Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27187

224 (2021) 302–307
June

Lead sorption by Togo rock phosphate as a sustainable solution to metal water depollution

Koffi A. Degbe[a,*], Diyakadola D. Bafai[a], Moursalou Koriko[a], Sanonka Tchegueni[a], Chahid Lhoussaine[b], Mohamed El Meray[c], Mohamed Hafidi[d,e], Gado Tchangbedji[a]

[a]*Université de Lomé, Faculté Des Sciences, Centre d'Excellence Régional Villes Durables en Afrique (CERViDA), Laboratoire Gestion Traitement et Valorisation des Déchets (GTVD), BP: 1515, Lomé, Togo, Tel. (+228)90903765/99635405; emails: koffiagbegnigan@gmail.com (K.A. Degbe), maryba01@hotmail.com (D.D. Bafai), moursalou7@hotmail.com (M. Koriko), tchegsani@gmail.com (S. Tchegueni), tchangbedji@gmail.com (G. Tchangbedji)*

[b]*Laboratoire Régional de la Direction Régionale de Tensift, Office National de l'Electricité et de l'Eau Potable, Marrakech, Maroc, email: hocinchahid@yahoo.fr*

[c]*Université Cadi Ayyad, Faculté des Sciences Semlalia, Laboratoire Physico-Chimie des Matériaux et Environnement (LPCME), Maroc, email: elmer.elmeray@gmail.com*

[d]*Cadi Ayyad University, Faculty of Sciences Semlalia, Laboratoire of Microbial Biotechnologies, Agrosciences and Environment Team of Agrosciences and Environment, Marrakech, Morocco, email: hafidi.ucam@gmail.com*

[e]*Mohammed VI Polytechnic University, AgroBioScience Program, Benguerir, Morocco*

Received 22 October 2020; Accepted 2 February 2021

ABSTRACT

The excessive use of chemical inputs in agriculture for wastewater irrigation, both on the surface and the groundwater. These pollutants are from the organic or inorganic origin. The treatment of these wastewaters is therefore very important and this is a great concern to many sustainable development goals such as preservation of human health, environmental protection and access to drinking water and sanitation. In Togo, no study has been carried out on the sorption capacity of rock phosphate. This work will lay emphasis on the lead chemical pollutant elimination by sorption on a mineral sorbent, the rock phosphate of Togo. The physicochemical characterization of the material by techniques such as X-ray diffraction, IR spectroscopy, pH of zero charge, Brunauer–Emmett–Teller surfaces was performed. The majority phase is fluoroapatite and traces of clay minerals have been found. Its specific surface is 20.78 $m^2 g^{-1}$ and its pH_{PZC} = 6.82. The batch method was used for the sorption study. Several experimentation parameters having an impact on the sorption process of the pollutant such as the pH of the solution, time of contact, the amount of sorbent and the initial concentration of the pollutant have been studied. The results of our study show that the maximum sorption capacity of lead is 166.67 mg g^{-1} over the rock phosphate of Togo. The best sorption is obtained for pH values $\leq pH_{PZC}$. The equilibrium time is 30 min. In view of these different results, rock phosphate constitutes an alternative to commercial sorbent that costs a lot in the water treatment.

Keywords: Wastewater; Rock phosphate; Depollution; Lead; Sustainable development

1. Introduction

The metallic trace elements or heavy metals are natural elements present in all compartments of our environment: air, water and soil [1]. On the one hand, as traces, they are necessary for all living beings [2,3], but on the other hand, at high concentrations, they constitute a serious threat to the fauna, flora and human beings due to their bioaccumulation, their non-biodegradable property and their toxicity

---

* Corresponding author.

[4]. The lead (Pb^{2+}) is one of the most dangerous metallic trace elements for human health that has no favorable biological activity [5–9]. Exposure to lead can have harmful health effects and can even be fatal in high doses [3]. It can cause anemia, muscle weakness and damage to the kidneys, liver and nervous system [10,11]. The emission of lead in the environment (air, water and soil) is respectively 332, 138 and 796 thousand tons y^{-1} [12]. 10%–20% of the lead consumed by humans may originate from water. The rest may come from food and dust from the air [13].

Considering everything that has been said above, therefore, it is necessary to treat these wastewaters before their utilization or reutilization according to their origin. Several treatment methods are being developed to comply with or satisfy restrictive international standards. Coagulation and flocculation, oxidation process, membrane filtration, chemical precipitation, cationic exchange are often used [14,15]. In recent years, much work has been done on techniques for the sorption of pollutants on porous materials. The activated carbons have remained one of the best sorbents but its preparation is expensive. This is why research focused on more available natural materials.

Togo has a significant reserve of rock phosphate and its production is mainly assigned to the export market. No study has been carried out on the sorption capacity of this natural resource to test its capacity for sorption of metallic trace elements. Previous work on this material has focused on its physicochemical characterization [16] and dissolution [17]. It is in this context that this work has been undertaken. It will therefore be necessary to characterize Togo's rock phosphate in order to use it as a sorbent to reduce the polluting load of wastewater containing lead ions (Pb^{2+}). The isothermals of Langmuir and Freundlich are used to determine the maximum sorption capacity of the material. The kinetics of lead sorption, the influence of the amount of the sorbent and the pH of the solution have been also studied.

2. Material and methods

2.1. Material

The merchant rock phosphate used is from the treatment factory based in Kpeme, Lomé-Togo. In order to obtain the powder, the material has been pulverized, sieved to 50 um, washed and dried up at 105°C in an oven for 5 h.

The solution of lead has been prepared by dissolving an appropriate quantity of nitrate of lead $Pb(NO_3)_2$ in distilled water. The initial pH is 3.4. The salt is of analytical purity and has been provided by Fluka Company (Munich).

2.2. Methods

2.2.1. Characterization of the rock phosphate

- *X-ray diffractometry*: It is a universal method used to identify the nature and structure of crystallized products. This method applies to crystalline environments (rocks, crystals, minerals, clays, etc.) only. The device used is an X-ray diffractometer of the type "X'PERT MPD" equipped with a monochromator using the ray K of the copper with $\lambda = 1.540598$ Å. The results have been treated by means of X'PERT HighScore software.
- *IR spectroscopy*: Fourier transform infrared spectroscopy has allowed determining in a qualitative way the functions of the surface of the material. The rock phosphate powder to be analyzed was mixed with dry KBr. The mixture is compressed into a hydraulic press to obtain a pastille. The specter is that of rock phosphate because KBr is transparent in infrared. The device used is a Fourier transform spectrometer VERTEX 70.
- *Specific surface*: The specific surface or mass area, expressed in $m^2\ g^{-1}$, represents the total area per unit of sorbent mass accessible to molecules [18]. This surface is obtained by applying the theory of Brunauer–Emmett–Teller [19], hence the name surface Brunauer–Emmett–Teller. The device used is an 'autosorb station 1'.
- *pH of zero charge*: The pH of zero charge pH_{PZC} is the pH setting for which the solid surface has a zero load. The method described by Ferro-Garcia et al. [20] and Sontheimer et al. [21] has been used.

2.2.2. Experimental protocol

The sorption of Pb^{2+} has been realized by 'batch method' [22,23]. During these studies, the agitation speed is settled at 4,000 rpm and the time of centrifugation of the mixtures (sorbent – pollutants) is 10 min. The experiments have been realized at ambient temperature evaluated to 25°C. The quantity of the sorbed pollutants Q_a (mg g^{-1}) is calculated using the following equation:

$$Q_a = \frac{\left(C_0 - C_e\right)V}{m} \tag{1}$$

where C_e is the concentration of sorbent at equilibrium (mg L^{-1}), C_0 the initial concentration of the sorbent (mg L^{-1}), V the volume of the pollutants solution (L) and m mass of the sorbent (g).

The pollutants retention rate is calculated by this equation:

$$T\left(\%\right) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{2}$$

The kinetic, the isothermal of sorption, the amount of sorbent and the pH of the pollutant solution have been studied. The isothermals of Langmuir and Freundlich are used to determine the maximum sorption capacity of the material.

3. Results and discussion

3.1. Characterization of the natural phosphate

3.1.1. X-ray diffraction analysis

The X-ray diffraction characterization of the material is reproduced in Fig. 1. The majority of the X-ray is attributed to the apatitic phase. Comparing the inter-reticular distance of the peaks and those of the apatitic phase of the database of ASTM field, the rock phosphate of Togo is fluorapatite of $C_{a5}(PO_4)_3F$ (PDF # 03-0736) formula confirming therefore the works of Tchangbeddji et al. [16]. Other minority phases attributed to the silica (SiO_2) and

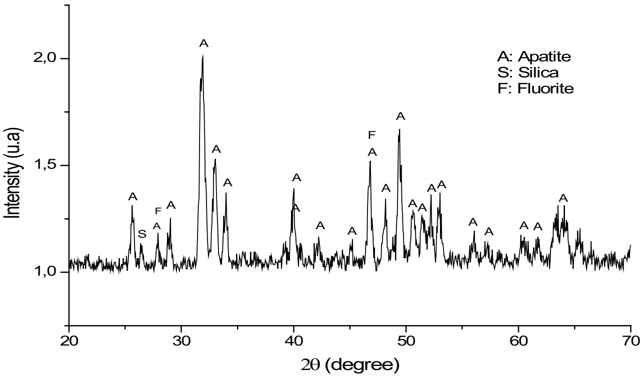

Fig. 1. Diffractogram of rock phosphate.

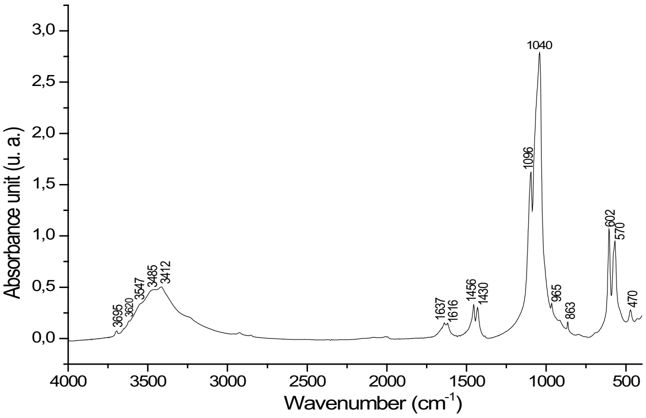

Fig. 2. IR spectra of rock phosphate.

the fluorite (CaF_2) have been observed. The good resolution of the peaks of the diffractogram is due to a better crystallinity of the material. X-ray diffraction analysis of the rock phosphate from the eastern region of Algeria [24] and Benguerir in Morocco [25] have led to the same results.

3.1.2. Infrared spectroscopy

Analysis of rock phosphate by infrared spectroscopy allowed to obtain the specter reported in Fig. 2. The bands raised at 1,096; 1,040; 602; 570 and 470 cm^{-1} characterize the phosphate ions. Bands found in the 3,500–3,700 cm^{-1} region frequently occur in laminate and fibrous clay containing Al, Si, and other elements [26]. The carbonates are well characterized by the bands at 1,456; 1,430 and 870 cm^{-1} [27].

The specter also shows the presence of a band at 3,695 cm^{-1}. The wavenumber of this band is high compared to the usual OH encountered in the case of water or in alcohol. It can therefore be attributed to structural hydroxyls in clay. The numbers of waves recorded correspond exactly to those of the kaolin. The peak at 3,620 cm^{-1} was attributed to the internal hydroxyls between the two layers [28]. The shoulders located at 3,654 and 3,695 cm^{-1} were assigned to the external hydroxyls located in the interfoliary space separating the adjacent leaflets that constitute the structure of the kaolinite [28,29]. The low intensity observed on our specter compared to that of the silica and phosphate bands (1,040 cm^{-1}) therefore reveals the presence of traces of clay in our samples. In this same region of hydroxyl elongation, there is a poorly resolved broadband strip on which three components can be pointed at 3,547; 3,485 and 3,412 cm^{-1}. At the same time, in the region of deformation vibration of water molecules (δH–O–H), there are two well-resolved peaks located at 1,637 and 1,616 cm^{-1}. These bands can be attributed to hydroxyls engaged by hydrogen bonds. The presence of two deformation bands and three hydroxyl elongation bands can be explained by the presence of at least two types of water molecules differently linked by hydrogen bond [30].

3.1.3. Specific surface

The specific surface is very important in interpreting the sorption of pollutants on the surface of the material. The specific surface of rock phosphate produced in Togo is 20.78 $m^2\ g^{-1}$. This value is very close to that of the rock phosphate (RP) produced in Tunisia (20.7 $m^2\ g^{-1}$) in the region of Bachouâ et al. [31] and much higher than that of the Eastern Algerian RP (5.20 $m^2\ g^{-1}$) [24]. Rock phosphate produced in the Khouribga region of Morocco has a specific surface area of 23.7 $m^2\ g^{-1}$ [32] greater than Togo's RP.

3.1.4. pH of zero charge

In view of the sorbent–pollutant electrostatic forces that play an important role in the sorption phenomenon, the pH at zero charge (pH_{PZC}) of the rock phosphate has been determined. It is slightly acidic and is worth 6.82. For $pH < 6.82$ values, the surface of the material is positively charged and for $pH > 6.82$ the surface is negatively charged.

The pH_{PZC} of rock phosphate produced in Togo is lower than Barka's found on the RP of the Khouribga-Morocco region ($pH_{PZC} = 7.9$) [33] and that found by Malash et al. on the Abu-Tartour region, which is also 7.9 [34].

3.2. Lead sorption studies

3.2.1. Effect of pH

The results reveal the increase of the lead elimination percentage in solution while the pH varies from 2 to 7. At pH = 7, the retention rate maximum value is 97.91% (Fig. 3). The effect of the pH has not been observed over the pH = 7 due to the precipitation of Pb^{2+} into a hydroxide. The low retention obtained at four low pH ($pH \leq 3$) would be explained by the competition between hydronium ions H_3O^+ and Pb^{2+} on the sorption sites of the rock phosphate [24]. Some authors explain the retention of lead ions at low pH on the RP by a dissolving reaction of the latter followed by a precipitate reaction in which the ions Pb^{2+} are substituted for the Ca^{2+} ions; with the appearance of new crystalline phases. This results in less stable crystallized fluoropyromorphite, which can develop into chloropyromorphite in the presence of Cl^- ions [35,36] as a solution according to the equations:

$$Ca_{10}\left(PO_4\right)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \tag{3}$$

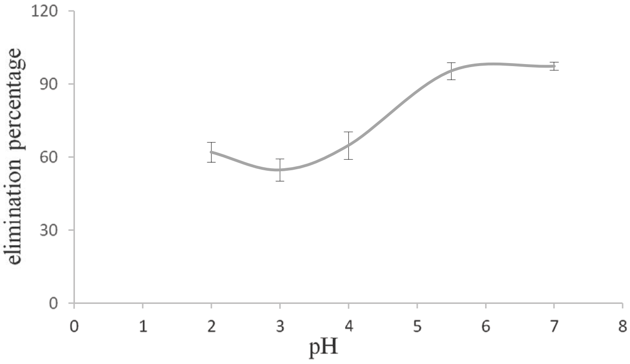

Fig. 3. Influence of pH of the solution.

$$10Pb^{2+} + 6H_2PO_4^- + 2F^- \rightarrow Pb_{10}\left(PO_4\right)_6 F_2 + 12H^+ \quad (4)$$

For pH > 3 where the dissolution of the rock phosphate is very low, in addition to the precipitation phenomenon, the retention of the Pb^{2+} would be the result of the complexation phenomenon due to the hydroxyl grouping discovered in the material or to the deprotonation of the surface and to the retention on the sorption sites [35].

3.2.2. Effect of the amount of the rock phosphate

The data obtained from the experiments on the effect of the amount of the material are shown in Fig. 4. The more the amount of the material increases, the higher the retention rate is. This can be due to the augmentation of the available surface which generates an augmentation of the active sites [23,37]. For R = 4 g L^{-1}, the retention rate is 89.71%. Filali et al. [24] obtained maximum sorption for the same R.

3.2.3. Influence of contact time

During the first 10 min of contact between the pollutant and the sorbent (Fig. 5), a high speed sorption is noticed and then the process becomes slower to reach the balance around t = 30 min. Former studies have reached 180 and 55 min during the elimination of the lead on the rock phosphate from Tunisia [38] and Benguerir in Morocco [39], respectively. This difference in balance time of Pb^{2+} sorption the different apatites would be a result of their structure which varies from an area to the other.

3.2.4. Kinetics models of lead sorption

The Kinetics study of the reaction of Pb^{2+} retention on the rock phosphate has been made using pseudo-first-order and second-order kinetic models. The coefficient to determine (Table 1) the pseudo-first-order kinetic model is 0.90. This value is proportionally high but the quantity of Pb^{2+} sorbed at resulted balance theoretically is different from the experimental value. We therefore conclude that the process of lead sorption on the material is not of the first order.

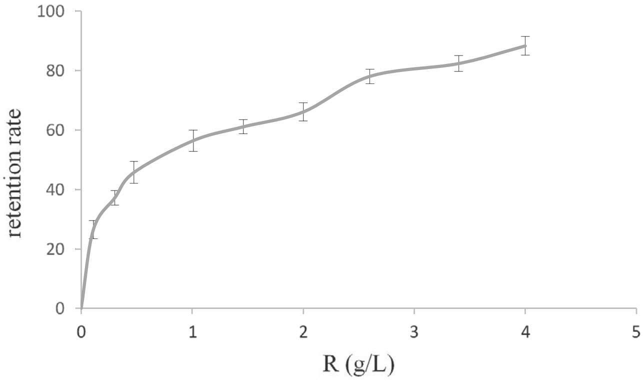

Fig. 4. Influence of the amount of the sorbent.

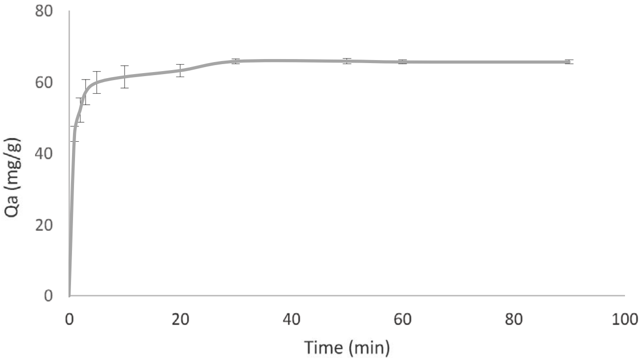

Fig. 5. Kinetic of lead sorption (R = 1 g L^{-1}; C_0 = 100 mg L^{-1}).

Applying the pseudo-second-order kinetic model, the coefficient of determination is close to the value of the experimental Q_e. The kinetic model of pseudo-second-order shows a better description of the kinetic of sorption of lead. The same result was obtained on the RP of the Jebel Onk deposit in Algeria [24].

3.2.5. Sorption isotherms of lead

The obtained isothermal is assimilated to the one of type S (Fig. 6) according to the classification of Giles et al. [40]. The type S shows a variable affinity of the sorbent to the sorbed substance and indicates multilayer sorption as Kifuani et al. [41] highlighted.

Table 1
Values of the constants of both kinetic models used

	Pseudo-first-order			Pseudo-second-order			$Q_{e,\exp}$ (mg g^{-1})
	k_1 (min^{-1})	$Q_{e,\text{theo}}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$Q_{e,\text{theo}}$ (mg g^{-1})	R^2	
RP	0.07	5.37	0.95	0.04	66.67	0.99	65.93

Table 2
Langmuir and Freundlich models constants values

	Pseudo-first-order			Pseudo-second-order			$Q_{e,\mathrm{exp}}$ (mg g^{-1})
	k_1 (min^{-1})	$Q_{e,\mathrm{theo}}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$Q_{e,\mathrm{theo}}$ (mg g^{-1})	R^2	
RP	0.07	5.37	0.95	0.04	66.67	0.99	65.93

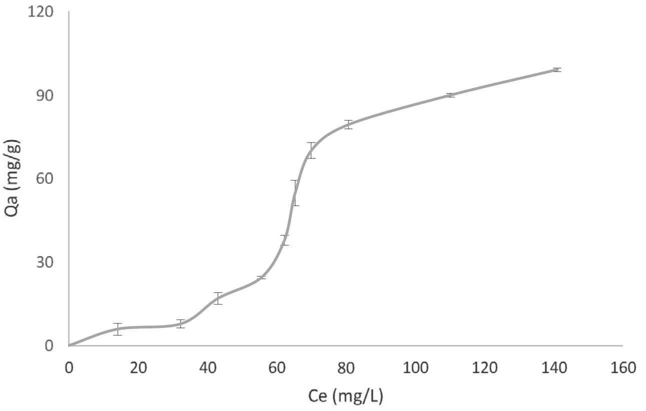

Fig. 6. Sorption Isotherm of Pb^{2+} on natural phosphate (m = 50 mg; V = 50 mL).

In order to determine the maximum quantity of sorption of the metallic ion studied and the type of sorption, we have simulated the experimental data by the equation of Langmuir and Freundlich. Fig. 6 shows the linear transforms of the isothermal of Langmuir and Freundlich. The coefficients of determination and the determined constants after the linearization of both models are recorded in Table 2.

The high values of the coefficients of determination of both models show that the isothermal of Langmuir and Freundlich describe best the sorption process of the lead ion on the rock phosphate. The maximum capacity of the sorption of the pollutant is 166.67 mg g^{-1} on the RP. The works of Filali et al. [24] have resulted in a maximum capacity of 15.15 mg g^{-1} during the fixation of the lead on the rock phosphate of Algeria. The value of K_F very high during the elimination of the lead by the rock phosphate shows a high affinity with the pollutant. The sorption of lead ions on apatites from other regions, was explained by the Langmuir isotherm [37,42,43].

4. Conclusion

The main objective of this work was to study the sorption capacity of lead ion on rock phosphate (RP) produced in Togo. The maximum sorption capacity of the pollutant calculated from the Langmuir isotherm is 166.67 mg g^{-1}. The time-based study showed that it is the kinetic model of the pseudo-second-order that explains this sorption. For the ratio solid/solution R = 4 g L^{-1}, the retention rate is around 90%. At the end of the work carried out on the retention of the metal ion, it should be retained that rock phosphate has a good capacity for sorption and is therefore an alternative to the commercial sorbent.

Acknowledgments

We are grateful to Pr. Detlef BAHNEMANN and Dr. Akpene DOUGNA for his help to achieve the surface specific.

Authors' contributions

G.T. (Professor) designed and supervised the study and approved the final manuscript.

M.H. (Professor) designed and supervised the study and approved the final manuscript.

M.E.M. (Professor) designed and supervised the study and approved the final manuscript.

K.A.D. (Doctor of chemistry) performed the research, managed the analyses of the study and wrote the manuscript.

C.L. (Doctor) helped us with the analyzes at SAA and approved the final manuscript.

M.K. (Doctor) performed protocol and literature research and approved the final manuscript.

S.T. (Doctor) performed protocol and literature research and approved the final manuscript.

D.D.B. (Doctor) performed protocol and literature research and approved the final manuscript.

References

[1] H. Saouli, Etude de l'influence de paramètres opératoires sur le rendement de rétention de métaux lourds sur des phosphates de calcium [Study of the Influence of Operating Parameters on the Rétention Efficiency of Heavy Metals on Calcium Phosphate], Mém. de magist., Université mouloud Mammeri Tizi-Ouzou-Algérie, 2008.

[2] A. Viala, Eléments de toxicologie [Toxicology Elements], Edit. Tec & Doc Lavoisier et édit. médic. inter., 1998.

[3] D. Mohan, C.U. Pittman Jr., P.H. Steele, Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent, J. Colloid Interface Sci., 297 (2006) 489–504.

[4] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, Water Res., 36 (2002) 2304–2318.

[5] K. Nomiyama, Toxicity of Cadmium—Mechanism and Diagnosis, Proc. of the Inter. Conf. Heal., 1973, pp. 15–23.

[6] D. Purves, Trace Element Contamination of the Environment, Elsevier Science, Amsterdam, Oxford, New York, 1977, pp. 170–182.

[7] G. Keck, E. Vernus, Déchets et risques pour la santé [Waste and Health Risks], Tech. de l'ing. (G2450), 2000, pp. 1–17.

[8] Y. Andrés, C. Brasquet Faur, C. Gérente, P. Cloirec, Elinimation des ions métalliques et des métalloides dans l'eau [Removal of metal ions and metalloids in water], Tech. de l'ing. (W 8000), 2007, pp. 1–14.

[9] R. Jocelyn, Calcination des Sédiments de Dragage Contaminés: Etudes des Propriétés Physico-chimiques [Calcination of Contaminated Dredged Sediments: Studies of Physicochemical Properties], Thèse de doctorat, Institut National des Sciences Appliquées de Lyon-France, 2008.
[10] S.S. Tahir, R. Naseem, Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay, Sep. Purif. Technol., 53 (2007) 312–321.
[11] A. Mathee, T. Khan, N. Naicker, T. Kootbodien, S. Naidoo, P. Becker, Lead exposure in young school children in South African subsistence fishing communities, 126 (2013) 179–183.
[12] J.O. Nriagu, J.M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature, 333 (1988) 134–139.
[13] J. Emmanuel, La production et le traitement des eaux destinées à l'alimentation et à la préparation de denrées alimentaires [The production and treatment of water intended for feeding and for the preparation of foodstuffs], Agence de l'eau Seine-Normandie.
[14] Y. Ku, I.-L. Jung, Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide, Water Res., 35 (2001) 135–142.
[15] S. Messeaouda, Etude de la capacité de rétention et d'élimination des cations métalliques par des adsorbants naturels [Study of the retention and elimination capacity of metal cations by natural sorbents], Thèse de doctorat, Université de Mustapha Stambouli, Mascara Faculté des Sciences de la Nature et de la Vie Département de Biologie-Algérie, 2015.
[16] G. Tchangbeddji, G. Djeteli, K.A. Kili, J.M. Savariault, J.L. Lacout, Chemical and structural characterization of natural phosphate of hahotoe (Togo), Bull. Chem. Soc. Ethiop., 17 (2003) 139–146.
[17] M. Koriko, A. Zanguina, G. Tchangbedji, M. El Meray, I. Natatou, M. Hafidi, M. Sarakha, Etude de la dissolution des phosphates de Hahotoé-Kpogamé (Togo) par les acides humiques naturels [Study of the dissolution of rock phosphate of Hahotoé-kpogamé by natural humic acids], J. Soc. Ouest-Afr. Chim., 30 (2010) 41–47.
[18] R.-L. Tseng, S.-K. Tseng, Characterization and use of high surface area activated carbons prepared from cane pith for liquid-phase adsorption, J. Hazard. Mater., 136 (2006) 671–680.
[19] S. Brunauer, P.H. Emmet, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc., 60 (1938) 309–315.
[20] M.A. Ferro-Garcia, J. Rivera-Utrilla, I. Bautista-Toledo, A.C. Moreno-Castilla, Adsorption of humic substances on activated carbon from aqueous solutions and their effect on the removal of Cr(III) ions, Langmuir, 14 (1998) 1880–1886.
[21] H. Sontheimer, J.C. Crittenden, R.S. Summers, Activated carbon for water treatment, DVGW Forschungsstells Enger-Bunte Institut, 1988.
[22] I. Tchakala, M.L. Bawa, T. Kodom, G. Djaneye-Boundjou, V.K. Doni, P. Nambo, Kinetics of the adsorption of anionic and cationic dyes in aqueous solution by low-cost activated carbons prepared from sea cake and cotton cake, Am. Chem. Sci. J., 4 (2014) 38–57.
[23] A.K. Degbe, M. Koriko, S. Tchegueni, E. Aziable, I. Tchakala, M. Hafidi, M. El Meray, G. Tchangbedji, Biosorption of methylene blue solution: Comparative study of the cactus (*Opuntia ficus indica*) of Lomé (CL) and Marrakech (CM), J. Mater. Environ. Sci., 7 (2016) 4786–4794.
[24] N. Filali, R. Mazouz, A. Hamel, Z. Hattab, K. Guerfi, Contribution to the study of the immobilization of lead ions from aqueous solution by adsorption on natural phosphate, Rev. Sci. Technol., 29 (2014) 88–99.
[25] S. El Asri, A. Laghzizil, A. Alaoui, A. Saoiabi, R. M'Hamdi, K. El Abbassi, A. Hakam, Structure and thermal behaviors of moroccan phosphate rock (Bengurir), J. Therm. Anal. Calorim., 95 (2009) 15–19.
[26] J. Madejová, P. Komadel, Baseline studies of the clay minerals society source clays: infrared methods, Clays Clay Miner., 49 (2001) 10–32.
[27] A.A. Flemming, B. Ljerka, Infrared spectra of amorphous and crystalline calcium carbonate, Acta Chem. Scand., 45 (1991) 1018–1024.
[28] R.L. Ledoux, J.L. White, Infrared studies of hydrogen bonding interaction between kaolinite surfaces and intercalated potassium acetate, hydrazine, formamide, and urea, J. Colloid Interface Sci., 21 (1966) 127–152.
[29] V.C. Farmer, J.D. Russell, The infra-red spectra of layer silicates, Spectrochim. Acta, 20 (1964) 1149–1173.
[30] R. Prost, Infrared study of the interactions between the different kinds of water molecules present in sepiolite, Spectrochim. Acta, Part A, 31 (1975) 1497–1499.
[31] H. Bachouâ, M. Othmani, Y. Coppel, N. Fatteh, M. Debbabi, B. Badraoui, Structural and thermal investigations of a Tunisian natural phosphate rock, J. Mater. Environ. Sci., 5 (2014) 1152–1159.
[32] N. Barka, A. Assabbane, A. Nounah, L. Laanab, Y.A. Ichou, Removal of textile dyes from aqueous solutions by natural phosphate as a new adsorbent, Desalination, 235 (2009) 264–275.
[33] N. Barka, L'élimination des colorants de synthèse par adsorption sur un phosphate naturel et par dégradation photocatalytique sur TiO_2 supporté [Removal of synthetic dyes by adsorption on a rock phosphate and by photocatalytic degradation on supported TiO_2], Thèse de Doctorat, Université Ibn Zohr-Maroc, 2008.
[34] G.F. Malash, M.I. El-Khaiary, Methylene blue adsorption by the waste of Abu-Tartour phosphate rock, J. Colloid Interface Sci., 348 (2010) 537–545.
[35] L.C.A. Koffi, K. Adouby, E.N. Wandan, B. Yao, K.P. Kotchi, Sorption and desorption of Pb(II) from aqueous solution using *Triplochiton scleroxylon* sawdust as sorbent, J. Appl. Sci., 10 (2010) 1536–1544.
[36] F. Naima, Utilisation des composes naturels (phosphate) dans les procedes de depollution des eaux contaminees par les metaux lourds [Use of natural compounds (phosphate) in processes for the depollution of water contaminated by heavy metals], Thèse de Doctorat, Universite Badji Mokhtar–Annaba (Algérie), 2015.
[37] E. Keleş, A. Kadir Özer, S. Yörük, Removal of Pb^{2+} from aqueous solutions by rock phosphate (low-grade), Desalination, 253 (2010) 124–128.
[38] H. Bachoua, H. Nasri, M. Debbabi, B. Badraoui, Using Tunisian phosphate rock and her converted hydroxyapatite for lead removal from aqueous solution, J. Eng. Res. Appl., 4 (2014) 171–178.
[39] S. El Asri, Nouveaux matériaux de structure apatite préparés à partir du phosphate naturel marocain à applications environnementales [New Apatite Structural Materials Prepared from Moroccan Rock Phosphate for Environmental Applications], Thèse de Doctorat, Université Mohammed V – Agdal-Maroc, 2009.
[40] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, J. Colloid Interface Sci., 47 (1974) 755–765.
[41] K.M.A. Kifuani, V.P. Noki, D.P.J. Ndelo, Adsorption de la quinine bichlorhydrate sur un charbon actif peu coûteux à base de bagasse de canne à sucre imprégnée de l'acide phosphorique [Adsorption of quinine hydrochloride on an inexpensive activated carbon based on sugar cane bagasse impregnated with phosphoric acid], Int. J. Biol. Chem. Sci., 6 (2012) 1337–1359.
[42] M. Mouflih, A. Aklil, N. Jahroud, M. Gourai, S. Sebti, Removal of lead from aqueous solutions by natural phosphate, Hydrometallurgy, 81 (2006) 219–225.
[43] Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi, A. Montiel, Heavy metal removal from aqueous solutions by activated phosphate rock, J. Hazard. Mater., 156 (2008) 412–420.