al. (2018) Nano-fibrillated cellulose-hydroxyapatite-based composite foams with excellent fire resistance. Carbohydrate Polymers, 195: 71.

[5] Zhang Y., Zhu Y., Chen F., et al. (2017) Biocompatible, ultralight, strong hydroxyapatite networks based on hydroxyapatite microtubes with excellent permeability and ultralow thermal conductivity. ACS Applied Materials & Interfaces, 9(9): 7918.

[6] Sarkar C., Chowdhuri A.R., Kumar A., et al. (2018) One pot synthesis of carbon dots decorated carboxymethyl cellulose-hydroxyapatite nanocomposite for drug delivery, tissue engineering, and Fe3+ ion sensing. Carbohydrate Polymers, 181: 710.

[7] Mirhosseini M., Biazar E., Saeb K. (2014) Removal of arsenic from drinking water by hydroxyapatite nanoparticles, Curr. World Environ. 9 (2): 331–338.

[8] Mobasherpour I., Salahi E., Pazouki M. (2011) Removal of divalent cadmium cations by means of synthetic nano crystallite hydroxyapatite, DES. 266: 142–148.