Elimination of copper (II) and lead (II) from wastewater using porous HAp: Comparative study

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Abstract

Adsorption phenomena are operative in the most normal physical, biological, and chemical systems. These adsorption operations have been widely applied in the industrial fields, drinking water purification and wastewater treatment. Elemental analyzes of water from drinking water treatment plants indicate the presence of many chemical elements, sometimes toxic, in significant concentrations. Moreover, in most cases, the presence of lead (II) and copper (II) in large quantities in drinking water generally poses a problem and can even be toxic, which makes its elimination necessary. Thus, the preparation of solid matrices capable of trapping these pollutants then proves to be of interest. For this, we synthesized using the method of precipitation of porous hydroxyapatite (HAp). The characterization of HAp by X-ray diffraction and also the study of the specific surface showed that the hydroxyapatites have a large specific surface and a disordered structure. This HAp was used as an adsorbent of Cu^{2+} and Pb^{2+} ions present in aqueous solutions. Pseudo-first-order and pseudo-second-order kinetics as well as Langmuir and Freundlich isothermal models were studied to confirm the mechanism of heavy metal adsorption on HAp.

Keywords: Pollutants, Hydroxyapatite, Copper (II), Lead (II), Adsorption

1. Introduction

In natural aquatic ecosystems, metals are found in low concentrations, usually in the order of nanograms or micrograms per liter [1]. In recent times, however, the presence of contaminating heavy metals, especially heavy metals at concentrations above natural loadings, has become a problem of increasing concern[2]. This is due to rapid population growth, increased urbanization, the expansion of industrial activities, exploration and exploitation of natural resources, the extension of irrigation and the spread of other modern agricultural practices, as well as the lack of environmental regulations[3] [4] [5]. Unlike other pollutants, such as petroleum-derived hydrocarbons, and the waste that invades the environment in plain sight, heavy metals build up surreptitiously, eventually reaching toxic levels [6] [7]. As industrial and urban activities are expected to increase in all parts of the continent, this issue now assumes even greater importance [8]. Some heavy metals, such as Zn, Cu, Mn and Fe, are essential for the growth and well-being of living organisms, including humans [9]. However, they can be expected to have toxic effects when organisms are exposed to higher levels of concentration than they normally require [10]. Other elements, such as Pb, Hg and Cd, are not essential

for metabolic activities and exhibit toxic properties [11]. Metals can be absorbed in the inorganic form or the organic form. For some elements, such as arsenic and copper, the inorganic form is the most toxic [12]. For others, like Hg, Sn and Pb, the organic forms are the most toxic [13]. At low concentrations, many heavy metals, including Hg, Cd, Pb, As and Cu inhibit photosynthesis and phytoplankton growth. Effects observed at higher trophic levels include delayed embryo development, malformations and poorer adult growth in fish, mollusks and crustaceans [14].

Over the past twenty years, many studies have been devoted to the toxicity of metals; Based on these results, several international and national organizations have developed water quality criteria for aquatic life [15]. For this, several researchers have worked on the elimination of heavy metals found in wastewater using different treatment methods namely, exchange [16], [17], chemical precipitation[18] and adsorption [19]. Adsorption is the most universal technique of all available physical techniques [20]. It is fast, efficient and inexpensive to set up and operate, so adsorption can be used for a wide variety of different treatments [21]. Research is already carried out on a wide variety of adsorbents such as

activated carbon, carbon nanotubes, zeolites, clays, and apatites [22]. In this context, porous hydroxyapatites were synthesized by the precipitation method at a temperature of 25°C, this synthesized HAp was used as adsorbents of heavy metals Cu(II) and Pb(II) found in the aqueous medium. An analysis by BET and XRD was carried out to study the specific surface and the crystal structure of the synthesized Hydroxyapatite. The following results show us that HAp has a high retention capacity for heavy metals.

2. Materials and methods

2.1. Materials

Porous hydroxyapatite (HAp) is prepared by the neutralization method of calcium hydroxide $Ca(OH)_2$ and by ammonium dihydrogen phosphate $NH_4H_2PO_4$ at room temperature and in an aqueous medium [16]. 20 grams of $Ca(OH)_2$ was dissolved in a volume of 200 mL of distilled water and then stirred for 1h30 min at room temperature (Solution 1). And, A mass of 18.6334 g of ammonium dihydrogen phosphate $NH_4H_2PO_4$ was dissolved in a mixture of 200 mL of distilled water (Solution 2). Finally, solution 2 was added to solution 1, and the reaction mixture was left under stirring for 48 hours. The precipitate obtained is filtered off under a vacuum and dried in an oven at a temperature of 100° C. overnight.

$$10(OH)_2 + 6\ NH_4H_2PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 6\ NH_4OH + 12\ H_2O$$

2.2. Characterization of adsorbent

The surface area of synthesized HAp was calculated according to the Brunauer-Emmett-Teller (BET) method using adsorption data in the relative range of 0.05 to 0.25, and the distribution was determined using the approximation of Barret-Joyner-Halenda (BJH) in the mesoporous range. Characterization by X-ray diffraction (Philips PW131 diffractometer, Cu Kα radiation) was made, to study the crystal structure of HAp. And to determine the characteristic bands of HAp, an analysis of the infrared spectra recorded on a spectrophotometer, (Bruker counter, IFS 66v FT-IR) with a resolution of 2 cm^{-1} was carried out.

2.3. Batch adsorption experiments

Discontinuous adsorption experiments were carried out in a volume of 100 ml taking an initial concentration of Cu^{2+}, Pb^{2+} of 20 mg/L and a mass of HAP of 0.2 g at a pH=5, the pH of the solution was adjusted to the desired point using solutions of 0.1 N HCl and 0.1 N NaOH. The solution was stirred at 160 rpm for a period of 30 min to reach equilibrium. The suspensions taken were then centrifuged at 4000 rpm for 20 min to eliminate the adsorbents and then analyzed by an atomic absorption spectrophotometer. The percent removal of Cu (II), and Pb(II) was calculated using the following equation:

$$\%R = \frac{Ci - Ct}{Ci} \times 100$$

Where: Ci and Ct are the Cu(II), and Pb(II) concentrations (mg/L) at the initial state and a given instant t respectively. The adsorption capacity was determined using the equation:

$$qe = \frac{Ci - Ce}{m} \times V$$

Where V is the volume of the solution, Ci is the initial concentration (mg/l), Ce is the equilibrium concentration (mg/l) and m is the mass of Hap (g).

3. Results and discussion

3.1. Characterization of synthesized HAp

To know the specific surface of synthesized HAp, the distributions of the pores on the surface of the hydroxyapatite and the isotherms of adsorption-desorption of N$_2$ (BET) were established. The results obtained show that the variation in reaction temperature influences the specific surface of the Hap. Hence, at a temperature of 25°C, the specific surface of HAp is equal to 235 (m²/g), and at a temperature of 70°C and 90°C, the specific surface is equal to 151 (m²/g) and 108 (m²/g), respectively. Then, the specific surface of the synthesized hydroxyapatite decreases by increasing the temperature of the reaction. X-ray diffraction shows that the HAp is poorly crystallized, and the crystalline phase develops by increasing the temperature of the reaction. XRD also shows that HAp consists of an apatitic phase and the lines are indexed in the hexagonal system of space group P6$_{3/m}$.7. To identify the characteristic bands of synthesized HAp, an analysis by infrared spectroscopy was carried out. Table 1 shows the characteristic bands indicated by the infrared spectra.

3.2. Adsorption studies

The process of adsorption of the Pb^{2+} and Cu^{2+} ions on the apatite is ensured by bringing 0.2 g of the apatite studied into contact with 100 mL of the lead Pb (II) and copper (II) solution. desired at a temperature of 30°C.

3.2.1. Effect of contact time

Samples were taken at time intervals, then filtered through a micro-filter with a diameter of 0.45 μm, and then analyzed by atomic absorption spectrophotometry.
During this study, we were interested in the kinetics of the phenomenon of adsorption of Pb^{2+} and Cu^{2+} ions by synthesized hydroxyapatites. The supernatant solution is instantly analyzed. In Figure 1, we see that the equilibrium time is quickly reached, after about 20 min. The equilibrium plateau is linked to the number of active sites present in a mass of 0.2 g of p-HAp and its saturation by the Pb^{2+} and Cu^{2+} ions [23].

3.2.2. Kinetic study

During this study, we are interested in the kinetics of the adsorption phenomenon of Pb^{2+} and Cu^{2+} ions by hydroxyapatite. The supernatant solution is instantly analyzed.During this study, we are interested in the kinetics of the adsorption phenomenon of Pb^{2+} and Cu^{2+} ions by hydroxyapatite. The supernatant solution is instantly analyzed. Figure 2 groups the linear representations of log(qe-qt) and t/qt as a function of time relating to the adsorption of copper (II) and lead (II) on the synthesized hydroxyapatite. The adsorption rate constants of Cu (II) and Pb (II) are determined graphically (Figure 2).

Table 1: Characteristics of bonds of HAP

Wave number (cm^{-1})	Characteristics bonds
510	PO_4^{3-}
1000	CO_3^{2-}
3500	HO^-

Table 2: Cu^{2+} and Pb^{2+} adsorption parameters on HAp according to the Langmuir and Freundlich model

		Cu(II)	Pb(II)
Langmuir isotherm	$q_{e,max}$	2.40	2.49
	β	0.42	0.48
	R²	0.9938	0.998
	1/n	0.3678	0.3145
Freundlich isotherm	lnK_f	0.1559	0.0157
	R²	0.8976	0.952
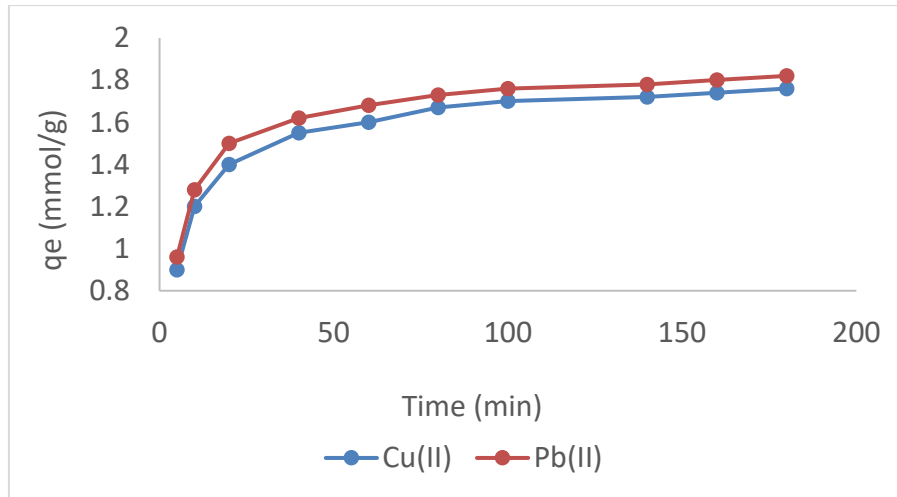
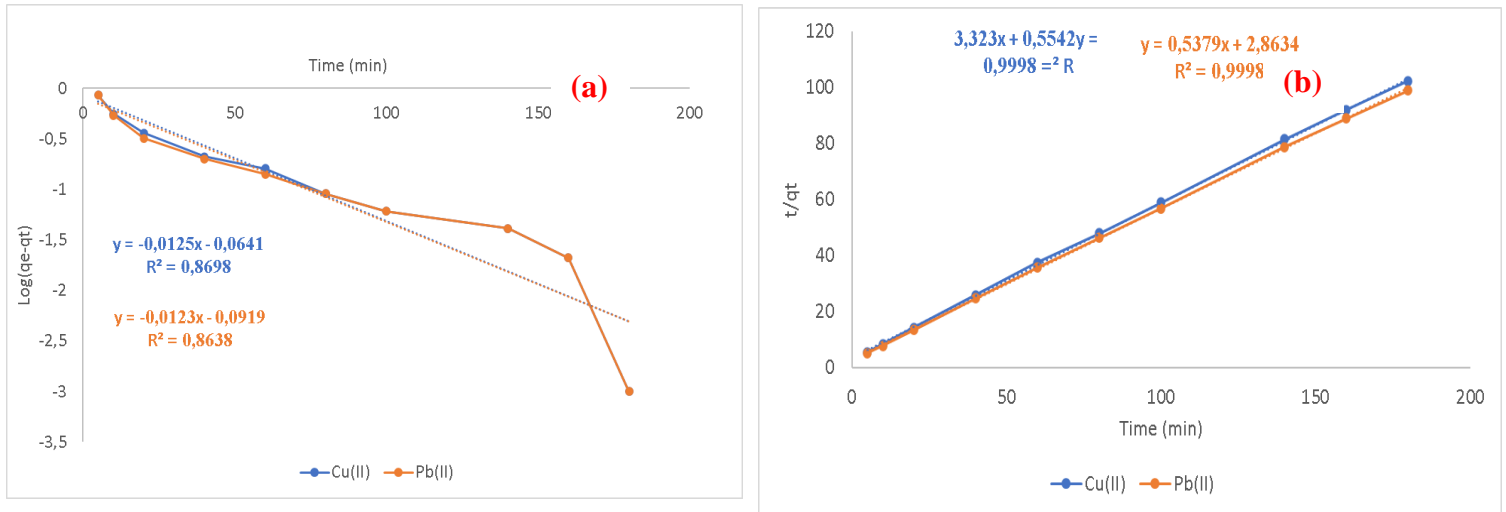**Figure 1**: Effect of contact time of Pb(II) and Cu(II) on HAp

Figure 2: Linear representations of the (a) pseudo-first-order and (b) pseudo-second-order kinetic model for HAP
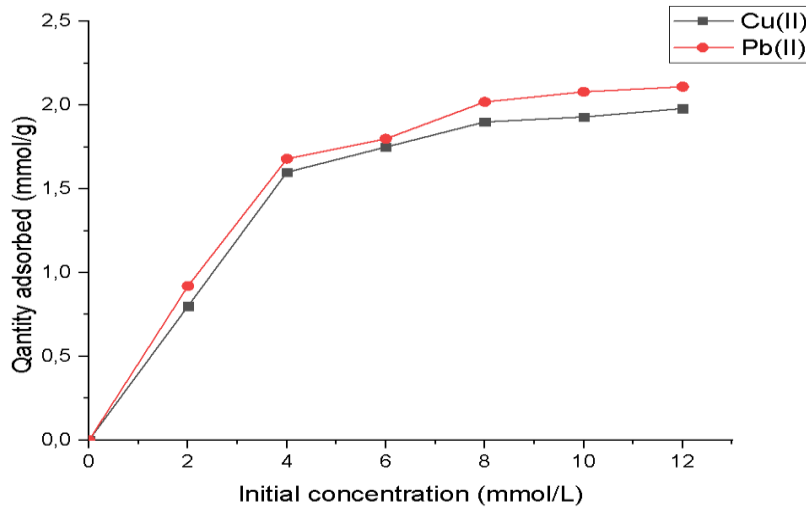

Figure 3: Effect of the initial concentration of Pb^{2+} and Cu^{2+} on the adsorption capacity of Hap
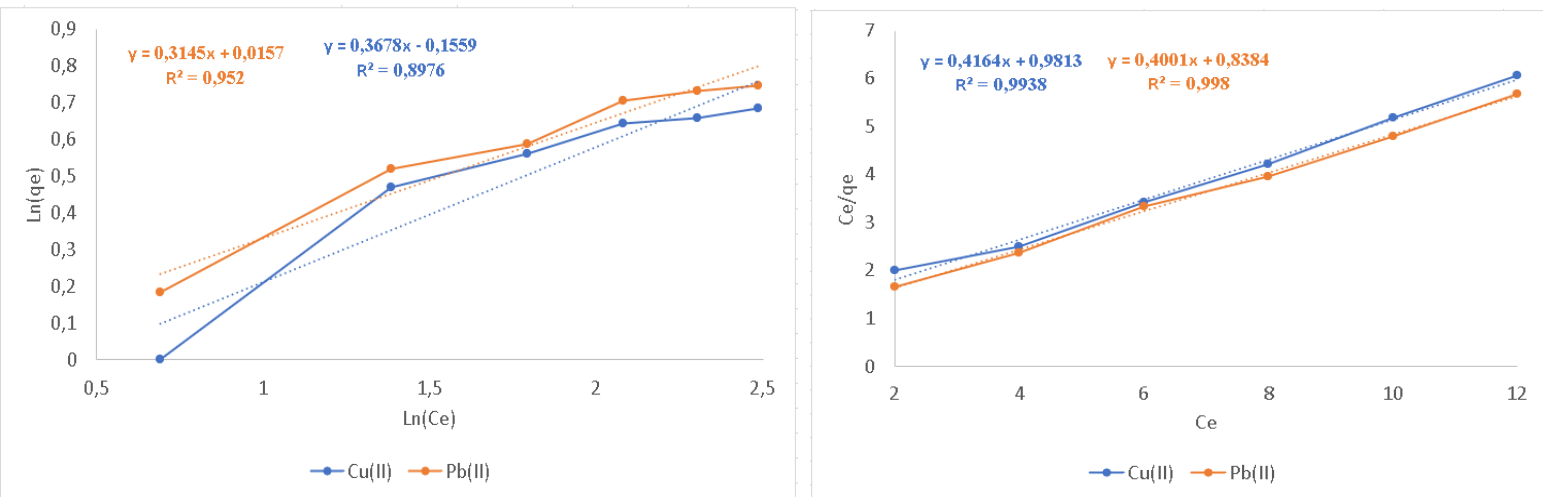

Figure 4: Model of the (a) Freundlich, (b) langmuir isotherms of HAp

From Figure 2, we can conclude that the pseudo-second-order equation gives the best correlation coefficient (R^2=0.9998) for the two pollutants (Cu^{2+} and Pb^{2+}), while the pseudo-first-order equation -order yields a low correlation coefficient (0.8638 and 0.8698 for Pb^{2+} and Cu^{2+}, respectively.) This suggests that chemical adsorption is the rate-limiting step for either adsorption process [24].

3.2.3. Effect initial concentration

Figure 1 shows the effect of the initial concentration of lead (II) and copper (II) on the adsorption capacity of the synthesized hydroxyapatite. Figure 3 shows us that the adsorbed quantity of Cu^{2+} ions and Pb^{2+} ions by HAp increases with the increase in the initial concentration of these ions, until a saturation plateau is obtained at 8 mmol/L for Cu^{2+} and also for Pb^{2+} with a maximum adsorption amount of 1.9 and 2.02 for Cu^{2+} and Pb^{2+}, respectively. The saturation plateau indicates that after a concentration of 8 mmol/L the active sites of the HAp have been exhausted, this is why the maximum adsorbed quantity is reached [25].

3.2.4. Isotherms models

From Figure 4 and Table 2 and based on the correlation coefficients (R^2) relating to the linearity of the lines of the adsorption isotherms of the two models, we can conclude that the Langmuir model is the most probable to characterize the adsorption of Pb^{2+} and Cu^{2+} ions on HAp. The value of the maximum adsorbed quantity $q_{e, max}$ is in good agreement with the maximum experimental value of the quantity of Pb^{2+} and Cu^{2+} ions adsorbed. This shows that HAp has a high affinity towards Pb^{2+} and Cu^{2+} ions.
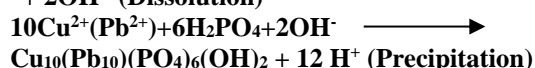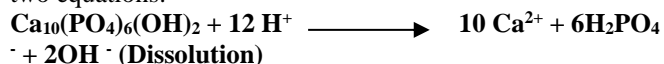
The adsorption process depends on the specific surface and therefore on the number of active sites present on the surface of the adsorbent. The mechanism of adsorption of Pb(II) and Cu(II) ions on HAp could therefore mainly be a combination of the three mechanisms, starting with the Complexation of Pb^{2+} and Cu^{2+} ions at the surface of the apatitic solid according to the following：
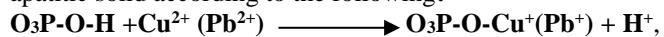
$O_3P\text{-}O\text{-}H + Cu^{2+} (Pb^{2+}) \longrightarrow O_3P\text{-}O\text{-}Cu^+(Pb^+) + H^+$, followed by ion exchange between the Pb2+ and Cu2+ ions contained in the contaminated solution and the Ca2+ ions present in the solid. This ionic exchange takes place thanks to a dissolution of the apatite followed by precipitation according to the equation below:

$Ca_{10}(PO_4)_6(OH)_2 + x\ Cu^{2+} (Pb^{2+}) \longrightarrow$
$Ca_{10\text{-}x}Cu_x(Pb_x)(PO_4)_6(OH)_2 + x\ Ca^{2+}$
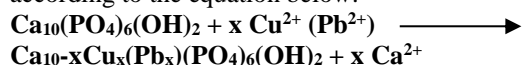
Then a dissolution-precipitation, the dissolution of the hydroxyapatite followed by the precipitation of a lead phosphate and copper phosphate according to the following two equations:

$Ca_{10}(PO_4)_6(OH)_2 + 12\ H^+ \longrightarrow 10\ Ca^{2+} + 6H_2PO_4^- + 2OH^-$ (Dissolution)

$10Cu^{2+}(Pb^{2+})+6H_2PO_4+2OH^- \longrightarrow$
$Cu_{10}(Pb_{10})(PO_4)_6(OH)_2 + 12\ H^+$ (Precipitation)

4. Conclusions

During this study, we have shown that it is possible to obtain apatites with large specific surface areas by preparing very fine particles using an appropriate method. Indeed, a porous hydroxyapatite HAp, with a very large specific surface, was prepared by precipitation at 25°C in a water-ethanol medium using the method of rapid neutralization of $Ca(OH)_2$ by $NH_4H_2PO_4$. The crystal

structure of the synthesized HAp and the specific surface area as well as the characteristic bands of these hydroxyapatites were studied by X-ray, BET and IR diffraction, respectively. The study of the behavior of porous apatites in an environment loaded with harmful elements is also studied.

The removal of lead and copper from an aqueous solution by apatite HAp is successful. To show the effect of the specific surface and consequently the crystallinity on the phenomenon of adsorption of the Pb^{2+} and Cu^{2+} ions, we compared the power of the trapping of the Pb^{2+} ions and the Cu^{2+} ions of the porous hydroxyapatite prepared. We have thus shown that the retention capacity of Pb(II) and Cu(II) ions by the porous apatite HAp is very important.

Finally, we studied the modeling of the phenomenon of adsorption of Pb^{2+} and Cu^{2+} ions on HAp according to the models of Langmuir and Freundlich. We noticed that in the case of the two ions, only the Langmuir model correlates well with the experimental points we have. Based on the correlation coefficients (R^2) relating to the linearity of the lines of the adsorption isotherms of the two models, we concluded that the Langmuir model is the most likely to characterize the adsorption of Pb(II) and Cu(II) ions by HAp. The very encouraging results of the phenomenon of adsorption Pb^{2+} and Cu^{2+} by the porous apatites that we have synthesized and characterized allow us to think that these apatitic materials could be advantageously used in the fields of catalysis of certain chemical reactions, depollution wastewater and industrial effluents or bone substitution.

Competing interests

The authors declare that they have no competing interests.

References

[1] L. Stetten, A. Mackevica, N. Tepe, T. Hofmann, and F. von der Kammer. (2022). Towards Standardization for Determining Dissolution Kinetics of Nanomaterials in Natural Aquatic Environments: Continuous Flow Dissolution of Ag Nanoparticles. Nanomaterials. 12(3): 519. doi: 10.3390/nano12030519.

[2] M. Mariana *et al.*, (2021). Recent advances in activated carbon modification techniques for enhanced heavy metal adsorption. Journal of Water Processing Engineering. 43: 102221. doi: 10.1016/j.jwpe.2021.102221.

[3] N. Akhtar, M. I. Syakir Ishak, S. A. Bhawani, and K. Umar. (2021). Various Natural and Anthropogenic Factors Responsible for Water Quality Degradation: A Review. Water. 13 (19): 2660. doi: 10.3390/w13192660.

[4] D. Fróna, J. Szenderák, and M. Harangi-Rákos, (2021). Economic effects of climate change on

global agricultural production. Natural Conservation Research. .44: 117–139. doi: 10.3897/natureconservation.44.64296.

[5] A.Y. Ahmad and M.A. Al-Ghouti. (2020). Approaches to achieve sustainable use and management of groundwater resources in Qatar: A review. Groundwater for Sustainable Development. 11: 100367. doi: 10.1016/j.gsd.2020.100367.

[6] I. Ayouch, I. Barrak, Z. Kassab, M. El Achaby, A. Barhoun, and K. Draoui. (2020). Impact of the drying process on the efficiency of alginate beads for cadmium removal from water: Kinetic, isotherm and thermodynamic study. Environmental Technology and Innovation. 20: 101157. doi: 10.1016/j.eti.2020.101157.

[7] C.S. Hsu and P.R. Robinson. (2019). Safety and Environment. Petroleum Science and Technology. pp. 395–480. doi: 10.1007/978-3-030-16275-7_18.

[8] J. Schmale et al., (2018). Local Arctic Air Pollution: A Neglected but Serious Problem. Earths Future. 6 (10): 1385–1412. doi: 10.1029/2018EF000952.

[9] H. Ali, E. Khan, and I. Ilahi. (2019). Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. Journal of Chemistry. 1-4. doi: 10.1155/2019/6730305.

[10] H. Zhang and M. Reynolds. (2019). Cadmium exposure in living organisms: A short review. Science of Total Environment 678: 761–767. doi: 10.1016/j.scitotenv.2019.04.395.

[11] H. M. Huseen and A. J. Mohammed. (2019). Heavy Metals Causing Toxicity in Fishes. Journal of Physics: Conference Series. 1294 (6): 062028. doi: 10.1088/1742-6596/1294/6/062028.

[12] J. Briffa, E. Sinagra, and R. Blundell. (2020). Heavy metal pollution in the environment and their toxicological effects on humans. Heliyon. 6 (9): e04691. doi: 10.1016/j.heliyon.2020.e04691.

[13] D. Raj and S. K. Maiti. (2020). Sources, bioaccumulation, health risks and remediation of potentially toxic metal(loid)s (As, Cd, Cr, Pb and Hg): an epitomised review," Environmental Monitoring and Assessment. 192 (2): 108. doi: 10.1007/s10661-019-8060-5.

[14] Z. Rahman and V. P. Singh. (2019). The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. Environmental Monitoring and Assessment. 191 (7): 419. doi: 10.1007/s10661-019-7528-7.

[15] R. Han, B. Zhou, Y. Huang, X. Lu, S. Li, and N. Li. (2020). Bibliometric overview of research trends on heavy metal health risks and impacts in 1989–2018. Journal of Cleaner Production. 276: 123249. doi: 10.1016/j.jclepro.2020.123249.

[16] S. Hussain and S. Ali. (2021). Removal of Heavy Metal by Ion Exchange Using Bentonite Clay," Journal of Ecological Engineering. 22 (1): 104–111. doi: 10.12911/22998993/128865.

[17] U. Ipek. (2005). Removal of Ni(II) and Zn(II) from an aqueous solutionby reverse osmosis. Desalination. 174 (2): 161–169. doi: 10.1016/j.desal.2004.09.009.

[18] Q. Chen, Y. Yao, X. Li, J. Lu, J. Zhou, and Z. Huang. (2018). Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. Journal of Water Processing Engineering. 26: 289–300. doi: 10.1016/j.jwpe.2018.11.003.

[19] T. Kouznetsova et al., "Sorption and mechanism studies of Cu2+, Sr2+ and Pb2+ ions on mesoporous aluminosilicates/zeolite composite sorbents," Water Science and Technology. 82 (5): 984–997. doi: 10.2166/wst.2020.407.

[20] V.E. Pakade, N.T. Tavengwa, and L.M. Madikizela. (2019). Recent advances in hexavalent chromium removal from aqueous solutions by adsorptive methods. RSC Advances. 9 (45). 26142–26164. doi: 10.1039/C9RA05188K.

[21] W. S. Chai et al., (2021). A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. Journal of Cleaner Production. 296: 126589. doi: 10.1016/j.jclepro.2021.126589.

[22] F.S.A. Khan et al., (2021). A comprehensive review on magnetic carbon nanotubes and carbon nanotube-based buckypaper for removal of heavy metals and dyes. Journal of Hazardous Materials. 413: 125375. doi: 10.1016/j.jhazmat.2021.125375.

[23] A.A. Keirudin, N. Zainuddin, and N.A. Yusof. (2020). Crosslinked Carboxymethyl Sago Starch/Citric Acid Hydrogel for Sorption of Pb2+, Cu2+, Ni2+ and Zn2+ from Aqueous Solution. Polymers. 12 (11): 2465. doi: 10.3390/polym12112465.

[24] A.R. Kaveeshwar, P.S. Kumar, E.D. Revellame, D.D. Gang, M.E. Zappi, and R. Subramaniam. (2018). Adsorption properties and mechanism of barium (II) and strontium (II) removal from fracking wastewater using pecan shell based activated carbon. Journal of Cleaner Production. 193. 1–13. doi: 10.1016/j.jclepro.2018.05.041.

[25] B.H.K. Azzaoui. (2022). Toxic heavy metals removal from river water using a porous phospho-calcic hydroxyapatite," Moroccan Journal of Chemistry. 10: 062-072. doi: 10.48317/IMIST.PRSM/MORJCHEM-V10I1.31752.