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Hydroxyapatite-Based Materials for Heavy Metal Removal in Wastewater Treatment

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Abstract

Nowadays, undisputable environmental pollution requests endeavors to treat wastewater, particularly containing heavy metal, where wastewater treatment technologies are improving hastily. Hydroxyapatite with micro-porous structure and the large surface area turns into an intense research topic as of its high adsorption capacity. Environmentally friendly Hydroxyapatite powder with the large specific surface is a promising cost-effective precipitation method, for the removal of heavy metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) from wastewater. Different studies have revealed the efficient removal of all metals using hydroxyapatite or by modified HA using zeolite or chitosan. The increase of Ca2+ ions content in the treated water suggests an ion exchange mechanism.

Keywords: Hydroxyapatite; Heavy metal removal; Wastewater; Nano hydroxyapatite; Adsorption

Introduction

Different conventional technologies are used for the removal of heavy metal ions from aqueous solution, such as “chemical precipitation”, “electrochemical treatment”, “ion exchange”, “reverse osmosis and electrodialysis” [1-9]. Recently, significant attention has been given to unconventional alternatives, one of the most encouraging approaches is the use of environmental friendly-cheap materials as a prospective sorbent for heavy metals removal from wastewater solutions [10]. The most prevalent materials used as sorbents have been carbons, zeolites, clays, biomass, and polymeric materials [1-9].

However, these reported materials exhibit low adsorption capacities towards heavy metals ions and suffer from separation troublesomeness. Therefore, broad endeavors are as yet required for the improvement of new materials that can be utilized as adsorbents in wastewater treatment applications. Several investigations were conducted in recent years have reported the utilization of mineral materials in the treatment of heavy metals contaminated wastewaters [11,12]. Materials such as zeolite [13,14], clay minerals [4,6,8] and other organo-derived clay materials [have been accounted for being excellent challengers in the treatment of wastewater because of their amazing surface qualities.

Recent studies have reported that phosphate minerals represent promising materials in the treatment of wastewaters for the removal of heavy metals [15-18]. Promising results have been reported on the effectiveness of phosphate minerals for the activity of hydroxyapatite (HAp) with the chemical formula $Ca_{10}(PO_4)_6(OH)_+$ as a remarkable material for removing long-term pollutants from contaminated water. The results showed that hydroxyapatite (HAp) has a high affinity for heavy metals, low water solubility, high stability, and low cost compared to other conventional methods [19,20].

Hydroxyapatite Properties and Characteristics

Hydroxyapatite (HAp) is a naturally occurring and non-toxic inorganic compound with the formula of $Ca_{10}(PO_4)_6(OH)_2$. Hydroxyapatite has a robust hexagonal atomic framework based on two distinct metal-cation sites (Ca(I), Ca(II)), a tetrahedral-phosphate site, and an anion column along four edges of the unit cell. The Ca(II), ion in the HA crystal lattice can be substituted by other metallic cations (e.g., Pb(II), Cd(II), Cu(II), Zn(II), Fe(III), etc.) by an ion exchange reaction [21-24]. The interaction between nano-hydroxyapatite and other conventional materials e.g. zeolite showed higher efficiencies than conventional materials alone. The metal-substituted nano-hydroxyapatite powder can effectively interact with chitosan structures, resulting in the augmentation of properties of the new nano-composites aiming to be applied in various applications [23].

Nevertheless, the most important characteristic of HAp is existing in the form of white powder. Consequently, separating the suspended fine solids from solutions after adsorption of heavy metal ions is challenging [25], therefore, bind HAp with a polymer to resolve this problem. There are quite a lot of polymers available in nature which can be utilized as a binding material for HAP. Hydroxyapatite–chitosan (HAp-C) composite was studied for the removal of heavy metals such as lead, cobalt, and nickel from aqueous solution [25-27]. Chitosan was selected as a binding material for HAP due to its availability in nature and the special characteristics of hydrophilicity, biodegradability, non-toxicity, biocompatibility, adsorption properties, as well as the existence of amino and hydroxyl groups in chitosan can function as the active sites for adsorption [26,27].

HAP has been broadly applied for the removal of various pollutants from aqueous solutions owing to their high sorption capacity, availability, porous nature, low cost, high stability under oxidizing and reducing environments, as well as low water solubility [28]. These properties permit strong interaction between the hydroxyapatite particles and pollutants. Various experimental studies have been reported on the adsorption of heavy metal ions [29], dye molecules [30], antibiotics [31] and others [32] on different Haps.

The adsorption properties of hydroxyapatite depend on their surface functional groups, surface area, and low water solubility [28]. Similarly, the photo-catalytic activities of hydroxyapatite-based nano-ceramics have been reported [33]. Mobasherpour, et al. had synthesized nano-hydroxyapatite to remove Ni_2^+ from Aqueous Solutions. The results showed that the efficiency of Ni_2+ adsorption is shown to be increased with the increase in the adsorbent dosage. Isotherm studies indicate that the Langmuir model is better than Freundlich [28].

Different parameters affect the adsorption capacity of hydroxyapatite; this includes the concentration of HAP ions in aqueous media as it has an impact on the "functional groups" of mHAP. Also the initial pH, the temperature and heavy metal concentration.

Synthesis of Hydroxyapatite Nanoparticles (HAP)

The solution–precipitation method presented by Mobasherpour, et al. [34], using $(NH_4)_2HPO_4$, and $Ca(NO_3)_2.4H_2O$ as starting materials, while ammonia solution as agents for pH adjustment. Another study performed for the adsorption of heavy metal ions on various low-cost minerals modified natural phosphate as mesoporous synthetic apatite as discussed by El Asri, et al [35]. Different synthesis methods using oyster shells, pig bones, and eggshells [35].

Some studies have tried to enhance the properties of hydroxyapatite (mechanical porosity, porosity, specific surface area, etc.) through the addition of gelatin, carboxymethyl cellulose chitosan, and alginate [25-26,36-38].

Heavy Metal Removal

The heavy metals presence in agricultural, industrial, or drinking water is a serious environmental hassle due to many health problems caused by these metal. Environmental policies have led to the establishment of strict standards regarding the emission of heavy metals. However, at trace aspect concentrations, these pollution are nevertheless dangerous, and for its elimination, adsorption is the most common method used [39]. HAp-related materials have been reported for the removal of metal ions from water; nevertheless some effort must be performed in order to allow their utilization at field conditions.

There are several reports about the removal of lead [39-43], copper [40,41], cadmium [41], chromium [41] manganese, and iron [44] and cobalt [45]. The mostly reported is the removal of lead, as some reports focused on the morphology and shape of HAp particlesas well as separtion effeciency.

Milonji´c SK [46] studied the factors affecting the use of hydroxyapatite sorption through sorption reactions. Suzuki Y, et al. [47] as well as [48] Babel S and Kurniawan TA [48] studied the uptake of divalent heavy metals using a fixed bed of hydroxyapatiteIn order to achieve a scalable application, a high sorption capability and a short equilibrium contact time are desirables; in this regard, Ahmed and co-workers reached a high sorption capacity and achieve a complete removal for lead ions at (pH = 5.6) containing 100 ppm lead ions, a sorbent dosage of 0.4 g HAp [49].

The removal efficiency varies according to the pH used (4-7), heavy metal concentration and the initial concentration of the Hap used.

Environmental Impact

Heavy metal water contamination could be adequately diminished and the beneficial outcome is reflected in regular effluents and the ensuing chain of every single living thing. In the other side, apatite is a consumable material with a restricted time uses, until it achieves saturation, as per this is important to treat the residual apatite material.

HAP as best candidates for application in adsorption of pollutants from the environment. Bio-adsorbent was successfully synthesized and studied with different characteristics for the application of the removal of heavy metals from contaminated water. Through continuous research, efforts will help in the production of economic synthesis approaches and can be applied in future research for different applications. In the end, the positive impact of using HAP is improving the quality of life, as well as decreasing the environmental impact.

Conclusion

Our study has evidenced that low crystallinity HAP can be successfully used in heavy metal removal from mine wastewater. For all the 10 metals reported (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), their content was rapidly reduced by contact with hydroxyapatite within and under the permissible limits for wastewater discharge characteristics into the natural environment. The application of hydroxyapatite advances the effective utilization of biocompatible and non-harmful nonmaterial's for ecological remediation.

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