Journal of Advanced Mechanical Sciences (JAMS)
ISSN: 2583-3790 (Online)
"J. Adv. Mech. Sci., vol. 1, no. 3, pp. 93-101, September 2022"

Investigation to Evaluate the Absorption Capacity of HApDuring Removal of Copper (II) from Aqueous Solution

Ankit Asthana[a]*, Abhay Kumar Mishra

[a]*Resarch scholar, M.Tech Department of Mechanical Engineering, Goel Institute of Technology and Management, Lucknow, Uttar Pradesh, India.*
[b]*Assistant Professor, Department of Mechanical Engineering, Goel Institute of Technology and Management, Lucknow, Uttar Pradesh, India*
**Corresponding Author Email and Phone Number: abhay.k.mishra@goel.edu.in, +919792132889*
Article received: 29/08/2022, Article Revised: 06/09/2022, Article Accepted: 08/09/2022
Doi: 10.5281/zenodo.7059339

Abstract

Present work illustrates the removal of copper ion (i.e. Cu2+) from water using hydroxyapatite (HAp) adsorbent. HAp powder was synthesized by chemical precipitation method. The developed HAp powders were characterized through FESEM images alongside the EDX analysis confirming the presence of calcium and phosphorous elements. Batch adsorption experiments were conducted mainly using HAP. The copper (II) ion adsorbed HAp was also characterized using, FESEM and EDX analysis. On the basis of the adsorption experimental results a treatment unit/set up has been developed for the purpose of removal of copper from water. The adsorption candle was made by mixing HAP and activated charcoal in a certain proportion. Activated charcoal was used mainly to increase the flow rate of water through the adsorbent candle. Prototypes were developed to investigate the initial copper ion concentration of 3mg/L and 6mg/L. The prototypes thus developed have proven to be successful as more than 1000 litres of copper contaminated water has been treated whilst maintaining the effluent copper concentration well below the permissible limit.

Keywords: *Hydroxyapatite (HAp), Adsorption, Copper, Fish scale.*

1. INTRODUCTION

The rapid rise in industrial development, increase in commerce, development of hospitals and health-care facilities has led to a significant increase in waste products. A large amount of toxic chemicals are also being generated which are highly hazardous in nature. The heavy metals are the most hazardous waste in liquid waste. The elements that have the specific gravity more than 5.0 alongside the atomic weights lie in the range of 63.5 and 200 are termed as heavy metals [1]. In the categories of heavy metal Cu, Pb, As, Fe, Zn, Hg, Ni, Cr and Cd are generally found in water and are highly toxic in nature. These heavy metals are of grave concern as these are toxic, have the affinity of bio-accumulation and are highly recalcitrant in the nature, consequences in the severe health related problems.

Some of these metals are trace elements e.g., manganese, zinc, iron and copper. These elements are always entering in the body through foodstuffs like vegetables, fruits and multivitamin products, moreover the high concentration of heavy metals present inside the water also responsible for the serious physiological and biological problems. For example, arsenic intake can lead to cancer and have the potential of causing skin and gastrointestinal effects. Lead also considered as a possible carcinogen, causes anaemia, high blood pressure, sterility and kidney problem. The metals like copper also responsible towards various diseases like headache, irritation in eyes, stomachache and diarrhoea [2]. The increasing number of food processing industries, using chemical for long term preservative may be responsible for the increasing the copper content in waste water. This contamination also prevails due to washing of copper container that contains food and water [3]. The earlier research suggested that when the contamination is more than 1.0 mg/l in drinking water it creates sever problems like gastrointestinal and hemochromatosis [4]. Therefore, it is indeed to develop such absorbent which have capacity to absorb heavy metals like copper from water to mitigate the water born diseases. Hence, the scientific community developed various methods for the removal of these metals from water. Some of these processes are precipitation, coagulation, ion-exchange, fluidized bed reactor, filtration, flue gas purification and adsorption. Each method has its own benefits and limitations. Precipitation method is deemed unsuitable if the amount of heavy metal dissolved in water is of very low concentration. Flocculation and Coagulation method is employed in conjugation with the precipitation process. This method leads to the formation of a large volume of sludge and usually some amount of heavy metals remain dissolved in water and is not beneficial for the treatment purpose [5]. Owing to the time and expense constraints, the aforementioned methods are not viable enough to be applied on large volume of waste water. However, the adsorption process is gaining popularity for the absorption of metals from polluted water. This method is suitable and potentially capable to treat water irrespective of the presence of heavy metal or the volume of water to be treated. There are many materials available, which can be used as an adsorbent. Among them the most commonly used adsorbent is activated carbon that commonly used as. The drawback that limits these absorbent is the expensiveness of material [6].

Now a days the primary focus of researchers is the use of cheaper adsorbents and easily available. They are in desire of having adsorbents that can be derived from some waste material and further use them with certain modifications for the removal of metals. Some of the adsorbents that was investigated so far are pea nut shells [7], olive cake [8], date pits and fruits [9], tea factory waste [10], maize cobs [11], wood saw dust [12] etc. The main bone of contention here lies in the selection of an optimal adsorbent which basically varies with the type of pollutant to be treated. An analysis is also required to get the optimal conditions needed for the removal of heavy metals by a particular adsorbent. The researches carried out on the Hydroxyapetite (HAp) as an absorbent show very efficient results towards purification of water. In this context researches illustrated that the Apatites possess well characterized surface properties and show potential of reacting with heavy metals. The reactions show both surface sorption reactions and precipitation reactions [13, 14]. The sorption of the divalent ions is governed by the ion exchange method. Ca^{2+} of the hydroxyapatite lattice is exchanged with Zn^{2+} and Cd^{2+} which caters its adsorption [15, 16]. The research suggested that dissolution with precipitation was more prominent towards the adsorption of Pb^{2+} ions rather than ion-exchange mechanism [17]. Heavy metals while reacting with the apatite minerals, first forms a poorly crystalline solid solution, which gradually then transforms to the purer and more highly crystalline products [18]. There are wide number of researches available to choose adsorbents for the purification of water. Amuda et al. [19] proposed composite absorbents made up of coconut shell carbon along with the chitosan and/ or oxidizing agent that have huge potential towards purification of water. These composites efficiently remove the zinc (II) present in synthetic industrial water. In the investigation the parameters like ion concentration zinc (II), pH and adsorbent concentration were varied and analyzed. Kadirvelu et al. [20] used chemical activation processes to extract the activated carbon from coirpith. The extracted activated carbon were used for the adsorption of heavy metals Cu(II), Pb(II), Ni(II), Cd(II) and Hg(II). Coir processing industries have huge wastage of coirpith as a waste. So, it may be available at cheaper rate that influences to develop cheaper absorbent. The analysis of adsorption showed that when pH from 2 to 6 increases the percent adsorption of heavy metals was found to be increase. Abdallah et al. [21] studied the purification of surface seawater in El-Max Bay through the bio-sorption of chromium, mercury, cadmium and lead ions present. The bio sorbent used was hybrid active carbon prepared by chemical treatment through acid, base followed by redox reaction. These sorbents were also processed through the surface loading of baker's yeast biomass which increased the adsorption capacity. Recent work on HAp as a absorbent is also shown by Balasooriya et al [22] and Zhu et al. [23].

In spite of availability of so many adsorbents it is incumbent upon researchers to come up with the new adsorbents which can be easily synthesized, is less expensive and can be effectively remove the copper from water. In this article, hydroxyapatite (HAp) is used as an adsorbent for complete elimination of copper (II) present in water. The article focused on HAp because it can easily be synthesized at cheaper cost by using bio wastes like fish scales, egg shells, animal bones or teeth etc. This will serve the dual purpose of waste minimization and pollutant treatment. Thus we will be having a waste to wealth approach through this. Hence an endavour has been made to see the absorption capability of HAp towards removal of copper ion from water.

2. SYNTHESIS OF HAP THROUGH CHEMICAL ROUTE

In this investigation the chemical used for preparation of HAp was Di-ammonium hydrogen phosphate, Calcium nitrate tetrahydrate and Ammonium hydroxide solution. The requisite amounts of chemicals were taken in an open beaker. The chemicals were mixed together in distilled water to form aqueous solution. The formed aqueous solution was further mixed with 0.1 molar ammonium hydroxide solutions to develop the precipitate of HAp. After formation of precipitate the water was decanted with help of filter unite. Wahtman filter paper was used during filtration. After filtration the cake was collected and placed in an hot environment for next 24 h. After drying the HAp powders having lump or bigger grain sizes were crushed manually using mortar pestle. After crushing the powders were decomposed at 1000 °C inside an high temperature furnace for calcination. The calcined powders were mechanically milled in an alcoholic media for 8 h inside an planetary ball mill to get fine sizes. Alumina balls were used for milling the HAp powders. The fine size powders collected from ball mill was again placed in hot environment also for 24 h. After drying again the powders were decomposed at 1000 °C to obtained crystalline morphology of HAp powder.

2.1. Set-up developed:

To carried out the experiments a filter unit has been developed by using plastic container. The systematic pictorial representation of the filter unit is shown in Figure 1. The filter unite having two PVC container capacity 10L has been taken. The cartridge used in it was of hydroxyapatite (HAP) powders inclusion with activated charcoal to enhance the porosity. Angular shaped activated charcoal was taken. The size of activated charcoal being larger than the powdered HAP, it was expected that the flow rate will improve after using it. The powdered HAP and activated charcoal were layer by layer filled up in the candle container. For the improvement in flow rate the pressure of the flow was also required to be increased. This being a gravity type flow system the pressure increment was done by increasing the height of the upper container. To carried out the experiments different concentrations of copper (II) contaminated water were prepared i.e. 3, 5, 6, 7 and 8 mg/l.

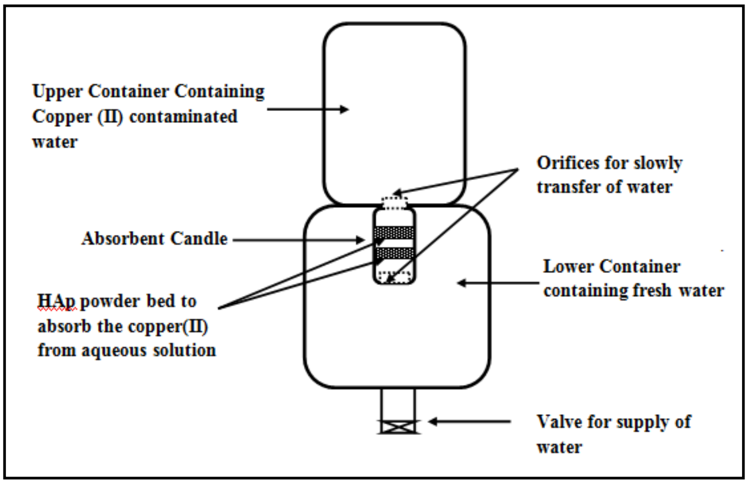

Figure 1. Experimental set up for removal of Copper (II) ion from aqueous solution

3. RESULTS AND DISCUSSION

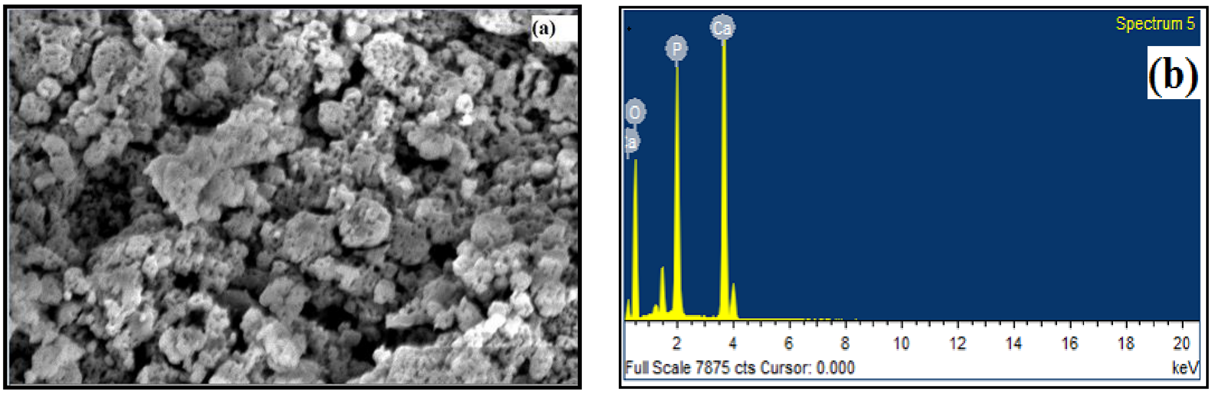

Figure 2. (a) FESEM image of HAp powder (b) EDX of Hap

The microstructure of developed HAp is shown in Figure 2. The EDX analysis confirms the presence of calcium and phosphorous in homogeneous amount throughout the matrix. The particles sizes were also uniform that resembles a good morphology of developed HAp powders.

3.1. Analysis on HAp as an Absorbent

The adsorption study of varying copper ion concentration on the same HAp dose with different contact time was observed. The different concentrations were of 3, 5, 6, 7 and 8 mg/l. In this analysis, the amount of HAp taken to investigate was 0.05 mg while the volume of water was 100 mL. The result illustrate that the when the concentration of ion was increases the percentage removal of copper (II) was decreases. This mainly happened due to presence of high ions of copper abruptly exposed to the HAp powder that consumes more time for settlement. The interesting result was observed with high concentration of copper (II) ions in water that requires high driving force during flow. The resistance offered by the mass of copper (II) ions provides favourable condition during purification of Copper through HAp powders [24-27]. The said resistance offer more time for the trapping of Copper (II) ions. Hence, with high concentration high purification was observed. The graph for the adsorption study has been shown Figure 3. The removal of copper ions found to be efficient for high concentration. The adsorption capacity at equilibrium for different concentrations has been tabulated in Table 1.

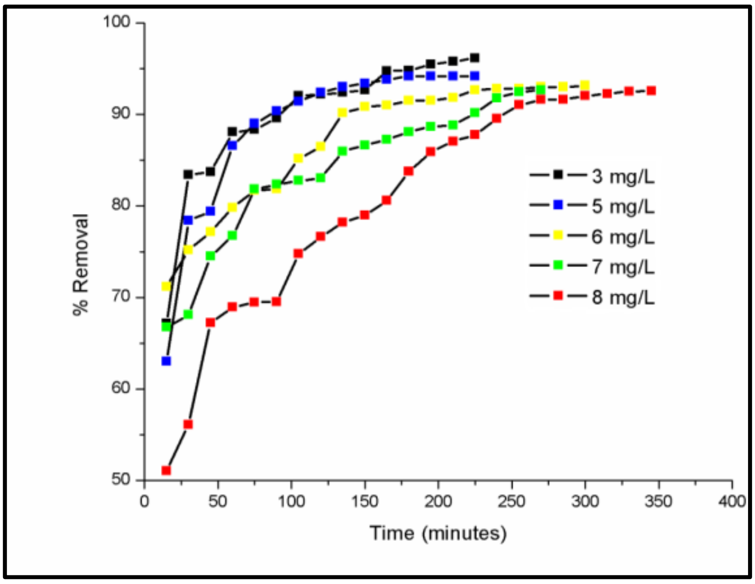

Figure 3. Removal of various initial copper ion concentration variations with time

Table 1. The removal efficiency, adsorption capacity and equilibrium concentration corresponding to different initial copper concentration.

Sl. No.	**Initial Concentration of Copper (mg/L)**	**% removal**	**Equilibrium adsorption Capacity (mg/g)**	**Equilibrium copper concentration (mg/L)**
1	3	96.17	5.77	0.1147
2	5	94.2	9.42	0.29
3	6	93.17	11.16	0.41
4	7	92.65	12.97	0.5145
5	8	92.54	14.82	0.5961

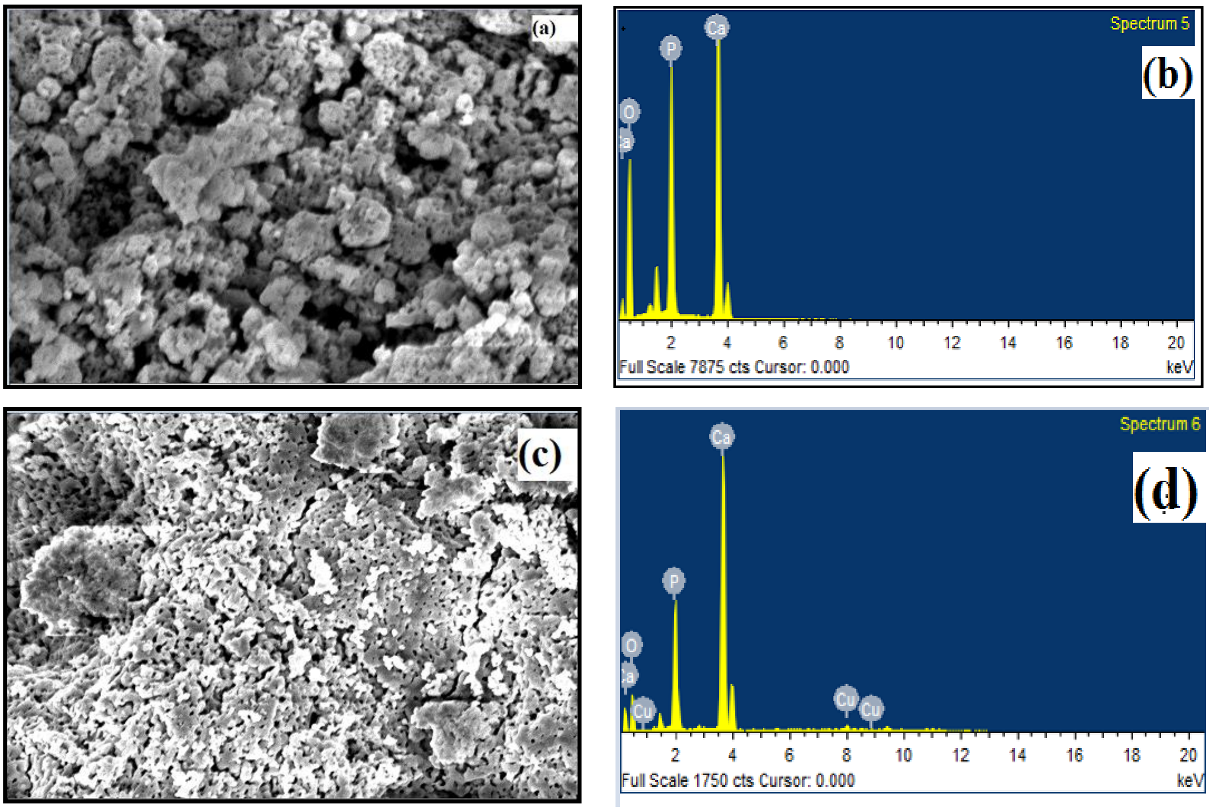

Figure 4. (a) FESEM image of HAP before adsorption, (b) EDX analysis of HAP before adsorption, (c) FESEM image of HAP after adsorption, and (d) EDX analysis of HAP after adsorption

From the above figure 4 it infer that in figure 4(b) there is no peak of copper while it is present in figure 4 (d). The composition of copper in HAp before adsorption is 0% but in the HAp after adsorption it is about 3% by weight. This can be seen in Table 2.

Table 2. Elemental composition of HAP and copper adsorbed HAP as per EDX analysis.

Elements	Before Adsorption		After Adsorption	
	% Weight	% Atom	% Weight	% Atom
O	56.8	74.85	34.86	56
P	15.67	10.67	13.96	11.59
Ca	27.54	14.49	48.06	30.93
Cu	0	0	3.16	1.28

5. CONCLUSION

This study successfully demonstrated the preparation of HAp power through chemical synthesized route. Furthermore a filter unite alongside cartridge has been develop for the entrapment of copper (II) ions from polluted or industrial contaminated water. The experiments successfully show that the presence of HAp efficiently removed the copper (II) ion from water. The amount of HAp have significant role towards removal of the copper ion. Hence, it can be concluded that the HAp is used as an efficient absorbent for removal of heavy metal from water.

Acknowledgement

The authors willing to thank theHoD and Director of GITM, Lucknow, U.P. for providing continuous support for completion of this article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

[1] Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of environmental management*, *92*(3), 407-418.

[2] Sud, D., Mahajan, G., & Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions–A review. *Bioresource technology*, *99*(14), 6017-6027.

[3] Gandhi, M. R., Kousalya, G. N., &Meenakshi, S. (2011). Removal of copper (II) using chitin/chitosan nano-hydroxyapatite composite. *International Journal of Biological Macromolecules*, *48*(1), 119-124.

[4] Kiran, B., &Thanasekaran, K. (2011). Copper biosorption on Lyngbyaputealis: application of response surface methodology (RSM). *International Biodeterioration& Biodegradation*, *65*(6), 840-845.

[5] Dąbrowski, A., Hubicki, Z., Podkościelny, P., &Robens, E. (2004). Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere*, *56*(2), 91-106.

[6] Varma, G., Singh, R. K., &Sahu, V. (2013). A comparative study on the removal of heavy metals by adsorption using fly ash and sludge: a review. *International Journal of Application or Innovation in Engineering and Management*, *2*(7), 45-56.

[7] Wafwoyo, W., Seo, C. W., & Marshall, W. E. (1999). Utilization of peanut shells as adsorbents for selected metals. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, *74*(11), 1117-1121.

[8] Doyurum, S., &Celik, A. (2006). Pb (II) and Cd (II) removal from aqueous solutions by olive cake. *Journal of Hazardous Materials*, *138*(1), 22-28.

[9] Banat, F., Al-Asheh, S., & Al-Rousan, D. (2002). A comparative study of copper and zinc ion adsorption on to activated and non-activated date-pits. *Adsorption Science & Technology*, *20*(4), 319-335.

[10] Malkoc, E., &Nuhoglu, Y. (2005). Investigations of nickel (II) removal from aqueous solutions using tea factory waste. *Journal of hazardous materials*, *127*(1-3), 120-128.

[11] Abdel-Ghani, N. T., Hefny, M., & El-Chaghaby, G. A. (2007). Removal of lead from aqueous solution using low cost abundantly available adsorbents. *International Journal of Environmental Science & Technology*, *4*(1), 67-73.

[12] Šćiban, M., &Klašnja, M. (2004). Wood sawdust and wood originate materials as adsorbents for heavy metal ions. *HolzalsRoh-und Werkstoff*, *62*(1), 69-73.

[13] Somasundaran, P., & Wang, Y. H. C. (1984). Surface chemical characteristics and adsorption properties of apatite. In *Adsorption on and surface chemistry of hydroxyapatite* (pp. 129-149). Springer, Boston, MA.

[14] Chander, S., &Fuerstenau, D. W. (1984). Solubility and interfacial properties of hydroxyapatite: a review. *Adsorption on and surface chemistry of hydroxyapatite*, 29-49.

[15] Suzuki, T., Hatsushika, T., & Hayakawa, Y. (1981). Synthetic hydroxyapatites employed as inorganic cation-exchangers. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, *77*(5), 1059-1062.

[16] Peld, M., Tõnsuaadu, K., & Bender, V. (2004). Sorption and desorption of Cd2+ and Zn2+ ions in apatite-aqueous systems. *Environmental science & technology*, *38*(21), 5626-5631.

[17] Prasad, M., &Saxena, S. (2004). Sorption mechanism of some divalent metal ions onto low-cost mineral adsorbent. *Industrial & engineering chemistry research*, *43*(6), 1512-1522.

[18] Kohn, M. J., Rakovan, J., & Hughes, J. M. (2002). Reviews in Mineralogy and Geochemistry. *Reviews in Mineralogy and Geochemistry*, *48*(1), 455-488.

[19] Amuda, O. S., Giwa, A., & Bello, I. A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering Journal*, *36*(2), 174-181.

[20] Kadirvelu, K., Thamaraiselvi, K., &Namasivayam, C. (2001). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource technology*, *76*(1), 63-65.

[21] Abdallah, M. A. M., Mahmoud, M. E., Osman, M. M., & Ahmed, S. B. (2017). New biosorbent in removing some metals from industrial wastewater in El Mex Bay, Egypt. *Applied Water Science*, *7*(4), 1931-1942.

[22] Balasooriya, I. L., Chen, J., KoraleGedara, S. M., Han, Y., &Wickramaratne, M. N. (2022). Applications of Nano Hydroxyapatite as Adsorbents: A Review. *Nanomaterials*, *12*(14), 2324.

[23] Zhu, Z., Yang, Y., Fan, Y., Zhang, L., Tang, S., Zhu, Y., & Zhou, X. (2022). Strontium-doped hydroxyapatite as an efficient adsorbent for Cd (II) removal from wastewater: Performance, kinetics, and mechanism. *Environmental Technology & Innovation*, *28*, 102575.

[24] Voudrias, E., Fytianos, K., &Bozani, E. (2002). Sorption–desorption isotherms of dyes from aqueous solutions and wastewaters with different sorbent materials. *Global Nest Int. J*, *4*(1), 75-83.

[25] Mohan, S. V., &Karthikeyan, J. (1997). Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal. *Environmental Pollution*, *97*(1-2), 183-187.

[26] Gokulsai, S. (2022). Studies on Stirling power cycles- A Review. *Journal of Advanced Mechanical Sciences*, *1*(2), 47-51.

[27] Pratap, A., Singh, B. K., &Sardana, N. (2022). Fracture in self-lubricating inserts: A case study. *Materials Today: Proceedings*.