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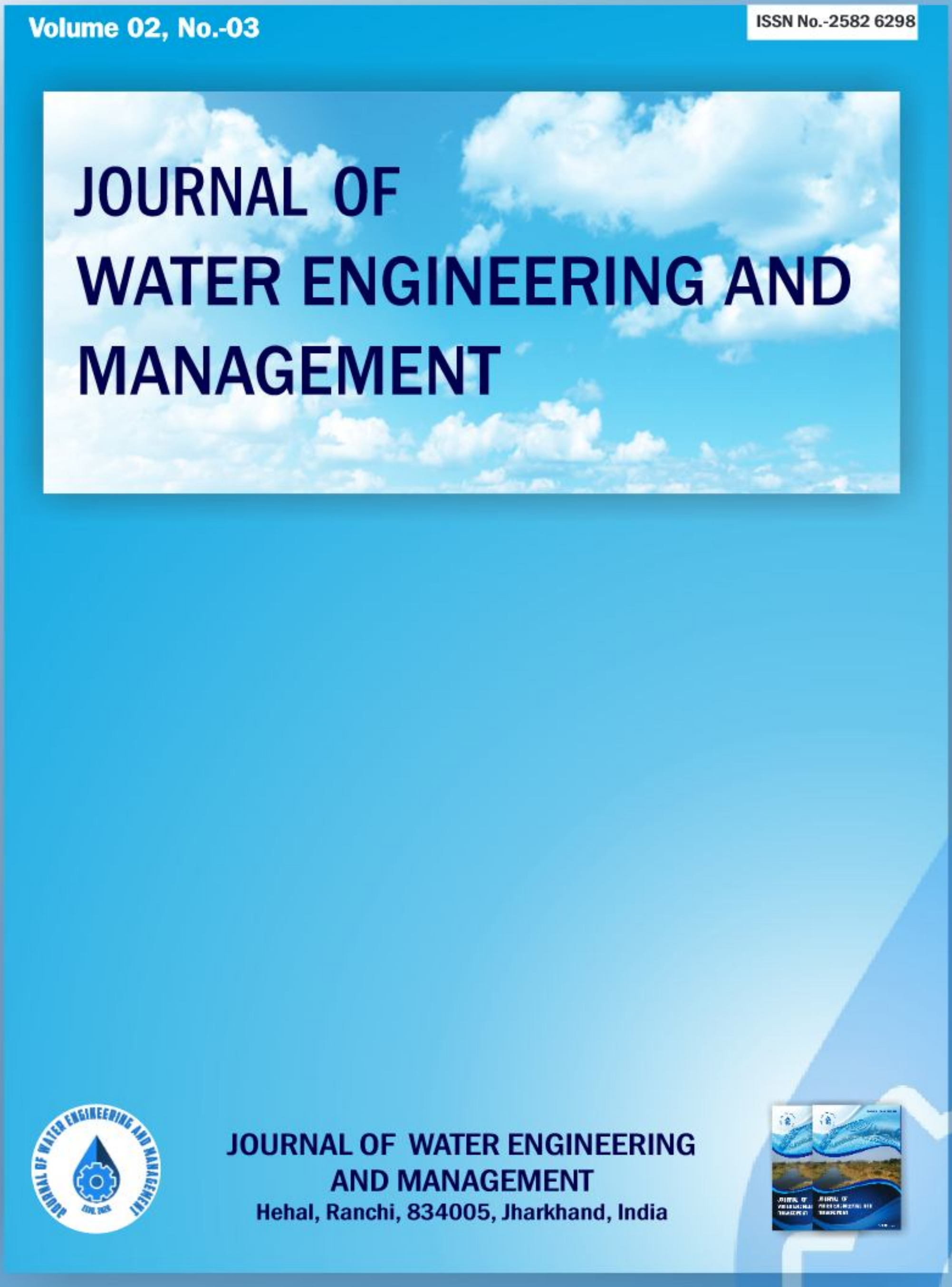

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Research Paper

Nano Hydroxyapatite: A Promising Material for Wastewater Remediation

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ABSTRACT

In recent years, increasing environmental issues, particularly relating to biogenic and chemical pollution of water, have become a significant threat to both human health and the ecosystems. Clean water, which is free from pathogens and toxic chemicals, is vital to human health. The blue planet is encountering remarkable challenges in meeting the ever-increasing demands of clean water. Hence, the removal of these toxic pollutants is necessary and, has attracted considerable efforts particularly via adsorption technology. The aim of this review is to summarize other synthesis methods and recent applications of hydroxyapatite-nanoparticles as adsorbents and catalysts. With the advances in materials science and nanotechnology, new materials have been regularly fabricated for several purposes. Hydroxyapatite is among the most representative ceramic materials and considered promising for long-term containment of toxic pollutants due to its large surface area, high reactivity, catalytic potential and presence of a large number of active sites. Surface properties of synthetic well-crystallized hydroxyapatite were also investigated by many researchers. Normally, two models of adsorption isotherms (Freundlich and Langmuir) are employed to correlate the data in order to understand the adsorption mechanism.The study on hydroxyapatite (HAp) nanopowder made from fish waste (skin, bones, and scales) has brought to its beneficial use as an adsorbent even for lead removal in water. These novel materials promise a feasible advance in the development of new, easy to handle and low-cost water purifying methods. The wastewater parametric conditions and the synthesized hydroxyapatite-based materials covered herein are expected to inspire and stimulate further applications of nanoceramic-based materials in the environmental science.

Keywords: Chemical pollution, Adsorption, Nanotechnology, Hydroxyapatite, Wastewater.

INTRODUCTION

Excessive Pollution due to increased industrial activities affects both flora and fauna which is disturbing ecological balance. Industries that use hazardous chemicals have the potential to pollute water resources through the discharge of the effluent to rivers and other water bodies. Industrial effluents include both organic and inorganic wastes. Heavy metal ions, aromatic compounds,and dyes are often present in the environment due to industrial pollution (Crini, 2005). As a result of the strict environmental regulations, it is required to remove dyes, heavy metals and organic matter from wastewater before being discharged into the water bodies as these are reported as lethal and carcinogenic in nature (Crini, 2006). Water, that contains heavy metals and dye wastes, can cause a serious threat to human beings, animals, and plants. Contaminants are broadly classified as inorganic, organic and biological contaminants. The inorganic contaminants are primarily zinc, cadmium, chromium, cobalt, copper, arsenic, selenium, strontium, fluoride, chloride, nitrate, oxalate etc.Organic contaminants include herbicides, pesticides, and plant and animal tissues, which cause adverse impacts on the environment. Waterborne diseases are caused by living organisms such as bacteria, enzymes, fungi, viruses or their products and are categorized as biological contaminants (Gledhill, 1987). World Health Organisation (WHO) has recommended a permissible limit for all of these contaminants. If the concentration of contaminants exceeds the permissible limit, it causes severe health issues. Zinc beyond permissible concentration limit of (3.0mg/l) stuntsthegrowth in children and leads to poor mental health(Oren and Kaya, 2006; Vatistas and Bartolozzi, 1999; Weng and Huang, 2004). Arsenic is known to be poisonous and the order of toxicity for different arsenic species are arsenite> arsenate >mono-methyl arsenic acid > dimethyl arsenic acid(WHO, 1981; Yamamura and Yamauchi, 1980).Higher concentration of cobalt beyond permissible concentration limit leads to vomiting, nausea, asthma,and carcinoma(John, 1990).It is also held responsible for thyroid, gastrointestinal and liver problems(Smiciklas et al., 2006; Rengaraj and Moon, 2006).Presence of anions such as nitrate, fluoride, phosphate,and oxalate in water leads to ill effects if present in higher concentration. For example, a highconcentration of Nitrate (>50mg/l) and fluoride leads to blue baby disease (methemoglobinemia) in children(Kross et al., 1992).

Removal of toxic materials from wastewater is necessary for health and environmental protection. It is required before discharging wastewater into the river and eventually provides safe drinking water to the people. Reverse osmosis, ultrafiltration, centrifugation, coagulation, screening, gravity separation, precipitation,and adsorption are some of the commonly used methods for removal of toxic materials. However,adsorption process is the most suitable method because of its high efficiency and economic consideration (Zare et al., 2015).The order of cost-effectiveness of different methods is as adsorption > evaporation > ion exchange > electro dialysis > micro- and ultra-filtration > reverse osmosis > precipitation > distillation > oxidation > solvent extraction (Masel, 1996; Condon, 2006).Design, operationandscale-up, high capacity, insensitivity to toxic substances, ease of regeneration, and low cost are the factors which make adsorption a preferred choice over other methods. It does not use toxic solvents and minimizes degradation(Gupta et al., 2011; Dargaville et al., 1996).Adsorbent has a high affinity towards the metal ions making the quality of the effluent generated better than the rest of the processes. The affinity towards metal ions may be due to the electrostatic forces of the solute to the adsorbent surface, van der Waals attraction or chemisorptions. It also has an advantage of reversibility, when the adsorptive bed gets exhausted with metal ions, it can be regenerated. This process is most preferred as it requires low maintenance cost, has high metal removal efficiency, easy to operate and uses solid adsorbent which resists degradation(Hua et al., 2012; Soto et al., 2011).The main selection parameters of adsorbents are the high adsorption capacity, fast kinetics, and low cost. The various adsorbents such as activated alumina, activated carbon, calcite, rare earth oxides, etc., are used for the removal of metal ions and other pollutants from wastewater streams.Adsorption encounters equilibrium when the concentration of contaminants present in water equals to that of adsorbed on the adsorbent. The relationship, thus derived, is known as adsorption isotherm and is helpful in estimatingdifferent parameters. Various models such as Langmuir, Freundlich, Halsey, Henderson, Smith, Elovich liquid film diffusion, Intraparticle diffusion, and Lagergren are used for explaining the results of adsorption studies. These models are similar in principle but differ in their approaches(Lewinsky, 2007).

Advancements in nanoscience and engineering have created more opportunities to develop cost-effective and environmentally friendly water treatment technology. The higher capacity of nanoparticles due to the larger specific surface area makes them one of the best adsorbents for the effective removal of heavy metals from wastewater. They also exhibit various advantages such as fast kinetics, and preferable sorption toward heavy metals in effluent streams(Gangadhar et al., 2012).In the present times, efforts are being made for synthesis of nanosized adsorbents and their utilization in water treatment. Hydroxyapatite is among the most representative ceramic materials and considered promising for holding toxic pollutants for a longer duration, due to its eco-friendly nature, good dispersibility, outstanding stability, and abundant modifiable surface functional groups (Meski et al., 2010).Photocatalysis is a phenomenon in which the rate of photo-reaction increases in the presence of a catalyst. It is broadly categorized as (a) catalyzed photolysis and (b) photo-generated catalysis. Hydroxyapatiteshow signs ofphoto-generated catalysis due to photo-induced electronic excitation. As a member of apatite mineral family, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) is an ideal material for discarding radioactive contaminants having long life because of its elevated sorption capacity for heavy metals, low water solubility, availability, low cost, and high stability under oxidizing and reducing conditions (Narwadeand Khairnar, 2017).Hydroxyapatite nanoparticles flash the properties such as large surface area, high reactivity and catalytic potential, the presence of a large number of active sites (Landi et al., 2000).Importance, role,and suitability of hydroxyapatite nanoparticles for removing inorganic, organic and biological contaminants have been discussed in the present paper.

SYNTHESIS AND CHARACTERISATION OF HYDROXYAPATITE NANOPARTICLES

The principal step towards employment of hydroxyapatite (HAP) nanoparticles in wastewater treatment is its synthesis and characterization. Hydroxyapatite (HAP) can be synthesized using various methods which are categorized into solid state and wet chemical methods (Table 1). These methods have been modified to develop controlled morphology. All these methods can synthesize different morphologies of HAP depending upon the reaction parameters. Solid State methods involve the addition of powdered calcium and phosphate precursor in the Ca:P ratio of 1.67. Aqueous solutions of calcium (calcium chloride, calcium oxide, etc.) and phosphate (orthophosphate, phosphorous pentoxide, etc.) precursors are added together while maintaining Ca:P ratio of 1.67 for the synthesis of HAP in wet state methods. These methods are most popular for the synthesis of controlled morphologies of HAP at relatively low temperature. Different methods for synthesis of hydroxyapatite nanoparticles are presented in Table 1.Different bio-waste materials are also used as a precursorto produce HAP (Fig. 1).

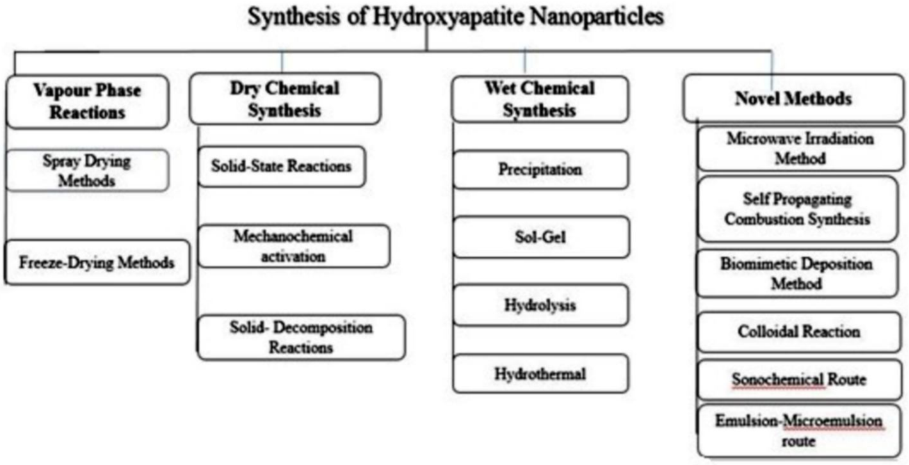

Fig. 1. Different synthesis routes of hydroxyapatite nanoparticles

Many researchers have prepared HAP by using raw eggshells as a calcium source (Rivera et al., 1999; Gargely et al., 2010; Ramli et al., 2011; Saeed et al., 2011; Lee and Oh, 2013). Several studies have been carried out by utilizing fish scales as a starting material (Venkatesan et al., 2015; Mondal et al., 2010).The potential of rice bran can also be used as a phosphate source during the preparation of hydroxyapatite (Puajindanetr, 1992).The conversion of bovine bones and corals into hydroxyapatite was discussed by several researchers (Nissan et al., 2004).The produce is subjected to various characterization tools such as X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Transmission electron microscope, Energy dispersive analysis of X-ray, Dynamic light scattering and zeta potential, Photoluminescence spectroscopy and Electron Spin Resonance to probe the particle size, morphology, and functionality of the prepared compound.

Table 1. Methods for synthesis of hydroxyapatite nanoparticles

Solid state	Solid State Reaction
	Mechano Chemical
Wet state	Chemical Precipitation
	Homogeneous Precipitation
	Emulsion
	Hydrothermal
	Sol-Gel

REMOVAL OF INORGANIC POLLUTANTS

Arsenic

Arsenic compounds are commonly found in natural water resources. It may occur naturally in water or might be the result of anthropogenic activities. Arsenic contamination in groundwater has become a serious problem affecting 150 million people in about 70 countries, particularly Bangladesh, Vietnam, China, Mexico, Chile and West Bengal in India(Brammer and Ravenscroft, 2009). Commonly occurring chemical forms of arsenic include arsenite, arsenate, monomethyl arsenic acid, dimethyl arsenic acid etc. WHO has recommended a permissible limit of 10 µ /ml of arsenic concentration in drinking water. Arsenic is considered to be carcinogenic in nature and can cause disturbances in RNA and DNA synthesis(Eblin et al., 2006).Increase in birth of unhealthy infants, underweight infants and high infant mortality rate duetoarsenic contamination has been reported in different places (Penrose, 2009).

Hydroxyapatite nanoparticle is described as a potential adsorbent for arsenate removal from water. The adsorption capacity was reported as 526mg/g andthe adsorption data fitted well to the Freundlich isotherm. The removal efficiency of 88% was achieved with a dose of 0.2g/l of hydroxyapatite nanoparticles (Mirhosseini et al., 2014).The increase in pH improved the adsorption capacity of HAP nanoparticle in acidic medium. At the early stages, an increased elimination rate of arsenate was observed probably due to the presence of more number of actives sites on the surface of hydroxyapatite. The proposed mechanisms for arsenate immobilization were the dissolution of hydroxyapatite nanoparticles and precipitation of hydroxyl pyromorphite. Sorption of arsenate on copper doped hydroxyapatite in groundwater was analyzed. Improved uptake by the factor of 1.6-1.9 was observed with respect to undoped HAP. The rate of sorption was found to be increasing with the increased level of copper doping and pH of the aqueous solution upto 8.0. The obtained sorption data was in agreement with linear sorption equation. The maximum removal efficiency was obtained at42%(Liu et al., 2010).The considerable arsenate removal could be achieved within the pH range of 6.0-9.0 with a calcium concentration range of 0-2.5mM. The increased sorption was attributed to the increase in surface area due to copper doping of hydroxyapatite. The dissolution of hydroxyapatite proved to be therestraining agent for arsenate removal. Sorption of arsenate was reported on cellulose – carbonated hydroxyapatite prepared (CCHA) within 60 minutes (Islam et al., 2011).The maximum adsorption was found to be as 12.72mg/g. The adsorption data followed the Langmuir isotherm with endothermic nature and was supported by pseudo-first order kinetics. The suitable pH for maximum removal was 4-8. The maximum removal efficiency was reported as 71 % at a pH value of 8.0.The author claimed the ion-exchange and adsorption process as removal mechanisms. Nature of sorption was discovered by determining the thermodynamic parameters (standard free energy, standard enthalpy, and standard entropy). The effects of pH, contact time, temperature, initial arsenate concentration and anions on arsenate removal were also investigated. Reduced removal of arsenate at higher pH can be explained by the estimated value of the point of zero charges for the synthesized composite, which was found to be 8. The presence of the sulfate and nitrate ions was trivial butthe phosphate and silicate ions restrained the arsenate removal.Adsorption of arsenate was studiedon cow bones derived hydroxyapatite (Czerniczyniec et al., 2007). The Plackett- Burman design test was conducted to evaluate the effects of various parameters such as pH, salinity, calcination temperature and alkalinity on the removal efficiency of the synthesized biogenic hydroxyapatite. The key factors influencing the restraint of arsenate were salinity, hardness, and pH. Maximumdeletion of impurities was achieved by high salinity, hardness, and low pH. An effective and enhanced elimination of arsenic from geothermal hot water was further reported (Nakahira et al., 2006). During the experiment, three different sources of hydroxyapatite were used namely pure hydroxyapatite, bovine bone, and silicon doped hydroxyapatite. The retention of arsenic in pure hydroxyapatite and bovine bone were reported to be3.6 ppm and 12.1 ppm, respectively when kept for 1 hour under hydrothermal conditions. While containment was found to be 38.2 ppm in modified HAP for the same duration and experimental conditions. Defect formation at phosphate sites in apatite structure during modification could be one of the prime reason for higher uptake of arsenic in silicon modified HAP.While, the defects in the apatite structure might be the reason behind the considerable retention of arsenic in bovine bone. The possible mechanism for arsenic retention is the replacement of phosphate ion by dihydrogen arsenate or hydrogen arsenate ion in the apatite structure.

Copper

Poorly crystalline and well-dispersed hydroxyapatite (HAP) nanoparticles were structured and used as novel adsorbents for the removal of Cu(II) from aqueous solution (Yang et al., 2016). Various factors affecting the adsorption such as adsorbent crystallinity, pH, adsorbent dosage, contact time, temperature, competing cations, and the presence of Humic acid were investigated. Results showed that the HAP calcined at lower temperature was poorly crystalline and had better adsorption capacity for Cu(II) than those calcined at a higher temperature.

The Cu(II) removal was increased with increase in pH, adsorbent dosage, temperature, and the presence of Humic acid, but decreased as the existence of competing for divalent cations. Kinetic studies showed that the pseudo-second-order kinetic model better described the adsorption process. Equilibrium data were best described by Langmuir model, and the estimated maximum adsorption capacity of poorly crystalline HAP was 41.80 mg/g at 313 K, displaying higher affinity towards Cu(II) removal than many previously reported adsorbents. The adsorption of Cu(II) by poorly crystalline HAP was reflected as spontaneous, endothermic, and entropy-increasing in nature. Humic acid (HA) was drenched over powdered activated carbon to catalyze its Cu(II) adsorption capability. The optimum pH value for Cu(II) removal was 6. The maximum adsorption capacity of HA- soaked activated carbon was 5.98 mg/g, which is five times the capacity of virgin activated carbon. Brisk adsorption processes were accompanied by changes in pH. Langmuir isotherm well demonstrated the equilibrium experimental data than by the Freundlich isotherm.

Synthesis of nano-hydroxyapatite (nHAP) composites with chitosan (nHAPCs) & chitin (nHAPC) and their role in copper (II) elimination from aqueous solution is discussed. The adsorption was carried in batch mode and several experimental parameters were studied like contact time, temperature, solution pH and interfering metal ions. The parameters optimized for maximum sorption capacity hada contact time of 30 minutes and solution pH was kept at 6.0. The maximum sorption capacity was obtained at4.7, 5.4 and 6.2 mg/g for nHAP, nHAPC,andnHAPCs, respectively. The adsorption data were in agreement with Freundlich isotherm. Ion exchange and adsorption were proposed as the removal mechanism by composites. The presence of a relatively greater number of amino groups was found to be responsible for its higher sorption capacity as compared to other prepared composites (Gandhi et al., 2011).Bone ash derived hydroxyapatite was recommended as the potential adsorbent for copper ion removal from wastewater(Lari et al., 2011). The removal efficiency of 88% was achieved at a pH value of 7.5. The maximum adsorption capacity was 1.631mmol/g. The adsorption data followed well to Freundlich isotherm with pseudo-second-order kinetics. The process was of endothermic nature as reflected in the estimation of thermodynamic parameters. Copper removal onto synthetic hydroxyapatite was studied.Batch mode technique was used to carry out the experiments. Depending upon the initial concentration of the metal solution, the removal efficiency of prepared sample varied between 97.3 - 98.6% whereas the sorption capacity was found to be in the range of 0.016-0.764mmol/g. Langmuir isotherm model was well correlated with the adsorption data. Surface complexation followed by ion exchange or dissolution of HAP and precipitation of heavy metal in some forms of hydroxyapatite were the proposed pathways for copper removal (Corami et al., 2008).

Cobalt

Cobalt radionuclide is one of the prime contaminants generated during operation of pressurized heavy water. The cobalt adsorption on hydroxyapatite (HAP) nanoceramic was studied. A modified wet chemical precipitation method was used for HAP synthesis. The HAPnano-material was characterized by XRD, FTIR, TG/DTA, AFM, SEM, and EDAX. Experiments were performed in batches to observe the effect of cobalt adsorption on HAP matrix. The adsorption of cobalt on HAP is examined at room temperature. According to isotherm and kinetic studies the most appropriate alternatives to illustrate the nature of adsorptionareFreundlich isotherm and pseudo-second-order kinetic model. The radiotracer technique was used to analyse the sorption of cobalt on prepared Hydroxyapatite via precipitation technique (Gogoi et al., 2012).The liquid nuclear waste containing sodium as a major fraction and 60Co as a radiotracer was used to investigate the cobalt removal. The adsorption data were in agreement withFreundlich model with pseudo-second-order kinetics. The mechanism for cobalt removal was attributed to chemisorption that took place on a heterogeneous surface. The higher removal efficiency of more than 97% was reported within first 30-40 minutes. The potential of hydroxyapatite in cobalt removal from aqueous solution has been studied.The synthesized adsorbent has lower crystallinity and a specific surface area of $67m^2/g$. The adsorption dataaligned with both the Langmuir and Dubinin–Kaganer–Radushkevich (DKR) isotherms with pseudo-second-order kinetics. Ion-exchange and surface complexation were the proposed mechanism for cobalt removal. The estimated adsorption capacity from the Langmuir equation was reported to be 20.92mg/g. Along with other experimental parameters, the presence of ethylenediaminetetraacetic acid (EDTA) on cobalt removal was also investigated. The results revealed a decrease in percent removal of cobalt with an increase in EDTA concentration. It was observed that the composition and pH of the leaching solution played a significant role in the desorption of adsorbed cobalt from hydroxyapatite. Studyof the cobalt removal from aqueous solution by synthesized hydroxyapatite was done. Aqueous precipitation technique was utilized for synthesis while experiments were conducted in batch mode. Among other experimental parameters, the effect of the presence of fulvic acid on cobalt removal was also observed. This was taken up because humic materials are well-known metal retaining agents due to their high reactive nature and excellent binding capability towards metal ions. Transition point was achieved at pH value of 7 for cobalt elimination in presence of fulvic acid. At lower pH value (<7), an increased sorption of cobalt onto HAP was observed whereas at the higher value it diminished. The sorption isotherm well followed the Langmuir model with pseudo-second-order kinetics. The estimation of thermodynamics parameters reflected endothermic nature of the sorption process. The sorption of cobalt was highly pH dependent and found to be increasing with an increase in pH up to pH 9 and afterward, no significant changes were observed(Huang et al., 2012).

Zeolites based hydroxyapatite composite was produced for adsorption of cobalt from aqueous solution. Increased removal efficiency was observed in the case of synthesized composite (65%) as compared to hydroxyapatite (58%) and zeolite (47%) individually [57].The study of several parameters affecting the cobalt removal was also carried out which involves initial cobalt concentration, the effect of pH, contact time and adsorbent dose. The optimized condition for achieving maximum removal efficiency included the adsorbent dose (2mg/l), pH 6.0, contact time of 20 minutes and temperature as 30ºC. The sorption kinetics was well explained by pseudo-second-order. The adsorption data were in agreement with both Langmuir and Freundlich isotherms. The discussion of the cobalt removal from aqueous solution by simulated body fluid (SBF) assisted synthesized hydroxyapatite. The prepared product hadrod-like morphology and specific surface area of $167m^2/g$. The maximum adsorption capacity was reported as 0.645mmol/g. The estimated thermodynamics parameters reflected endothermic nature of the sorption process. Furthermore, a positive value of the change in entropy indicated towards the possible structural changes that might take place between adsorbate and adsorbent during the process. Ion exchange and surface complexation were the main mechanisms behind cobalt removal (Ma et al., 2010).

Cadmium

The adsorption of cadmium ion on hydroxyapatite in single and multi-metal aqueous solution was demonstrated. An improved uptake was observed in the single metal system and adsorption capacity varied from 0.058-1.681 mmol/g of hydroxyapatite. The adsorption followed well the Langmuir isotherm. Surface complexation and ion exchange were proposed as a removal mechanism. The decreased removal capacity in multi-metal system varied between 63%-83% due to competition among interfering ions (Corami et al., 2008). A rapid elimination of cadmium ion was reported in the range of 0.01-0.005 molar ratios (Lusvardi et al., 2002).Sorption phenomenon was the prime cause of metal ion removal. The magnetic separation technology for cadmium ion adsorption was reported. Magnetic hydroxyapatite nanoparticle (MNHAP) with high specific surface area 142.5m^2/g was used as a potential adsorbent for removal of cadmium. The maximum adsorption capacity was found to be 1.964mmol/g. The data fitted well to the Langmuir model with pseudo-second-orderkinetics (Feng et al., 2010). The removal of cadmium cation was discussed using nanocrystallite hydroxyapatite. The maximum adsorption capacity was reported as 142.857 mg/g. The adsorption data fitted well to the Langmuir model as compared to Freundlich and D-K-R models. The chemical adsorption and surface complexation of cadmium ions on the available P-OH sites were the prominent cause behind this removal. The increased adsorption capacity with increasing temperature pointed towards the endothermic nature of the process (Mobasherpour et al., 2011). The hydroxyapatite nanorods (nHAP) and nano-hydroxyapatite chitosan composites (nHAPCs) were utilized for divalent cadmium ion removal from wastewater. The experiment was carried out in batch mode and several parameters affecting adsorption such as initial cadmium ion concentration, pH, contact time and sorbent dose were discussed. The maximum adsorption capacity was reported as 243.90mg/g for nHAP. The pseudo-second-order kinetics supported the adsorption data. The results showed that the optimized dosage of 100 ppm initial cadmium concentration in 200 ml, pH of 5.6 along with sorbent dosage of 0.4 g could remove upto 92% cadmium ions. The possibility of regeneration of used adsorbent has also been practiced(Salah et al., 2014).

Chromium

Chromium removal from water using hydroxyapatite derived from fish bone was studied. The fishbone, subjected to heating at 600ºC, showed maximum removal efficiency of 26% over duration of 2 h(Ozawa et al., 2003).The adsorption study of chromium (VI) over hydroxyapatite micro-fibrillated cellulose composite (CHA/MFC) was described.The removal efficiency of 94% was reported within 5 minutes. The maximum adsorption capacity of the synthesized composite was found to be2.208mmol/g. The adsorption data followed well to Langmuir adsorption isotherm with pseudo-second-order kinetics. The suitable pH for maximum removal ranges from 5-7. The effect of pH, temperature, contact time and initial chromium concentration on adsorption mechanism was also analyzed. A precise calculation of thermodynamic parameters indicated the endothermic nature of the adsorption process (Hokkanen et al., 2016).The potential of modified nanohydroxyapatite with chitin and chitosan towards chromium ion removal was investigated. The adsorption data was found to be in agreement with Freundlich isotherm with pseudo-second-order kinetics. The sorption capacity of synthesized composites n-HAPCs and n-HAPC were 3450mg/kg and 2845mg/kg, respectively whereas it was limited to 2720mg/Kg for nano-hydroxyapatite. The maximum containment of chromium ion was achieved after 10 min of contact time. A number of steps have been proposed during elimination of chromium by n-HAPCs and n-HAPC which includes ion exchange, electrostatic attraction, complexation,and reduction. According to the study, the presence of a large number of amino groups in chitosan might be responsible for higher sorption capacity in comparison to other synthesized composites. The estimation of thermodynamic parameters revealed the endothermic nature of the adsorption process. The intraparticle diffusion model supported the adsorption results(Natarajan et al., 2010). The adsorption of chromium ion on syntheticn-HAP at neutral pH was studied. The removal efficiency of 98% was reported at pH 7.Theoptimized dose of n-HAP was 0.1g/l with an adsorption capacity of 2.18mg/g. The point of zero chargeof n-HAP powders was found to be at 7.8. The adsorption data fitted well to the Langmuir model with pseudo-second-order kinetics. Dubin in- Radushkuvich isotherm model revealed the chemisorption nature of the adsorption process occurring on to n-HAP (Asgari et al., 2012).

Uranium

The sorption of Uranium (VI) onto hydroxyapatite was demonstrated. The removal efficiency of more than 99.5% was reported. The equilibrium time for the sorption process was less than 1 h. The proposed mechanism was the formation of surface complexes(Fuller et al., 2002). Hydroxyapatite was utilized as a reactive material for the elimination of uranium in permeable reactive barriers. The uranium sorption was conducted in long-term column experiment as well as in radiotracer column mode. The columns, used in radiotracer experiment, had a length of 165 mm and the inner diameter of 22mm whereas; these figures were 500mm and 59mm in case of a long-term experiment. The maximum adsorption capacity of 51.3 mg/g was reported in long-term column experiment. The precipitation of uranium as uranyl phosphate was observed by the author in the reactive material (Simon et al., 2003).A magnetic composite consisting of calcium aluminum layered double hydroxides and hydroxyapatite as a potential adsorbent for uranium removal from aqueous solution was proposed. In this study, eggshells were used as a calcium source. The amount of uranium retention was found to be increasing with an increase in pH range from 2 to6. At solution pH 6.0, 98.5 % adsorption of the contaminant was claimed by the author. The optimal parameters for the conducted experiments were adsorbent dose, equilibrium time, and solution pH of 0.05g, 1h and 6.0 respectively. The adsorption data fitted well with Langmuir isotherm with pseudo-second-order kinetics. The author reported sodium bicarbonate as promising eluant for considerable regeneration of synthesized composite (Li et al., 2012).

Mercury

Adsorption technology was used along with magnetic separation technique for successful removal of toxic mercury (II) ions from aqueous solution. They prepared a nano-adsorbent consisting of magnetic Iron oxide (Fe_3O_4) modified hydroxyapatite. The maximum adsorption capacity of the synthesized adsorbent was found to be 492.2 mg/g.The removal efficiency of 98% was achieved within the first 10 min. The adsorption data fitted well with the Langmuir isotherm with pseudo-second-order kinetics. Investigation of the mercury elimination was conducted in batch mode and optimized experimental conditions had pH 7.0, temperature 25ºC, adsorbent dose 50mg and initial mercury concentration of 1mg/ml. Adsorption capacity increased with increasing temperature which indicated towards endothermic nature of the sorption process and this was found to be in agreement with the estimation of thermodynamic parameters. The higher removal efficiency was due to the higher surface area of prepared adsorbent as well as electrostatic attraction between active sites present on the surface of Fe_3O_4-Hydroxyapatite and mercury ions (Hardani et al., 2015). The role of Carboxymethyl Cellulose (CMC) based nanohydroxyapatite composite for mercury removal from aqueous solution was investigated. The maximum removal was obtained within the pH range of 5-6. Furthermore, a higher initial concentration of mercury ions resulted in an increased adsorption capacity of the synthesized composite. The adsorption data fitted well with the Langmuir isotherm with pseudo-second-order kinetics. Estimation of thermodynamic parameters revealed the endothermic nature of the adsorption process (Roushani et al., 2015).

Zinc

Magnetic $CoFe_2O_4$–hydroxyapatite coreshell nanoparticles were synthesized by reverse microemulsion method and used it as an adsorbenttoremoveZn(II) from aqueous solution. The synthesized products were studied by X-ray diffraction, Brunauer–Emmett–Teller surface area analysis, vibrating sample magnetometer and transmission electron microscopy. The effect of parameters, including adsorbent dosage, contact time, and zinc concentration on the adsorption properties was investigated. The results revealed that hydroxyapatite was coated on the CoFe2O4 surface formediocre–shell structure. The adsorption of Zn (II) on to the nanoparticles increased sharply within 60min and equilibrium conditionwere obtainedgradually. Adsorption data were well described by the Freundlich model (Foroughi et al., 2015).The kinetic study illustrated that the adsorption of Zn (II) on to the nanoparticles surface fits the pseudo-first-order model. Hydroxyapatite–chitosan composite for sorption of zinc (II) ions were prepared from wastewater. The maximum sorption capacity was 1.692mmol/g at a solution pH of 7.5. The adsorption data fitted well to Freundlich isotherm with pseudo-second-order kinetics. The estimation of thermodynamic parameters reflected the endothermic nature of the sorption process. The removal efficiency of 99% was achieved under optimized conditions. The estimated particle size of the prepared sorbent was 47.6 nm(Lari et al., 2011). The use of magnetic hydroxyapatite nanoparticle was demonstrated for zinc cation removal from aqueous solution. The studied experimental parameters affecting sorption process were solution pH, contact time, initial metal ion concentration, adsorbent dosage and presence of interfering ions. The prepared adsorbent had a maximum adsorption capacity of 2.151mmol/g with an initial dose of 0.1g/l. The adsorption data fitted well to Langmuir isotherm with pseudo-second-order kinetics. The sorption process was pH dependent. The author claimed the enhancement in the uptake of the metal ion with an increase in pH range of 4-8. The pH value of 8.0was an inflection point when a sudden increase in adsorption amount was recorded. Cation–exchange mechanism was proposed behind the zinc removal(Fenf et al., 2010).Calcium hydroxyapatite (CaHAP) and barium doped hydroxyapatite (BaHAP) were proposed as potential sorbents for zinc ion removal from aqueous solution. Batch mode technique was utilized to carry out the process. The adsorbed amount showed increment with an increase in pH range 2-8. The adsorption capacity of 36.62mg/g and 102.04mg/g was reported for BaHAP and CaHAP, respectively. A higher removal efficiency of 98% was achieved. The adsorption data fitted well to Langmuir isotherm with pseudo-second-order kinetics. Several mechanisms were involved in zinc removal namely, the formation of surface complexes, ion exchange and precipitation of metal ions as phosphate salt. In the desorption study, the use of cupric chloride as an eluant showed remarkable advantage as compared to other eluants(Sheha, 2007). A comparative analysis of zinc sorption on cheap and naturally available apatite resources with that of synthetic hydroxyapatite was carried out . Bovine and billy goat bones were used as natural adsorbents. The removal efficiency was higher for synthetic hydroxyapatite (93%) followed by billy goat bone (90%) and bovine bone (82%). The adsorption data for natural apatites fitted well with Langmuir isotherm while for synthetic HAP Dubinin-Radushkevich isotherm model holds good. The sorption kinetics were explained by pseudo-second-order. Furthermore the intraparticle mass transfer model supported this sorption study (Meski et al., 2010). The retention of zinc ion from groundwater onto hydroxyapatite nanoparticles was discussed. The utilized material had total pores volume of $0.25 cm^3/g$ and specific surface of $82.7 m^2/g$. The maximum adsorption capacity was reported to be as 94mg/g. The adsorption data fitted well to the Langmuir isotherm (Ignat et al., 2011).

Lead

Hydroxyapatite (HAP) $Ca_{10}(PO_4)^6(OH)^2$ has been shown to play a crucial role in the immobilization of heavy metals as well as for the remediation of groundwater pollution in contaminated soil. HAP has the advantages of biocompatibility, non-toxicity, and chemical inertness as well as a high ion exchange capacity leading to a variety of potential applications in bio-ceramics, protein purification, catalyst, and methane oxidation. The hydroxyapatite nanorods (nHAP) and hydroxyapatite/chitosan nanocomposite (nHAPCs) were explored as potential sorbents for the removal of lead ions from aqueous lead-containing solutions in a batch adsorption experiment. The high-resolution transmission electron microscopy, energy dispersive X-ray analysis, X-ray diffraction, Fourier transform infrared spectrophotometry and Zeta potential measurements were all combined to reveal the morphology, composition, crystal structure, functionality,and stability of the prepared sorbents. The equilibrium concentration of Pb^{+2} ions was identified by the atomic absorption spectrophotometry. The sorption process followed pseudo-second-order kinetics, where 20 min was quite enough to attain equilibrium. Two models of adsorption isotherms (Freundlich and Langmuir) were employed to correlate the data in order to understand the adsorption mechanism. Interestingly, in one of the experiments, for a 200 ml solution (pH = 5.6) containing 100 ppm lead ions, a sorbent dosage of 0.4 g nHAP achieved a complete removal of lead ions. However, typically, the sorption capacities of nHAP and nHAPCs to lead ions were 180 and 190 mg/g respectively, which appear excellent for lead removal (Mohammad et al., 2017). Granular HAPB composite adsorbents, with dimensions of 4 mm × 4 mm were prepared for the removal of lead from an aqueous solution. The effectiveness of the composites for Pb^{+2} removals from an aqueous solution with different initial concentrations, adsorbent doses and reaction times were examined. The Langmuir isotherms, Freundlich isotherm models,andpseudo-second-order kinetic model were used in this analysis. It was found that the Langmuir model fitted the experimental data better than the Freundlich model, with a maximum adsorption capacity of 93.37 mg/g. The pseudo-second-order kinetic model also fitted the experimental data well with an adsorption capacity of 70.73 mg/g after being reused for 3 times (Do et al., 2016).

The lead removal from water by using nano-hydroxyapatite and alginate biocomposites and derived the hydroxyapatitefrom bovine bone. The adsorbents were in two shapes bead and film form and include two different content of hydroxyapatite e.g. 20 and 50 wt. %.The cluster formation of nano HAP on the bead surface decreased the adsorption capacity of bead-shaped adsorbent. However among synthesized composites 50 wt.%

film type adsorbent showed better removal efficiency over a duration of 6 h and pH value of 5. The maximum adsorption capacity was found to be 270.3 mg/g. The data followed the Langmuir isotherm with pseudo-second-order kinetics (Googerdchian et al., 2012). The lead removal capability of synthesized hydroxyapatite polyurethane composite foams from aqueous solution over a wide range of pH ranging from 2 to 6 and various initial lead concentrations was studied. The HAP contents maintained in the composite were identical as reported by Fahimeh Googerdchian. The adsorption capacity was found to be increasing with increased HAP content along with the reduced rate of removal due to agglomeration of HAP particles in the prepared foams. The solution pH played a major role in the determination of the removal mechanism. Dissolution of HAPand precipitate formation of hydroxypyromorphite prevailed at lower pH value of 2-3 while adsorption of lead ions on the adsorbent surface followed by ion exchange between the calcium ions of hydroxyapatite and lead ions from the solution took place at higher pH of 5-6. The synthesized composite with 50 wt. % HAP content showed higher removal efficiency with maximum adsorption capacity of 150mg/g. The adsorption data fitted well to the Langmuir isotherm model with pseudo-second-order kinetics(Jang et al., 2008).Divalent lead was removed by using hydroxyapatite magnetite composite having a specific surface area of 109m^2/g. The maximum adsorption capacity was 598.8mg/g at an optimized dose of 0.5g/l. It proved to be a better adsorbent due to higher removal efficiency at neutral pH. The data fitted well to both Langmuir and Freundlich isotherm with pseudo-second-order kinetics. The effect of the presence of humic acid along with competitive ions was also investigated during the experiment. The two pathways responsible for lead adsorption on composite were dissolution-precipitation and surface complexation (Liao et al., 2017). The waste eggshells were utilized for the synthesis of carbonate Hydroxyapatite estimated the lead removal capability of prepared adsorbent. Batch mode technique was employed for the adsorption studies and its dependence on various parameters such as pH, initial lead concentration, contact time etc. was investigated. The adsorption data were supported by Langmuir isotherm with pseudo-second-order kinetics. The maximum adsorption capacity reported was 101mg/g with a contact time of 1 h (Kongsri et al., 2013). Carbonate hydroxyapatite (CHAP) was synthesized from domestic hen egg shells and characterized by X-ray diffraction and Fourier transform infrared spectroscopy and investigated as metal adsorption for Pb^{+2} from aqueous solutions. The results showed that the removal efficiency of Pb^{+2} by carbonate hydroxyapatite calcined at 600 °C reached 99.78%, with an initial Pb^{+2} concentration of 200 mg/l, pH of 3.0, and a solid/liquid ratio of 1g/l. The equilibrium removal process of lead ions was well described by the Langmuir isotherm model, with a maximum adsorption capacity of 500 mg/g at 25 and 35°C. The thermodynamics of the immobilization process indicates an exothermic sorption process of Pb^{+2} (Meski et al., 2010).

Selenium

Selenite removal was discussed by using nanocrystalline Hydroxyapatite derived from fishbone (FHAP) via alkaline heat treatment method. They also compared other available adsorbents such as commercial hydroxyapatite (CHAP), chitosan (CS) and fish scale (FS) with the prepared Selenite adsorption. The adsorption experiments were conducted in batch mode and the effects of various parameters involving solution pH, contact time, adsorbent dosage and initial selenium concentration were investigated. An increased adsorption of selenite was observed within the pH range of 3 to 6 which was largely attributed to the electrostatic attraction between positively charged FHAP Nanopowder and negatively charged selenite ions. The maximum adsorption capacity reported was 1.58

mg/g at an initial selenium concentration of 0.02mg/l. Furthermore, an adsorbent dose of 0.1 g exhibited different adsorption percentages in the case of other used adsorbents. Adsorption percentages were recorded at100, 72.4, 55.5 and 44% for FHAP, CS, FS,and CHAP, respectively. The contact time of 90 min was provided during the experiment. The author opined that high porosity along with high specific surface area (110.56m^2/g) was responsible for enhanced adsorption capacity as compared to other sorbents. The adsorption fitted well to Freundlich isotherm with pseudo-second-order kinetics (Kongsri et al., 2013). Selenite removal on hydroxyapatite was also reported. The prepared adsorbent has a specific surface area of 77m^2/g and 70m^2/g, respectively (Rivera et al., 1999; Duc et al., 2003). The maximum adsorption capacity of 0.34 mmol/g was reported(Rivera et al., 1999).

Iron and Nickle

The presence of iron in water is one of the essential reasons for water pollution. Iron is the fourth element of the earth's crust and the second most abundant metal in the earth. Fe^{+3}ions are mainly present in the groundwater, but they can also be found in the surface waters. The presence of iron ions in the natural sources is due to the decomposition of rocks, acid mine, and drainage water. Excess iron causes degradation of water quality, corrosion, and clogging of pipes and reservoirs, which accompanied by precipitation of Fe^{+3}. There are various methods for removing Fe^{+3} from water, including ion exchange, reverse osmosis, chemical precipitation, and adsorption. However, most of these technologies are either extremely expensive or too ineffective to reduce metal concentration levels from the water. Modified hydroxyapatite was used as adsorbentto remove Fe^{+3} from groundwater. Different parameters such as contact time, pH, and initial concentration, the dosage of adsorbent, agitation speed, and temperature were studied. The results revealed that the pseudo-second-order is the best model to describe the adsorption process. Adsorption capacity from the Langmuir model was found to be 0.389 mg/g (Seafelnasr et al., 2017). Homogeneous magnetic powders were obtained with iron oxide content up to 50 wt%, without perturbation of the magnetite structure or formation of additional calcium phosphates. The surface area of the composite powder was significantly increased after incorporation of magnetite due to the better apatite particle dispersion. The magnetic properties of magnetite nanocrystals were preserved upon association with hydroxyapatite. Full recovery of the composite powder after lead removal could be achieved using a simple magnet at a relatively low iron oxide content (20 wt%) (Yang et al., 2015).

An adsorbent called chitosan-coated magnetic hydroxyapatite nanoparticles (CS-MHAP) was prepared to improve the removal efficiency of Ni^{+2}ions and textile dye by co-precipitation. Structure and properties of CS-MHAP were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and vibrating sample magnetometer (VSM). The weight percent of chitosan was investigated by thermal gravimetric analysis (TGA). The prepared CS-MHAP presented a significant improvement on the removal efficiency ofNi^{+2}ions and reactive blue 19 dye (RB19). Interestingly, the prepared adsorbent could be easily recycled from an aqueous solution by an external magnet and reused for adsorption with high removal efficiency (Nguyen and Pho, 2014). Nanocrystalline Hydroxyapatite (nano HAP) was synthesized from Persian Gulf coral by a hydrothermal method in order to remove nickel ions from aqueous solutions. The primary powder was characterized using XRD, FTIR,and SEM. The powder surface area was determined by BET. The influence of different adsorption parameters, such as initial concentration of metal ion, contact time, adsorbent dosage, and the temperature on the adsorption amounts of Ni^{+2} ions were studied. Nickel uptake was quantitatively evaluated using the Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) models. The results indicated that the adsorption reactions were spontaneous, endothermic and the pseudo-second-order model fitted better the adsorption kinetics of Ni^{+2} on HAP (Zamani et al., 2013).

Phenol

Wastewater from various types of industries such as synthetic resins, plywood, paper and pulp, gas and coke oven plants, paints, coal gas, tanning, textile, plastic, rubber, pharmaceutical, petroleum and mine discharges, contain different types of phenols. Phenolic compounds are toxic substances and some of them are known or suspected carcinogens. Therefore it is important to remove phenol and phenolic compounds from contaminated industrial aqueous streams before being discharged into any water bodies. Adsorption of phenol and its derivatives from aqueous solution by activated carbon is one of the most investigated of all liquid phase applications of carbon adsorbents. Several adsorbents have been used for the treatment of wastewater and removal of phenolic compounds. Various adsorption processes and adsorbents such as pistachio nut shell ash, Moringaperegrina tree shell ash, agricultural fibers, red mud, low-cost clay, olive mill waste, natural zeolites, rubber seed coat, peat, fly ash, and bentonite have been used for the removal of phenol and its derivatives.The chemical, biological and physical treatment processeshave their own advantages and disadvantages. It is worth mentioning that economic aspects of these processes are important, for example,biosorptionwas found to be an effective method with scope for further research in terms of cost-effectiveness and regeneration (Bazrafshan et al., 2016). Magnetic hydroxyapatite (HAP) was prepared which combined super-paramagnetic Fe_3O_4 nanoparticles and HAP, by ultrasound method and found that these materials have the ability to absorb phenol in wastewater. The magnetic materials were investigated by scanning electron microscope, X-ray diffraction, Fourier transform infrared spectroscopy, thermal gravimetric analysis, vibrating sample magnetometer, and N_2 adsorption in order to elucidate the morphology, structure, and other properties. When the prepared magnetic materials were calcined at 200^0C, the prepared Fe_3O_4 was oxidized to Fe_2O_3, possessing loose-shaped holes with a high specific area of 325.2 m^2/g, a magnetization intensity of 12.5 emu/g, and the N_2 adsorption isotherm belongs to porous adsorption. Experiments confirmed that the Freundlich adsorption isotherms model applies to lower phenol concentrations (0–50 mg/l), while the Langmuir adsorption isotherms model fits for high phenol concentrations (50–500 mg/l). The efficiency of adsorption was reduced only by 10% over a six-time use period (Wang et al., 2011).

The potential of n-HAP powder was explored for the removal of phenol from aqueous solution. The effect of contact time, initial phenol concentration, pH, adsorbent dosage, solution temperature and adsorbent calcining temperature on the phenol adsorption was investigated. The results showed that the n-HAP powder possessed good adsorption ability to phenol. The adsorption process was fast, and it reached equilibrium in 2 h of contact. The initial phenol concentration, pH,and the adsorbent calcining temperature played obvious effects on the phenol adsorption capacity onto n-HAP powders. The maximum phenol sorption capacity was obtained at 10.33 mg/g for 400 mg/l initial phenol concentrations at pH 6.4 and 60^0C (Lin et al., 2008). Adsorbent materials were used based on the apatites (non-substituted and substituted with Sr and Ba) for adsorption of phenol from aqueous solution at 10, 20 and 30 °C and three pH values (3, 6 and 10.5). Structural studies showed the formation of the apatite materials and the replacement of Ca by Sr and Ba. The adsorption isotherms of phenol were determined and modeled with three parameter equations (Langmuir, Freundlich,andTemkin) or with two parameter equations (Sips and Dubinin–Radushkevich). Taking into account the Sips isotherm, the maximum amount of phenol uptake was 220 mg/g for Ba based adsorbent (Fierascu et al., 2017). It was also shown that phenol molecules were absorbed by hydrogen bonding between apatite metal ion or oxygen atom from P–O group and the hydrogen of the phenol functional group. The kinetic data indicated that physical and chemical adsorption might be involved in the adsorption process. Combined calorimetric and adsorption techniques showed that in the case of phenol adsorption from either dilute or concentrated aqueous solutions, water is always adsorbed preferentially by the oxygen-containing surface groups of the carbon. This reduces the surface and/or the micropore volume accessible to the phenol molecule and quantitatively explains the decrease in the limiting adsorption of phenol on a given carbon after oxidation (Fernandez et al., 2003).

Anions - Fluoride

Nano-HAP and nano-HAP/Chitosan composite were used for fluoride removal with a defluoridation capacity of 1845.0 mg/kg and 2840.0 mg/kg, respectively and thus making evident, the better efficiency of the latter composite. They followed ion-exchange and adsorption as mechanisms of fluoride removal (Siaram et al., 2008). An adsorbent was prepared by loading Al (III) ions into the bone char and studied its performance through batch adsorption experiments. The factors considered were types of the aluminium salts ($AlCl_3$, $Al(NO_3)_3$, $NaAlO_2$, $Al_2(SO_4)_3$), initial fluoride ion concentration (2–20 mg/l), mass of the adsorbent (0–14 g/l) and the adsorption time (0–72 h). The fluoride removal efficiency was determined as 97% at a pH of 7.25 for 10 g/l modified bone char in the 10 mg/l fluoride solution. The study reflects good prospects as a potential defluoridation system(Zhu et al., 2011). Eggshell powder was investigated as an adsorbent for fluoride removal from aqueous solution. The fluoride adsorption was studied in a batch system and the maximum removal efficiency was observed at pH6.0. The study indicated the effectiveness of eggshell powder as a low-cost adsorbent (Bhaumik et al., 2012). Fluoride removal was evaluated with respect to the optimization of composite synthesis conditions like aluminum loading, calcination temperature, the ratio of the eggshell membrane and eggshell in the composite. The eggshell composite showed adsorption capacity of 37.0 mg/g at 30 °C and performed in the pH range 3-9 (Lunge et al., 2012). The surface hydroxyl groups were reported as the active site for heavy metal adsorption and therefore the efficiency of removal could be enhanced by increasing the number of such groups in the nano-HAP (Nie et al., 2012). Fluoride adsorption was studied on HAP at pH (2.6, 4.6, 7.1, 8.9 and 11.5) with contact time (7 min–23 h), initial fluoride concentration (2.0–20 mg/l) and adsorbent dose (0.01–0.1 g/25ml). The maximum adsorption of fluoride ion took place in the pH range of 5-7.3(Reyes et al., 2010).Cellulose was synthesized at hydroxyapatite nanocomposite in NaOH/thiourea/urea/H_2O and studied its adsorption characteristics regarding defluoridation i.e. effects of contact time, pH, initial adsorption concentration and coexisting ions. They noted higher adsorption capacity at low pH. An increase in adsorbent dose improved fluoride removal due to increase in a number of available adsorption sites. The maximum adsorption capacity was recorded at 4.2 mg/g. Also, other coexisting ions did not adversely affect the fluoride adsorption (Yu et al., 2013).

Fluoride adsorption was examined onto HAP and Apatitic-Tri-calcium Phosphate in two different studies. The adsorption was characterized by temperature, initial solution pH, adsorbent dose and initial fluoride concentration as the parameters. fluoride removal efficiency of 88.9% was recorded for HAP with initial concentration up to 20 mg/l under the conditions (pH = 4.16, temperature of 39 °C, adsorbent dose of 0.28 g) while the efficiency was 82.3% for Apatitic-Tri-calcium Phosphate with initial fluoride concentration of up to 60 mg/l under the conditions (pH = 4, temperature of 40 °C and adsorbent dose of 0.29 g) (Mourabet et al., 2015). Defluoridation was investigated with magnesium substituted HAP keeping parameters as pH (6-9), initial fluoride concentration (1.5–13 mg/l), contact time (0.5–24 h) and co-existing ions (bicarbonate, sulfate, chloride, and nitrate).The maximum fluoride uptake by the magnesium substituted HAP was reported as 2.66 mg/g. The fluoride removal was found to depend on all the parameters except the co-existing ions. The hexavalent chromium toxicity forces the aluminum finishing industry to use fluoride-containing chemicals in order to improve aluminum passivation. Disposal of industrial wastewaters containing an excess concentration of fluoride to surface and ground waters can cause several health hazards. Effluents containing fluoride need treatment to reduce their concentration to disposable values before being discharged into public sewage (Garg and Chaudhari, 2012). The fluoride-containing wastewater from the aluminum finishing industry was treated by precipitation at pH 12.5 and achieved residual fluoride concentrations of 8.69±1.84 mg/l from an initial concentration of 74.5±4.6 mg/l. Further, remaining solution was processed by adsorption onto hydroxyapatite (HAP) which resulted in fluoride effluent concentrations of 4.09±0.16 mg/l. The total fluoride removal efficiency was 94.5 %. The sorption onto HAP data fitted well the Freundlich (r^2=0.992) and Langmuir (r^2=0.994) models. It was concluded that the adsorption step using HAP can be used as a post-treatment method to remove fluoride from aluminum finishing industry wastewater (Melidis, 2015).

REMOVAL OF ORGANIC CONTAMINANTS

The health hazards associated with commonly found organic contaminants warrant ways of effective removal. Adsorption and photocatalytic degradation are two such methods for water treatment. The widely reported usage in treating dyes, pesticides, and pharmaceutical compounds speaks volume about their utility. Studies were performed on the adsorption of acid black 172 dye using uncalcined hydroxyapatite nanopowder. They have reported the removal efficiency as 95.78% in batch mode experiments after 1 h of adsorption under the optimum conditions (pH 3, adsorbent dosage of 28 g/l, initial dye concentration 400 mg/l and temperature 20°C).The adsorption kinetics followed the pseudo-second-order model and the Langmuir isotherm represented the equilibrium state with a maximum adsorption capacity of 312.5 mg/g (Ciobanu et al., 2014). Studies on adsorption of reactive blue 19 dye, used both uncalcinedand calcined hydroxyapatite in batch mode. The parameters optimized by them were adsorbent dosage, contact time, initial dye concentration, pH, and temperature. At pH-3 and 20°C, both uncalcined and calcined hydroxyapatite exhibited a high removal rate of 95.58% and 86.95%, respectively. The kinetic studies indicated a pseudo-second-order model with equilibrium data fitting well to Langmuir isotherm. The maximum adsorption capacity of uncalcined and calcined adsorbent was reported as 90.09 mg/g and 74.97 mg/g, respectively(Ciobanu et al., 2016).The batch adsorption of disperse blue SBL dye was studied on hydroxyapatite synthesized by co-precipitation method. The experiment took into consideration the factors which might influence the adsorption such as contact time, adsorbent dosage, initial dye concentration, temperature, and pH. The removal efficiency increased with increase in adsorbent dose until complete discoloration of the solution. The adsorption isotherm followed Langmuir model with high dependence on pH and temperature.It was concluded that the nature of the interaction between dye and the adsorbent was electrostatic(Noureddine et al., 2008).Alow-cost adsorbent was developed in the form of hydroxyapatite/chitosan composite for the removal of Remazol blue dye. The hydroxyapatite was extracted from eggshell and conjugated with commercially available chitosan. The maximum removal efficiency stood at 95% at pH 6 with an adsorbent dose of 60 mg. However, the study runs short on adsorption kinetics (Ciobanu et al., 2014). Batch mode adsorption experiments were performed for crystal violet dye on nanocrystalline hydroxyapatite. The removal rate was 90.71% under optimum conditions (pH 10, adsorbent dosage 4g/l, the initial dye concentration of 80 mg/l, contact time 3 hr and temperature 20°C). The adsorption took place due to the electrostatic interaction between the adsorbent and the dye. This explained high adsorption at a low adsorbent dose. However, there is no mention of kinetic studies (Hamzah and Salleh, 2015).A cost-effective adsorbent called chitosan-coated magnetic hydroxyapatite nanoparticles was prepared through co-precipitation method. These nanoparticles were used to conduct batch adsorption studies for reactive blue 19 and Ni (II) ions. The experiment underlined the influence of several factors such as contact time, initial dye concentration, adsorbent dosage and pH. The maximum removal of dye and Ni (II) ions took place at pH 5 and pH 6, respectively. The work established chitosan-coated magnetic hydroxyapatite as a better adsorbent with respect to pure chitosan and magnetic hydroxyapatite. Chitosan (CS) has marked potential in environmental adsorption applications but typically suffers from low specific gravity and sensitivity to pH (Hamzah and Salleh, 2015).A hydroxyapatite-CS (HAP-CS) composite was developed via embedding of HAP into CS and used for removal of Congo red (CR) dye from aqueous solution. Effects of different weight contents of CS in HAP-CS composite, adsorbent dosage, initial pH, contact time and the initial dye concentration on CR removal were studied using batch adsorption at room temperature. The kinetic data were best described by the pseudo-second-order model ($R^2 > 0.9999$), while a thermodynamic investigation of CR adsorption by HAP-CS composite confirmed a spontaneous adsorption. HAP-CS composite containing 50 wt% of CS exhibited adsorption capacity of 769 mg/g for CR (Langmuir model), which was much higher than that of pure CS, HA and other previously reported adsorbents (Huijuan et al., 2012).

Hydroxyapatite prepared through combined precipitation-microwave method was used in batch adsorption studies for the removal of methylene blue. Temperature, pH, and adsorbent dose were the chosen factors with the first two influencing adsorptions. The adsorption kinetics data was closer to the pseudo-second-order model with the best fit for the Langmuir isotherm. The maximum dye adsorption was 33.3 mg/g (Allam et al., 2016).Poorly crystalline hydroxyapatite nanoparticles were synthesized to conduct batch mode experiments towards the removal of humic acid. The effects of crystallinity, pH, adsorbent dosage, contact time & the presence of inorganic salts at room temperature were considered. The adsorption obeyed pseudo-second-order kinetics while the adsorption data was described well by Sips model. The maximum adsorption of 123.44 mg/g was recorded at 298 K. It was observed that the adsorption rate decreased with increasing initial adsorbent dose. Surface complexation between the oxygen atoms of functional groups of humic acid and calcium ions of hydroxyapatite was suggested as the possible mechanism of adsorption. Moreover, the adsorbent could be regenerated using neutral phosphate buffer (Wei et al., 2015).In another study, hydroxyapatite/gelatine nanocomposite, synthesized through precipitation route, and was used for the removal of nitrobenzene from aqueous solution in batch studies. Authors investigated effects of contact time, adsorbent dose, temperature, pH, ionic strength, humic acid and the presence of solvent on adsorption. It was observed that an increase in the amount of adsorbent improved nitrobenzene removal while an increase in pH and temperature decreased it. The experimental data fitted well to both the Langmuir andFreundlich isotherm with a maximum adsorption of 42.373 mg/g. Reusability of the adsorbent was also possible using methanol (Wei et al., 2014).

The adsorption properties of norfloxacin (NOR) and ciprofloxacin (CIP) by nano-hydroxyapatite (n-HAP) were studied using batch adsorption experiments. The adsorption curves of fluoroquinolone antibiotics (FQs) by n-HAP were simulated by Langmuir and Freundlich isotherms. The results showed that NOR and CIP can be adsorbed effectively by the adsorbent of n-HAP, and the adsorption capacity of fluoroquinolone antibiotics increases with increasing dosage of n-HAP. The maximum removal efficiency occurred when pH was 6 for both FQs. The adsorption isotherm of FQs fits well for both Langmuir and Freundlich equations and the adsorption of both FQs by n-HAP follows second-order kinetics (Chen et al., 2015).Carbonated hydroxyapatite (CHA) nanorods were prepared by using the hydrothermal method. The crystallinity and chemical structure of synthesized CHA nanorodswere characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Carmine was selected as a representative organic dye to study the adsorption capacities of CHA nanorods. Mechanistic studies of carmine adsorption by CHA nanorods showed that the adsorption processes both followed the pseudo-second-order kinetic model and fitted the Langmuir isotherm model well. The CHA nanorods exhibited a high adsorption capacity of 85.51 mg/g for Carmine at room-temperature. The experimental results prove that CHA nanorods can be used as promising absorbents for removing organic dye pollutants in wastewater from paper and textile plants (Liu et al., 2017).

Metal and polymer-mediated porous crystalline hydroxyapatite (HAP) nanocomposites were prepared for environmental applications. Four different nano-HAP systems were synthesized, namely, microwave irradiated HAP (M1), Zn doped HAP (M2), Mg-doped HAP (M3) and sodium alginate incorporated HAP (M4), and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, nuclear magnetic resonance (NMR), X-ray fluorescence, thermogravimetric analysis and Brunauer–Emmett–Teller (BET) analyses. Surface area estimates using BET isotherm reflected the highest surface area for M3 and M1>M2>M4. Four systems of M1–M4 were used as potential adsorbent materials for the removal of metal-containing azo dye from aqueous system. This study highlights the possibility of developing Hap nanocomposites for the effective removal of dye contaminants in the environment (Manatungate al., 2018).

REMOVAL OF BIOLOGICAL CONTAMINANTS

Biological contaminants such as bacteria, virus, fungi, mycoplasma etc. are a profound challenge as these are often associated with the waterborne diseases. Though hydroxyapatite has found numerous mentions as a suitable platform for amplification, detection,and purification of compounds with the biological origin, its role in microbe removal from water is somewhat less documented. Biocompatible nano hydroxyapatite-curcumin bio-coated activated carbon wasinvestigated for microbe removal/anti-microbial application. The filtering matrix was validated against both gram-positive (E.coli) and gram-negative (S.aureus) concluding that the antibacterial property of the above-said matrix was higher than the hydroxyapatite/activated carbon and pure granular activated carbon. The matrix was developed by attaching a layer of curcumin molecules atop hydroxyapatite coating of granular activated carbon. This work aimed to get over the problem of disinfection-by-product generation associated with the usual filtering apparatus (Udayakantha et al., 2015).Microbes removing material based on hydroxyapatite were studied. On the basis of work carried out, inventors claim that the hydroxyapatite whiskers as synthesized by hydrothermal reaction, with a mean C-axis length of from 1- 1000 micron & an aspect ratio of 5 or more (preferably 10) can selectively separate microbes. Also, they add that their invention is sensitive to the difference in the functional groups existing on the surfaces of microbes. The microbes referred in the work included not only bacteria but also virus, rickettsiae, chlamydia, mycoplasma, spirochete and fungi (Okamoto, 1998).

CONCLUSIONS

The purpose of this review was to highlight the competency and advancement in use of hydroxyapatite nanoparticles as adsorbents and catalysts took place for the last couple of years. It is evident from the study carried out so far that the use of hydroxyapatite composites as adsorbents is well immersed and widely practiced across the world. An in-depth study of hydroxyapatite nanoparticles as an adsorbent indicates its potential to be used for the removal of metal ions, anions, organic and biological contaminants from water efficiently. It works well under a wide range of conditions (pH, temperature, the initial concentration of impurities etc. It is also capable of removing the toxicants even at a lower concentration. Meanwhile, the dose required for removal is quite low, thereby making it economical. The composite materials are characterized by the standard methods such as FTIR, SEM, XRD, TG, and XPS, and the adsorption of various impurities has been investigated. Adsorption kinetics indicates the rapid adsorption equilibrium and the adsorption process is well described by the pseudo-second-order kinetic model. In most of experiments, the Langmuir and Freundlich isotherm models fitted the experimental data well. Adsorption and photocatalytic degradation are two methods, which have been found suitable for water treatment to remove the organic contaminants. **S**urface complexation, ion exchange, and hydrogen bonding are found suitable for a possible mechanism for dye adsorption.

Hydroxyapatite has found numerous mentions as a suitable platform for amplification, detection and purification of compounds with the biological origin. Its role in microbe removal from water is somewhat less documented. The synthesis of Hydroxyapatite by biowastes makes it ideal to be used as an inexpensive method for water and wastewater treatment. It is also evident that the synthesized nano-composite can be categorized as a bactericidal nano-composite. It is worth to note that all research works have carried out adsorption in batch mode which reflected remarkable results but no such use is employed at industrial scale. This needs further research for its utilization at alarge scale. The experiments carried out in batch mode should be transformed into columns operations in order to get the best out of nano adsorption technology. The waste management system should be developed for the proper disposal of recovered pollutants and used nanoparticles. A joint effort of research institutions and industries is required to solve the issue of water contamination at the global level.

REFERENCES

Allam, K., Bouari, A. E., Belhorma, B. And Bih. L. 2016. Removal of Methylene Blue from Water Using Hydroxyapatite Submitted to Microwave Irradiation. Journal of Water Resource and Protection, 8(3):358-371.

Asgari, G., Rahmani, A. R., Faradmal, J. and Mohammadi, A. M. S. 2012. Kinetic and Isotherm of Hexavalent Chromium Adsorption onto Nano Hydroxyapatite. Journal of Research in Health Sciences, 12(1):45-53.

Bazrafshan, E., Amirian, P., Mahvi, M/ H. And Ansari-Moghaddam, A. 2016. Application of adsorption process for phenolic compounds removal from aqueous environments: a systematic review, Global NEST Journal, 18:146.

Bhaumik, R., Mondal, N. K., Das, B., Roy, P., Pal, K. C., Das, C., Banerjee, a. and Datta, J. K. 2012. Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies. E-Journal of Chemistry, 9(3):1457-1480.

Brammer, H. and Ravenscroft, P. 2009. Arsenic in groundwater: a threat to sustainable agriculture in South and South-East Asia. Environment International, 35: 647.

Chen, Y., Lan, T., Duan, L., Wang, F., Zhao, B., Zhang, S. and Wei, W. 2015. Adsorptive Removal and Adsorption Kinetics of Fluoroquinolone by Nano-Hydroxyapatite. 10(12):e0145025.

Ciobanu, G., Barna, S. and Harja, M. 2016. Kinetic and equilibrium studies on adsorption of Reactive Blue 19 dye from aqueous solutions by nanohydroxyapatite adsorbent. Archives of Environmental Protection, 42(2):3-11.

Ciobanu, G., Harja, M., Rusu, L., Mocanu, A. M. and Luca, C. 2014. Acid Black 172 dye adsorption from aqueous solution by hydroxyapatite as low-cost adsorbent. Korean Journal of Chemical Engineering, 31:1021-1027.

Ciobanu, G., Harja, M., Diaconu, M., Cimpeanu, C., Teodorescu, R. and Bucur, D. 2014. Crystal violet dye removal from aqueous solution by nanohydroxyapatite. Journal of Food, Agriculture & Environment, 12(1):499-502.

Condon, J. B. 2006. Surface Area and Porosity Determinations by Physisorption: Measurements and Theory. Elsevier, New York.

Corami, A., Mignardi, S. and Ferrini, V. 2008. Cadmium removal from single and multi-metal (Cd + Pb +Zn+ Cu) solutions by sorption on hydroxyapatite. Journal of Colloid and Interface Science, 317:402.

Crini, G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog. Polym. Sci., 30: 38.

Crini, G. 2006. Non-conventional low-cost adsorbents for dye removal: A Review. Bioresource Technology, 97:1061.

Czerniczyniec, M., Farias, S. S., Magallanes, J. and Cicerone, D. S. 2007. Arsenic (V) Adsorption onto Biogenic Hydroxyapatite: Solution Composition Effects. Water Air Soil Pollution, 180(1):75-82.

Dargaville, T. R., Guerzoni, F. N., Looney, M. G. and Solomon, D. H. 1996. The Adsorption of Multi nuclear Phenolic Compounds on Activated Carbon. Journal of colloid and interface science.182(1): 17-25

Do, T.H., Tran, P. T., Ton, A. K. and Le, M. V. 2016. A Novel Method for the Fabrication of Granular Hydroxyapatite-bentonite Composite Adsorbents for the Removal of Pb2+ from an Aqueous Solution. Journal of Environmental Science and Engineering, 5:371-378.

Duc, M., Lefevre, G., Fedoroff, M., Jeanjean, J., Rouchaud, J. C., Monteil-Rivera, F., Dumonceau, J. and Milonjicet, S. 2003. Sorption of selenium anionic species on apatites and iron oxides from aqueous solutions. Journal of Environmental Radioactivity, 70(1-2):61-72.

Eblin, K.E., Bowen, M. E., Cromey, D. W., Bredfeldt, T. G., Mash, E. A., Lau, S. S. and Gandolfi, A J .2006. Arsenite and monomethylarsonous acid generate oxidative stress response in human bladder cell culture. Toxicology and applied pharmacology, 217(1):7-14.

Feng, Y., Gong, J. L., Zeng, G. M., Niu, Q. Y., Zhang, H. Y., Niu, C. G., Deng, J. U. and Yan, M. 2010. Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. Chemical Engineering Journal, 162:487-494.

Fernandez, E., Hugi-Cleary, D., Lopez-Ramon, M. V. and Stoeck, F. 2003. Adsorption of Phenol from Dilute and Concentrated Aqueous Solutions by Activated Carbons, Langmuir, 19(23):9719-9723.

Fierascu, L., Avramescu, S. M., Petreanu, I., Marinoiu, A., Soare, A., Nica, A. and Fierascu, R. C. 2017. Efficient removal of phenol from aqueous solutions using hydroxyapatite and substituted hydroxyapatites. In (Ed) C. S. Hsu and P. R. Robinson Reaction Kinetics, Mechanisms and Catalysis, 122:155-175.

Foroughi, F., Hassanzadeh-Tabrizib, S.A., Amighiana, J. and Saffar-Teluric, A. 2015. A designed magnetic CoFe2O4 – hydroxyapatite core–shell nanocomposite for Zn(II) removal with high efficiency. Ceramics International, 41:6844-6850.

Fuller, C. C., Bargar, J. R., Davis, J. A. and Piana, M. J. 2002. Mechanisms of Uranium Interactions with Hydroxyapatite: Implications for Groundwater Remediation. Environmental Science and Technology, 36(2): 158-165.

Gandhi, M. R., Kousalya, G. M. and Meenakshi, S. 2011.Removal of copper(II) using chitin/chitosan nano-hydroxyapatite composite. International Journal of biological macromolecules, 48:119.

Gangadhar, G., Maheshwari, U. and Gupta, S. 2012. Application of Nanomaterials for the Removal of Pollutants from Effluent Streams. Nanoscience and Nanotechnology-Asia, 2:140.

Garg, P. and S. Chaudhari. 2012. Adsorption of Fluoride from Drinking Water on Magnesium Substituted Hydroxyapatite. Proceedings of the 2012 International Conference on Future Environment and Energy, 180.

Gergely, G., Weber, F., Lukacs, I. E., Toth, A. L., Horvath, Z. E., Mihsly, J. And Balazsi, C. 2010. Preparation and characterization of hydroxyapatite from eggshell. Ceramics International, 36(2):803-806.
Gledhill,W. E. 1987. Microbial Toxicity and Degradation Test Methodology: An Industrial Perspective. Toxicity Assessment, 2: 89.

Gogoi, D., Kumar, T., Shanmugamani, A. G., Rao, S. V. S. and Sinha, P. K. 2012. Studies on removal of cobalt from an alkaline waste using synthetic calcium hydroxyapatite. Journal of Radio analytical and Nuclear Chemistry, 298(1): 337-344.

Googerdchian, F., Moheb, A. and Emadi, R. 2012. Lead sorption properties of nanohydroxyapatite–alginate composite adsorbents. Chemical Engineering Journal, 200:471.

Gupta, N., Kushwaha, A.K. and Chattopadhyaya, M. C. 2011. Adsorption of cobalt (II) from aqueous solution onto hydroxyapatite/zeolite composite. Advanced Material Letters, 2: 309.

Gupta, V. K., Agarwal, S. and Saleh, T. A. 2011. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. Journal of Hazardous Materials.185: 17.

Hamzah, S. and Salleh, M. F. M. 2015. Hydroxyapatite/ Chitosan Biocomposite for Remazol Blue Dyes Removal. Applied Mechanics and Materials, 695:106.

Hardani, Kh., Buazar, F., Ghanemi, K., Kashisaz, M., Baghlani-Nezhad, M. H., Khaledi-Naseb, a. and Badri, M. 2015. Removal of toxic mercury (II) from water via Fe3O4/Hydroxyapatite nano adsorbent: An efficient, economic and rapid Approach. AASCIT Journal of Nanoscience, 1(1):11-18.

Hokkanen, S., Bhatnagar, A., Repo, E., Lou, S. and Sillanpaa, M. 2016. Calcium hydroxyapatite microfibrillated cellulose composite as a potential adsorbent for the removal of Cr (VI) from aqueous solution. Chemical Engineering Journal, 283:445-452.

Huang, Y., Chen, L. and Wang, H. 2012. Removal of Co (II) from aqueous solution by using hydroxyapatite. Journal of Radio analytical and Nuclear Chemistry, 291: 777.

Huijuan, H., Zhou, R., Wu, P. and Wu, L. 2012. Removal of Congo red dye from aqueous solution with hydroxyapatite/chitosan composite. Chemical Engineering, 211-212:336-342.

Ignat, M., Alexandroaei, M. and Lungu, N.C. 2011. The removal of Zn2+ ions from groundwater using hydroxyapatite nanoparticles. Revista de Chimie, (Bucharest), 62:787.

Islam, M., Mishra, P.C. and Patel, R. 2011. Arsenate removal from aqueous solution by cellulose-carbonated hydroxyapatite nanocomposites. Journal of Hazardous Materials, 189:755.

Jang, S.H., Min, B. G., Jeong, Y. G., Lyoo, W. S. Lee, S. C. 2008. Removal of lead ions in aqueous solution by hydroxyapatite/polyurethane composite foams. Journal of Hazardous Materials, 152(3):1285-1292.

John, D. Z. 1990. Handbook of Drinking Water Quality: Standards and Controls. Van Nostrand Reinhold, New York.

K. Okamoto. 1998. United States Patent, 5755969.

Kongsri, S., Janpradit, K., Buapa, K., Techawongstien, S. and Chanthai, S. 2013. Nanocrystalline hydroxyapatite from fish scale waste: preparation, characterization and application for selenium adsorption in aqueous solution. Chemical Engineering Journal, 215-216:522-532.

Kross, B. C., Ayebo, A.D. and Fuortes, L. 1992. Methaemoglobinaemia: nitrate toxicity in rural America. Journal of American family physician, 46: 183.

Landi, L., Tampieri, A., Celotti, G. And Sprio, S. 2000. Densification behaviour and mechanisms of synthetic hydroxyapatites. Journal of the European Ceramic Society, 20(14-15):2377-2387.

Lari, R. B., Bahrololoom, M. E. and Nemati, A. 2011. Sorption behavior of Zn (II) ions by low cost and biological natural hydroxyapatite/chitosan composite from industrial waste water. Journal of Food, Agriculture & Environment, 9: 892.

Lee, S. J. and Oh, S. H. 2013. Fabrication of calcium phosphate bio ceramics by using eggshell and phosphoric acid. Materials Letters, 57:4570.

Lewinsky, A. A. 2007. Hazardous Materials and Wastewater: Treatment, Removal and Analysis. Nova Science Publishers, New York.

Li, S., Bai, H., Wang, J., Jing, z., Liu, Q., Zhang, M., Chen, R., Liu, L. and Jiao, C. 2012. In situ grown of nano-hydroxyapatite on magnetic CaAl-layered double hydroxides and its application in uranium removal. Chemical Engineering Journal, 193-194: 372-380.

Liao, D., Zheng, W., Li, X., Yang, Q., Yue, X., Guo, L., Zeng G. 2010. Removal of lead (II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste. Journal of Hazardous Materials, 177(1-3):126-130.

Lin, K., Pan, J., Chen, Y., Cheng, R. and Xu, X. 2008. Adsorption of Phenol from Aqueous Solution by Hydroxyapatite Nanopowders. Part I: Synthesis and Factors Affecting the Adsorption Characteristic Studies, 2nd International Conference on Bioinformatics and Biomedical Engineering (ICBBE 2008), May 16-18, Shanghai, China.

Liu, G., Talley, J. W., Na, C., Larson, S. L. and Wolfe, L. G. 2010. Copper doping improves hydroxyapatite sorption for arsenate in simulated ground waters. Environment Science Technology, 44(4):1366-1372.

Liu, G., Xue, C. and Zhu, P. 2017. Removal of Carmine from Aqueous Solution by Carbonated Hydroxyapatite, Nanorods, 7:137.
Lunge, S., Thakre, D., Kamble, S., Labhsetwar, N. and Rayalu, S. 2012. Alumina supported carbon composite material with exceptionally high defluoridation property from eggshell waste. Journal of Hazardous Materials, 237-238: 161-169.

Lusvardi, G., Malavasi, G., Menabue, L. and Saladini, M. 2002. Removal of cadmium ion by means of synthetic hydroxyapatite. Waste Management, 22(8): 853-857.

Ma, B., Shin, W. S., Oh, S., Park, Y. J. and Choi, S. J. 2010. Adsorptive Removal of Co and Sr Ions from Aqueous Solution by Synthetic Hydroxyapatite Nanoparticles. Separation Science and Technology, 45(4):453-462.

Manatunga, D.C., de Silva, R. M., de Silva, K. M. N., de Silva, N. and Premala, E. V. A. 2018. Metal and polymer-mediated synthesis of porous crystalline hydroxyapatite nanocomposites for environmental remediation. 5, https://royalsocietypublishing.org/doi/10.1098/rsos.171557.

Masel, R.I. 1996. Principles of Adsorption and Reaction on Solid Surfaces. John Wiley & Sons, New York.

Meski, S., Khireddine, H., Ziani, S., Rengaraj, S. and Sillanppa, M. 2010. Comparative study on the removal of zinc (II) by bovine bone, billy goat bone and synthetic hydroxyapatite. Desalination and Water Treatment, 16(1-3):271-281.

Meski, S., Ziani, S. and Khireddine, H. 2010. Removal of Lead Ions by Hydroxyapatite Prepared from the Egg Shell. J. Chem. Eng. Data, 55:3923.

Ming, H.,Shujuan, Z.,Bingcai, P., Weiming, Z., Lu, L. and Quanxing, Z.2012. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. Journal of Hazardous Materials. 211-212:317-321.

Mirhosseini, M., Biazar, E. and Saeb, K. 2014. Removal of arsenic from drinking water by hydroxyapatite nanoparticles. Current World Environment, 9:331.

Mobasherpour, I., Salahi, E. and M. Pazouki. 2011. Removal of divalent cadmium cations by means of synthetic nano crystallite hydroxyapatite. Desalination, 266:142.

Mohammad, A.M., Saleh Eldin, T. A., Hassan, M. A. and El-Anadouli, B. E. 2017. Efficient treatment of lead-containing wastewater by hydroxyapatite/chitosan nanostructures. Arabian Journal of Chemistry, 10(5):683690.

Mondal, S., Mahata, S., Kundu, S. and Mondal, B. 2010. Processing of natural resourced hydroxyapatite ceramics from fish scale. Advances in Applied Ceramics, 109(4):234-239.

Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M., El Hamri, R. and Taitai, A. 2015. Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology. Journal of Saudi Chemical Society, 19(6):603-615.

Nakahira, A., Toshihiro, O., Tetsuo, H., Satoshi, Y. and Isao, T. 2006. Arsenic removal by hydroxyapatite-based ceramics. Chemistry Letters, 35(8):856-857.

Narwade, V. N. and Khairnar, R.S. 2017. Cobalt adsorption on the nano-hydroxyapatite matrix: isotherm and kinetic studies. Bulletin of the Polish Academy of Sciences Technical Sciences, 65:131.

Natarajan, K., Muniyappan, R.G. and Sankaran, M. 2010. Removal of Toxic Cr(VI) Ions from Aqueous Solution Using Nano-hydroxyapatite-based Chitin and Chitosan Hybrid Composites. Adsorption Science & Technology, 28:49.

Nguyen, V. C. and Pho, Q. H. 2014. Preparation of Chitosan Coated Magnetic Hydroxyapatite Nanoparticles and Application for Adsorption of Reactive Blue 19 and Ni+2Ions, Scientific World Journal, https://doi.org/10.1155/2014/273082.

Nie, Y., Hu, C. and C. Kong. 2012. Enhanced fluoride adsorption using Al (III) modified calcium hydroxyapatite. Journal of Hazardous Materials, 233:194.

Nissan, B. B., Milev, A. and Vago, R. 2004. Morphology of sol-gel derived nano-coated corraline hydroxyapatite. Biomaterials, 25:4971.

Noureddine, Q., Qourzal, S., Assabbane, A., Nounah, A. and Ait-Ichou, Y. 2008. Adsorption of Disperse Blue SBL dye by synthesized poorly crystalline hydroxyapatite. Journal of Environmental Sciences, 20(10):1268-1272.

Oren, A. H. and Kaya, A. 2006. Factors affecting adsorption characteristics of Zn2+ on two natural zeolites. Journal of Hazardous Materials B., 131: 59.

Ozawa, M., Satake, K. and Suzuki, R. 2003. Removal of aqueous chromium by fish bone waste originated hydroxyapatite. Journal of Materials Science Letters, 22:513.

P. Melidis. 2015. Fluoride Removal from Aluminium Finishing Wastewater by Hydroxyapatite. Environ. Process, 2:205.

Penrose, W.R. 2009. Arsenic in the marine and aquatic environments. Analysaism, occurrence and significance. Critical Reviews in Environmental Control, 1:465.

Puajindanetr, S. 1992. Characterisation and sintering of precipitated hydroxyapatite. Queen Mary and Westfield College London, Great Britain.

Ramli, R. A., Adnan, R., Bakar, M. A. and Masudi, S. M. 2011. Synthesis and Characterisation of Pure Nanoporous Hydroxyapatite. Journal of Physical Science, 22(1): 25-37.

Rengaraj, S. and Moon, S. H. 2002. Kinetics of adsorption of Co (II) removal from water and wastewater by ion exchange resins. Water Research, 36: 1783.
Reyes, J.M. and Solache-Ríos, M. 2010. Sorption behavior of fluoride ions from aqueous solutions by hydroxyapatite. Journal of Hazardous Materials, 180:297.

Rivera, E. M., Araiza, M., Witold, B., Victor, M. C., Dıaz-Estrada, J.R., Hernandez, R. and Rogelio, J.R. 1999. Synthesis of hydroxyapatite from eggshells. Materials Letters, 41:128-134.

Rivera, F. M., Masset, S. and J. Dumonceau. 1999. Sorption of selenite ions on hydroxyapatite. Journal of Materials Science Letters, 18:1143.

Roushani, M., Abbasi, S. and Khani, H. 2015. Synthesis and application of ionimprinted polymer nanoparticles for the extraction and preconcentration of mercury in water and food samples employing cold vapor atomic absorption spectrometry. Environ Monit Assess, 187: 4820.

Saeed, A. M., Hassan, R. A. and Thajeel, K. M. 2011. Synthesis of calcium hydroxyapatite powder from hen's eggshell. Iraqi Journal of Physics, 9:24.

Sairam, S.C.,Viswanathan, N. and Meenakshi, S. 2008. Defluoridation chemistry of synthetic hydroxyapatite at nano scale: Equilibrium and kinetics studies. Journal of Hazardous Materials, 155:206.

Salah, T.A., Mohammad, A. M., Hassan, M. A. and El-Anadouli, B. E. 2014. Development of nano-hydroxyapatite/chitosan composite for cadmium ions removal in wastewater treatment. Journal of the Taiwan Institute of Chemical Engineers, 45(4):1571-1577.

Seafelnasr, T.A., Soliman, M.H. and Ayash, M.A.A.A. 2017. Modified Hydroxyapatite Adsorbent for Removal of Iron Dissolved in Water Wells in Sohag, Egypt. Chemistry of Advanced Materials, 2:1

Sheha, R. R. 2007. Sorption behaviour of Zn (II) ions on synthesized hydroxyapatites. Journal of Colloid and Interface Science, 310:18.

Simon, F.G., Biermann, V. and Csicsak, J. 2003. Uranium removal using elemental iron and hydroxyapatite in permeable reactive barriers. – In: Nel, P. J. L.: Mine Water and the Environment, Johannesburg (Proceedings, 8th International Mine Water Association Congress), 43.

Smiciklas, I., Dimovic, I. and Mitricet, M. 2006. Removal of Co2+ from aqueous solutions by hydroxyapatite. Water Research. 40(12): 2267-2274.

Soto, M. L.,Andres, M., Herminia, D. and Juan, C. P. 2011. Recovery, concentration and purifi cation of phenolic compounds by adsorption: A review, Journal of Food Engineering. 105(1):1-27.

Udayakantha, K. S. M., de silva, R. M., de silva, K. M. N. and Hettiarachchi, C. 2015.Biocompatible nano hydroxyapatite – curcumin bi-coated antibacterial activated carbon for water purification. RSC Advances, 75:64696-703.
Vatistas, N. and Bartolozzi, M. 1999. Zinc contamination in the cathodic material of exhausted alkaline manganese dioxide batteries. Journal of Power Sources, 79: 199.

Venkatesan, J., Lowe, B., Manivasagan, P., Kang, K. H., Chalisserry, E. P., Anil, S., Kim, D. G. and Kim, S. K. 2015. Isolation and Characterization of Nano-Hydroxyapatite from Salmon Fish Bone. Materials, 8(8):5426-5439.

Wang, X. 2011. Preparation of Magnetic Hydroxyapatite and Their Use as Recyclable Adsorbent for Phenol in Wastewater, Clean – Soil, Air, Water, 39(1):13-20.

Wei, W., Sun, R., Jin, Z., Cui, J. and Zhenggui, W. 2014. Hydroxyapatite–gelatin nanocomposite as a novel adsorbent for nitrobenzene removal from aqueous solution. Applied Surface Science, 292:1020.

Wei, W., Yang, L., Zhong, W. Cui, J. and Wei, Z. 2015. Mechanism of Enhanced Humic Acid Removal from Aqueous Solution using Poorly Crystalline Hydroxyapatite Nanoparticles. Digest Journal of Nanomaterials and Biostructures, 10(2):663-680.

Weng, C. H. and Huang, C. P. 2004. Adsorption characteristics of Zn (II) from dilute aqueous solution by fly ash, Colloids and Surfaces. Physicochemistry Engineering Aspects, 247: 137.

WHO. 1981. Environmental Health Criteria 18. World Health Organization, Geneva.

WHO.1993. Guidelines for Drinking-Water Quality, World Health Organization, Geneva, 2nd Edition, Vol. 1.

Yamamura, Y. and Yamauchi, H. 1980. Arsenic metabolites in hair, blood and urine in workers exposed to arsenic trioxide. Industrial Health, 18: 203.

Yang, H., Masse, S., Rouelle, M., Aubry, E., Li, Y., Roux, C., Journaux, Y., Li, L. and Coradin, T. 2015. Magnetically recoverable iron oxide–hydroxyapatite nanocomposites for lead removal. International Journal of Environmental Science and Technology, 12(4):1173.

Yang, L., Zhong, W., Cui, J., Wei, Z. and Wei W. 2016. Enhanced Removal of Cu(II) Ions from Aqueous Solution by Poorly Crystalline Hydroxyapatite Nanoparticles. Journal of Dispersion Science and Technology, 37(7):956-968.

Yu, X., Tong, S., Ge, M. and Zuo, J. 2013. Removal of fluoride from drinking water by cellulose@hydroxyapatite nanocomposites. Journal of Carbohydrate Polymers, 92(1):269-275.

Zamani, S., Salahi, E. and Mobasherpour, I. 2013. Removal of Nickel from Aqueous Solution by Nano Hydroxyapatite Originated from Persian Gulf Corals.Canadian Chemical Transactions, 1: 173.

Zare, K., Gupta, V. K., Moradi, O., Makhlouf, A. S. H., Sillanpaa, M., Nadagouda, M. N., Sadegh, A., Shahryari-ghoshekandi, R., Pal, A., Wang, Z., Tyagi, I. and Kazemi, M. 2015. Comparative study on the basis of adsorption capacity between CNTs and activated carbon as adsorbents for removal of noxious synthetic dyes: a review. J. Nanostruct. Chem. 5(2): 227-236.

Zhu, H., Wang, H., Wang, G. And Zhang, K. 2011. Removal of Fluorine from Water by the Aluminium-Modified Bone Char. Proceedings of the International Conference on Biology, Environment and Chemistry, IACSIT Press, Singapore, 1:455-457.

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