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Compositional and structural characterization of *Corbula trigona* shells for their valorization in water treatment

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Abstract

Biowastes such as *Corbula trigona* shell powder are used for practical applications because of their adsorptive properties in the treatment of pollutants in aqueous solution. In order to determine its physico-chemical properties in relation to its purifying capacity, *Corbula trigona* shell powder is characterized by inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results revealed the presence of $CaCO_3$ (97.8 %), two crystalline polymorphs, calcite and aragonite and functional groups such as C–O and C=O on the surface of the material. The results of this study suggest that the $CaCO_3$ contained in this material can be used in various fields of science despite the presence of some metallic trace elements that can improve its adsorption capacity.

1. Introduction

Bivalve shells are underutilized biological waste, available in large quantities with an estimated mass of 1,147,000 tons [1]. They are inexpensive and non-toxic [2]. They are a solid multilayer material, composed mainly of calcium carbonate in the form of calcite [3]. In addition to calcium carbonate, they contain some metallic trace elements (Fe, Mn, Cu, Zn, Pb, Co, Cd, As, Sr, etc.) [4,5]. Calcium carbonate contained in bivalve shell powder is a naturally occurring inorganic biomaterial. According to Widyastuti *et al* [6], bivalve shells is a potential biomass resource as a bone repair material especially designed for cancer patients [7]. Calcium carbonate is also used in a wide variety of products, including paper, plastics, rubber, pharmaceuticals, and in the treatment of polluted water [8–11]. Recently, this material has received enormous attention from researchers due to its adsorption capacity. It has been the subject of some research work for the removal in aqueous solution of thorium [12], malachite green [13], methylene blue [3].

The bivalve shells of *Corbula trigona* could be an alternative adsorbent, natural to be used in the treatment of pollutants. The characterization of this one is therefore essential for a better understanding of its properties and its use. The aim of this study is to characterize the shell powder of *Corbula trigona* in order to evaluate its chemical properties and its performance in the treatment of pollutants in aqueous solution. This could expand the list of non-toxic adsorbent materials for the treatment of contaminated waters.

Corbula trigona shell powder was characterized using different analytical techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) the specific surface, using the Brunauer-Emmet-Teller (BET) equation.

2. Methodology

2.1. Sourcing and preparation of Corbula trigona shells

Corbula trigona shells (CTS) were collected from the shore of the Aby lagoon (Ivory Coast). In addition, they are characteristic species found on a variety of substrates ranging from sandy to muddy sediments [1,14]. The bivalves of *Corbula trigona* are small species (21 mm maximum), with a color that varies from white to light green, then to ferruginous brown **(Figure 1)**.They live, also, in brackish waters (for example, estuaries, lagoons and lakes) and in temperate and tropical areas. They are often abundant in eutrophic waters and have an increased ability to survive in heavily polluted areas [15]. They are under-exploited wastes and available in large quantities. The use of these waste *Corbula trigona* shells as adsorbent is a way to valorize them in the treatment of pollutants in aqueous solution.

Figure 1. Shells of *Corbula trigona*

In order to remove impurities, 100 g of *Corbula trigona* shells were immersed in 200 mL of hydrogen peroxide (50 volumes or 15 % mass) for 24 hours. These shells were then washed several times with distilled water before being dried in an oven at 105 °C for 24 hours. After cooling in a desiccator, they were crushed and ground in a porcelain mortar. Two successive sieving operations using 250 µm and 100 µm mesh sieves resulted in powdered materials with a particle size between 100 and 250 µm. The choice of the diameters of the shells of *Corbula trigona* were made according to the work of Turner *et al* [16]. Because according to them, the shells of granulometry included between 100 µm and 250 µm have a good capacity of adsorption.

2.2 *Product characterization*

The pH of zero charge point (pHpzc) was determined with reference to the work of Lopez-Ramon *et al*. [17]. Thus, six solutions of NaCl at 0.1 mol/L and pH between 2 and 10 were previously prepared using NaOH or HCl solutions of concentration 0.1 mol/L). 0.1 g of CTSP was put in contact with 20 mL of each of the six solutions under stirring with a magnet bar for 48 hours. These reaction mixtures were then filtered using filter paper, Whatman of porosity = 0.45 µm. The final pH is measured using a pH/Ionometer XL250. pHzpc corresponds to the point where the curve of variation ΔpH versus the initial pH crosses the x-axis. The elemental composition of *Corbula trigona* shell powder (CTSP) was determined using an Agilent 5800 ICP-OES instrument. The Rigaku brand diffractometer - Miniflex II, Japan (voltage 40 kV, current 200 mA, CuKα radiation (λ = 1.5406 Å), scan rate $4min^{-1}$) for 2θ ranging from 0 to 90° allowed us to identify the crystalline phases present in the CTSP. Brukers brand Alpha-p infrared spectrophotometer was used to identify functional groups on the surface of CTSP in the range of 4000 to 400 cm^{-1}. The surface properties of CTSP were investigated using a multipoint BET surface. CTSP was characterized by N_2 adsorption test at 77 K. 100 mL/min of dry nitrogen was introduced into the sample tube to avoid contamination of the clean surface. The sample tube was then removed and the sample weighed.

3. Results and Discussion

3.1 *pH of zero charge point (pHpzc) of CTSP*

The pHpzc is defined as the pH of the aqueous solution in which the solid exists under a neutral electrical potential. CTSP has a pHpzc of 8.2 **(Figure 2)**. This parameter plays an important role in the adsorption mechanism. Thus, when the pH of the solution is below 8.2, the surface of the adsorbent becomes positively charged. On the other hand, for a pH of the solution higher than pHpcn, the surface of the adsorbent is negatively charged.

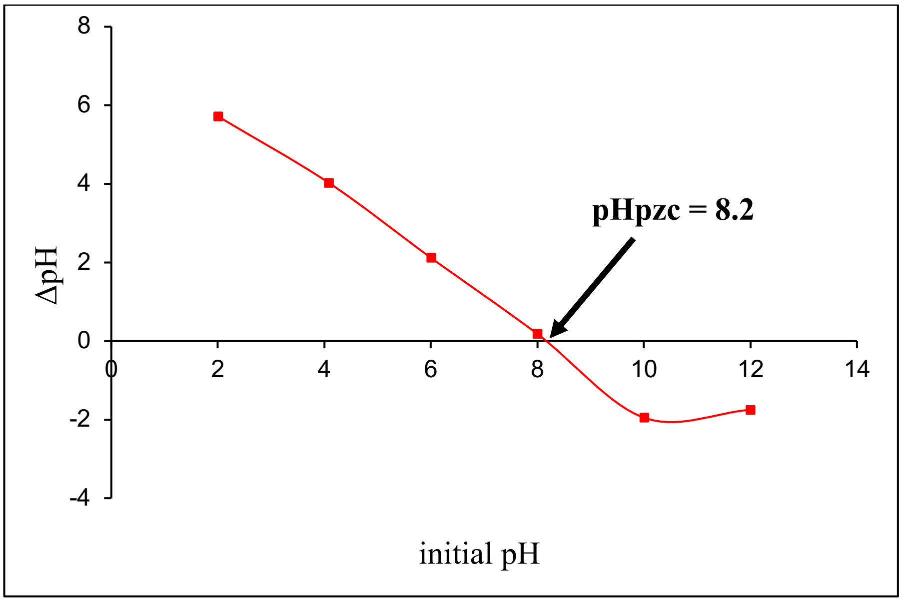

Figure 2. pHpzc of *Corbula trigona* shell powder

3.2 *Mineral composition*

The elemental composition of *Corbula trigona* shell powder (CTSP) is presented in **Table 1.** It shows that this material consists of 97.8 % calcium carbonate, 0.46 % chromium, 0.3 % mercury and lead as well as other metallic trace elements (As, Cd, Ni, Sb, Se). This CTSP has a composition close to that determined by Jacob *et al.*[5] in bivalve shell powder. The $CaCO_3$ present in the bivalve shell is calcite, which is very stable and less soluble in water at standard temperature and pressure. Previous studies have revealed the presence of $CaCO_3$ and trace metal elements such as Fe, Mn, Cu and Ca increases the adsorption capacity in the treatment of pollutants in aqueous solution [18,19]. The presence of trace metals, particularly mercury in *Corbula trigona* shells (0.3%) is below the toxicity threshold (≤ 2 µg/L), which suggests that its presence does not constitute a hazard in water treatment [20].

Table 1. Chemical composition of the shell of *Corbula trigona*

Chemical compounds	Pourcentage (%)
$CaCO_3$	97.8
Cr	0.46
Hg	0.3
Pb	0.3
As	0.26
Cd	0.25
Ni	0.23
H_2O	0.23
Sb	< 0.1
Se	< 0.1
Insoluble matter	< 0.1

3.4 X-ray analysis

X-ray diffraction was used to identify the crystalline phases in the CTSP material. **Figure 3** shows the diffractogram of CTSP obtained with the different phases identified from the Joint Committee on Powder Diffraction Standards (JCPDS) databases. The composition of the microspheres of this adsorbent indicates two crystalline polymorphs, namely calcite and aragonite. The characteristic peaks obtained at 29.5°, 26.9, 39.5°, 42.9°, 48.5° and 62.3° correspond to reflections (104), (101), (113), (202), (116) and (124), respectively. These are attributed to calcite ($CaCO_3$), while aragonite ($CaCO_3$) peaks are observed at 27.5° (021), 33.4° (012) and 37.9° (112).

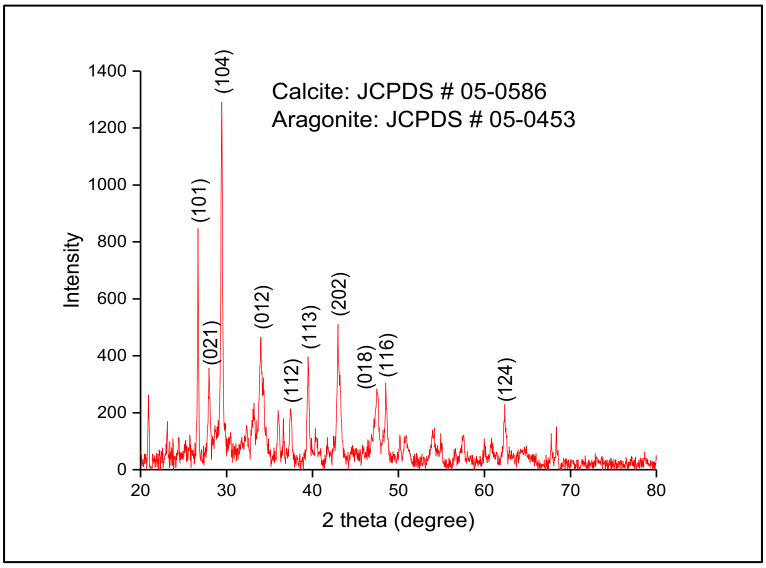

Figure 4. XRD of raw CTSP

3.3 FTIR analysis

Examination of the spectrum in **Figure 3** allowed the association of characteristic peaks with functional groups. The main peaks obtained were located at 1385 cm^{-1}, 871 cm^{-1} and 710 cm^{-1} respectively. Thus, the low intensity peak obtained at 1776 cm^{-1} could be attributed to the $C = O$ bond of the carbonate while the peaks located at 1385 cm^{-1}, 871 cm^{-1} and 710 cm^{-1} are associated with the $C-O$ bond. The functional groups obtained are in agreement with the structure of bivalve shells studied by Elwakeel *et al* [3]. For example, the absorption bands at 1776 cm^{-1}, 1385 cm^{-1}, 871 cm^{-1} and 710 cm^{-1} are also consistent with calcite and the band at 710 cm^{-1} is a common peak for both calcite and aragonite [21–24].

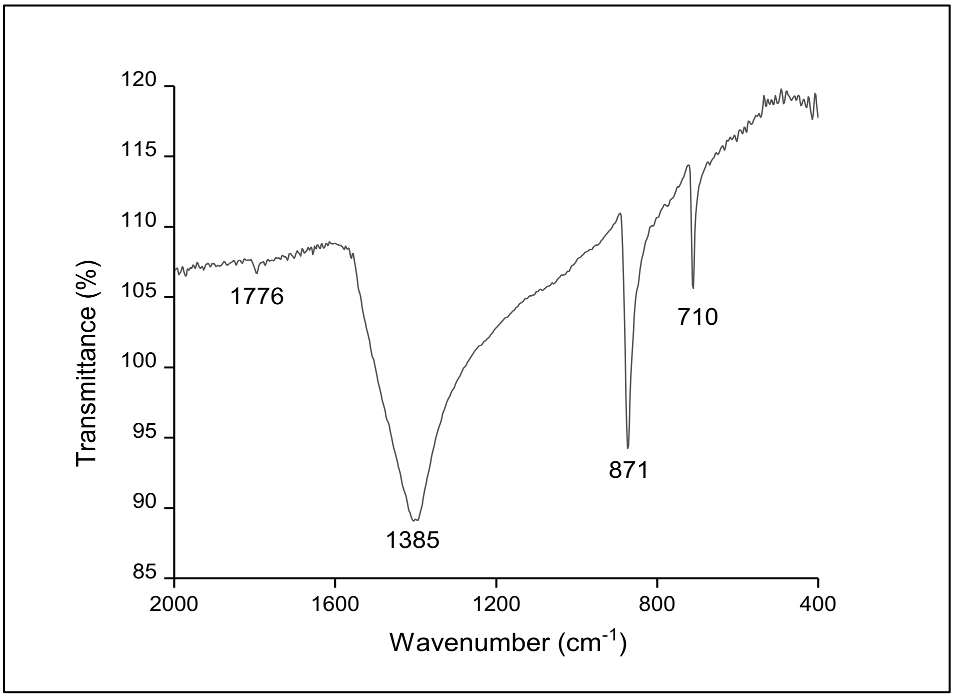

Figure 3. FTIR spectrum of CTSP

3.5 Surface morphology of CTSP

Scanning electron microscopy (SEM) was used to illustrate the different surface morphologies and characteristics of CTSP. **Figure 5** shows the scanning electron microscopy (SEM) snapshot of the studied adsorbent. The SEM photographs of the CTSP were recorded at 300 x, 500 x and 1000 x magnifications to highlight the perceived nuances in the topography of the adsorbent. These pictures clearly indicate that the CTSP surface is flaky and coarse. In addition, we observe the appearance of numerous gaps that could facilitate the adsorption mechanisms.

3.6 Spectrum analysis and EDS mapping

The spectrum **(Figure 6a)** and EDS mapping **(Figure 6b)** were performed to know the elemental chemical composition of CTSP. It appears that this material consists mainly of calcium (51.23 %), oxygen (40.29 %) and carbon (8.37 %). This composition is close to that determined by Elwakeel *et al* [3] in bivalve shells (47.6% Ca, 41.1 % C and 11.1 % O) from beaches located on the coast of Port Said in Egypt.

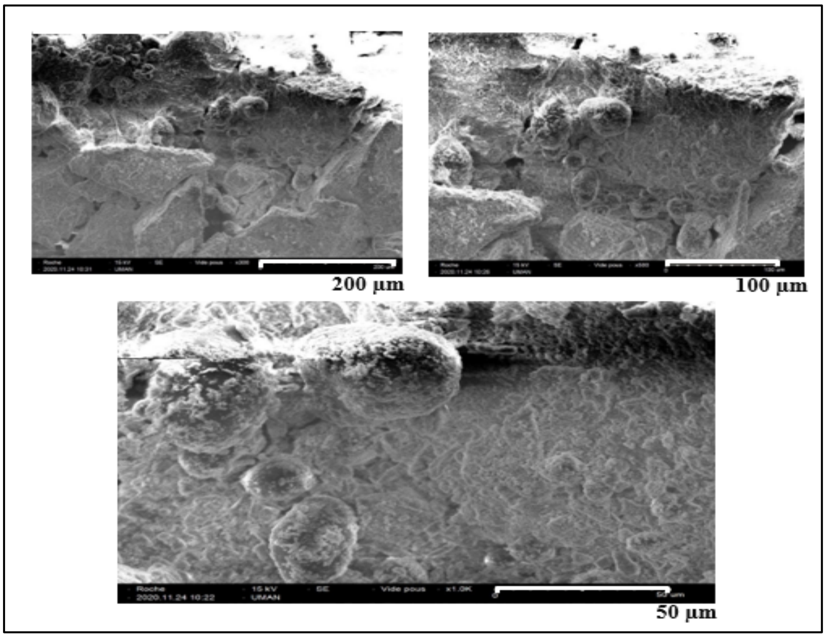

Figure 5. SEM photograph of the CTSP

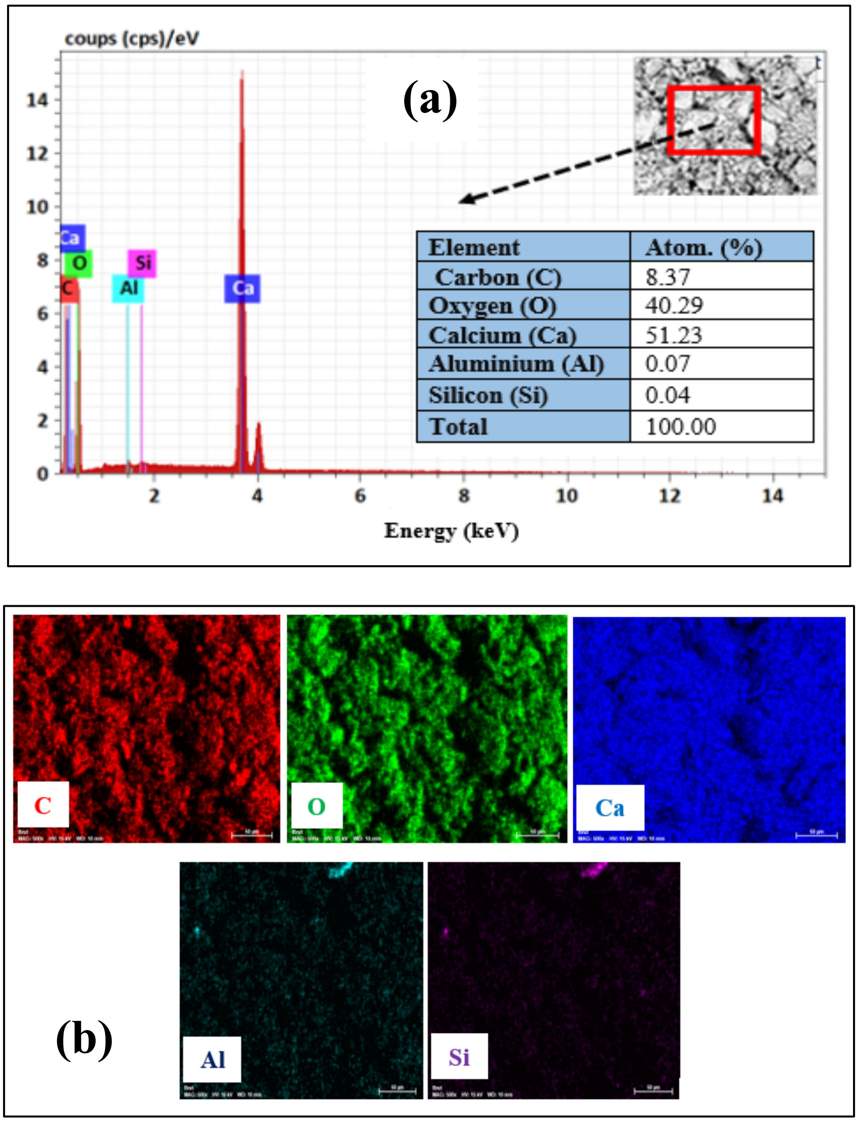

Figure 6. EDS spectrum **(a)** and mapping images **(b)** of chemical elements in the CTSP

3.7 BET analysis

Specific surface area is one of the characteristics that plays the main role in the adsorption capacity. The shells of *Corbula trigona* have a relatively low specific surface area [25]. The value found in our study is 4.85 m^2/g. Despite the low value of the specific surface, they represent a potential source for the removal of certain pollutants in solution such as fluoride by precipitation [26]. Their activation could also increase their specific surface and make them good adsorbents in the treatment of pollutants in aqueous solution. It is one of the characteristics that plays the main role in adsorption capacity [9,27,28].

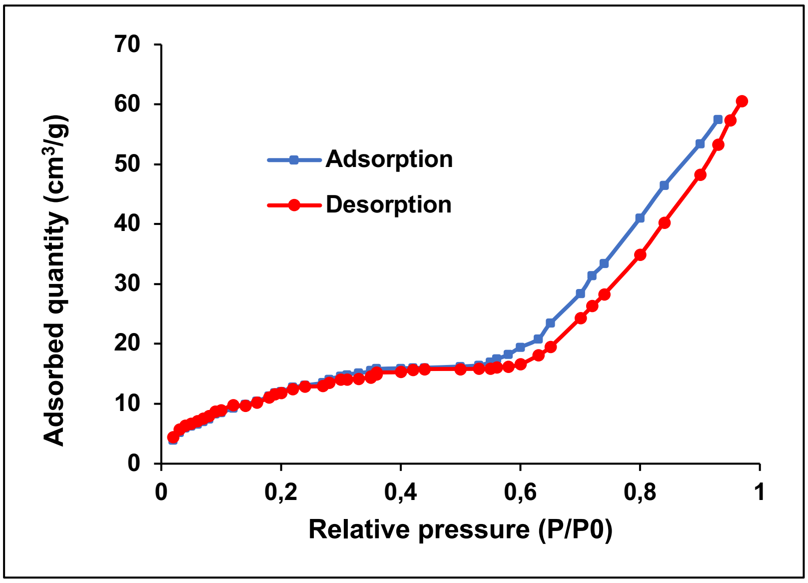

Figure 7. Adsorption-desorption profiles of CTSP

Conclusion

This study showed that the crude *Corbula trigona* shell powder can be used in various scientific fields. ICP-MS analysis showed that CTSP was predominantly $CaCO_3$ (97.8%) with a specific surface area of 4.85 m^2/g. The DRX analysis showed that it was constituted by two crystalline polymorphs, calcite and aragonite, recognized by their capacity of adsorption of pollutants in aqueous solution. Moreover, the characterization of the surface allowed to highlight the presence of functional groups such as $C-O$ and $C=O$. Therefore, the valorization of these shells of *Corbula trigona* is necessary by transforming them into other products with high added value. In this perspective, the use of *Corbula trigona* shell powder in the treatment of contaminated water could be an effective solution given its comparative advantages due to its chemical composition rich in $CaCO_3$.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest. *Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

References

[1] J. Polet, Première approche d'une industrie sur coquillage identifiée dans un amas coquillier de Basse Côte d'Ivoire (Nyamwan), *J. Afr.* 65 (1995) 93–109. doi.org/10.3406/jafr.1995.2433.

[2] T.R. Bouye, A. Sika, J.D. Memel, M. Karamoko, A. Otchoumou, Effets de la teneur en poudre de coquilles de bivalves (*Corbula trigona*) du substrat sur les paramètres de croissance d'*Achatina*

achatina (Linné, 1758) en élevage hors-sol, *Afr. Sci. Rev. Int. Sci. Technol.* 9 (2013) 142–153. https://doi.org/10.4314/afsci.v9i2.142–153.

[3] K.Z. Elwakeel, Ahmed.M. Elgarahy, S.H. Mohammad, Use of beach bivalve shells located at Port Said coast (Egypt) as a green approach for methylene blue removal, *J. Environ. Chem. Eng.* 5 (2017) 578–587. https://doi.org/10.1016/j.jece.2016.12.032.

[4] F. Marin, N. Le Roy, B. Marie, The formation and mineralization of mollusk shell, *Front. Biosci. Sch. Ed.* 4 (2012) 1099–1125. https://doi.org/10.2741/s321.

[5] D.E. Jacob, A.L. Soldati, R. Wirth, J. Huth, U. Wehrmeister, W. Hofmeister, Nanostructure, composition and mechanisms of bivalve shell growth, *Geochim. Cosmochim. Acta.* 72 (2008) 5401–5415. https://doi.org/10.1016/j.gca.2008.08.019.

[6] S. Widyastuti, I.A.K. P., Synthesis and characterization of CaCO3 (calcite) nano particles from cockle shells (Anadara granosa Linn) by precipitation method, *AIP Conf. Proc.* 1855 (2017) 030018. https://doi.org/10.1063/1.4985488.

[7] S.K. Mahmood, M.Z.A.B. Zakaria, I.S.B.A. Razak, L.M. Yusof, A.Z. Jaji, I. Tijani, N.I. Hammadi, Preparation and characterization of cockle shell aragonite nanocomposite porous 3D scaffolds for bone repair, *Biochem. Biophys. Rep.* 10 (2017) 237–251. https://doi.org/10.1016/j.bbrep.2017.04.008.

[8] Z. Alhalili, H. Souli, M. Smiri, Effect of LEO (Lycium Essential Oils) as Green Inhibitors of Calcium Carbonate Scale on Nanoparticles-Doped Ultrafiltration Membrane (UFM) and Water Treatment, *Arab. J. Sci. Eng.* 47 (2022) 6233–6243. https://doi.org/10.1007/s13369-021-06183-5

[9] N.S. Yapo, S. Aw, B.G.H. Briton, P. Drogui, K.B. Yao, K. Adouby, Removal of fluoride in groundwater by adsorption using hydroxyapatite modified *Corbula trigona* shell powder, *Chem. Eng. J. Adv.* 12 (2022) 100386. https://doi.org/10.1016/j.ceja.2022.100386.

[10] Y. Shan, J. Zhao, H. Tong, J. Yuan, D. Lei, Y. Li, Effects of activated carbon on liquefaction resistance of calcareous sand treated with microbially induced calcium carbonate precipitation, *Soil Dyn. Earthq. Eng.* 161 (2022) 107419. https://doi.org/10.1016/j.soildyn.2022.107419.

[11] L. Poudyal, K. Adhikari, M. Won, Nano Calcium Carbonate (CaCO3) as a Reliable, Durable, and Environment-Friendly Alternative to Diminishing Fly Ash, *Materials.* 14 (2021) 3729. https://doi.org/10.3390/ma14133729.

[12] M. Zuykov, E. Pelletier, R. Saint-Louis, A. Checa, S. Demers, Biosorption of thorium on the external shell surface of bivalve mollusks: The role of shell surface microtopography, *Chemosphere.* 86 (2012) 680–683. https://doi.org/10.1016/j.chemosphere.2011.11.023.

[13] A.A. Jalil, S. Triwahyono, M.R. Yaakob, Z.Z.A. Azmi, N. Sapawe, N.H.N. Kamarudin, H.D. Setiabudi, N.F. Jaafar, S.M. Sidik, S.H. Adam, B.H. Hameed, Utilization of bivalve shell-treated Zea mays L. (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green, *Bioresour. Technol.* 120 (2012) 218–224. https://doi.org/10.1016/j.biortech.2012.06.066.

[14] L. Aké Assi, G. Paradis, Malacofaune et flore holocènes d'un forage en bordure de la lagune Adjin (Côte d'Ivoire), *Geobios.* 15 (1982) 43–52. https://doi.org/10.1016/S0016-6995(82)80057-0

[15] L. Etim, Y. Sankare, T. Brey, W. Arntz, The dynamics of unexploited population of *Corbula trigona* (Bivalvia Corbulidae) in a brackish-water lagoon, Cote d'Ivoire, *Arch. Fish. Mar. Res.* 46 (1998) 253–262. https://doi.org/10013/epic.11353.

[16] B.D. Turner, P. Binning, S.L.S. Stipp, Fluoride Removal by Calcite: Evidence for Fluorite Precipitation and Surface Adsorption, *Environ. Sci. Technol.* 39 (2005) 9561–9568. https://doi.org/10.1021/es0505090.

[17] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon.* 37 (1999) 1215–1221. https://doi.org/10.1016/S0008-6223(98)00317-0.
[18] K.Z. Elwakeel, Ahmed.M. Elgarahy, S.H. Mohammad, Use of beach bivalve shells located at Port Said coast (Egypt) as a green approach for methylene blue removal, *J. Environ. Chem. Eng*. 5 (2017) 578–587. https://doi.org/10.1016/j.jece.2016.12.032.
[19] H.E.S. Nour, Distribution and accumulation ability of heavy metals in bivalve shells and associated sediment from Red Sea coast, Egypt, *Environ. Monit. Assess.* 192 (2020) 353. https://doi.org/10.1007/s10661-020-08285-3.
[20] B.-J. Ye, B.-G. Kim, M.-J. Jeon, S.-Y. Kim, H.-C. Kim, T.-W. Jang, H.-J. Chae, W.-J. Choi, M.-N. Ha, Y.-S. Hong, Evaluation of mercury exposure level, clinical diagnosis and treatment for mercury intoxication, *Ann. Occup. Environ. Med.* 28 (2016) 5. https://doi.org/10.1186/s40557-015-0086-8.
[21] X. Luo, X. Song, Y. Cao, L. Song, X. Bu, Investigation of calcium carbonate synthesized by steamed ammonia liquid waste without use of additives, *RSC Adv.* 10 (2020) 7976–7986. https://doi.org/10.1039/C9RA10460G.
[22] R.-J. Qi, Y.-J. Zhu, Microwave-Assisted Synthesis of Calcium Carbonate (Vaterite) of Various Morphologies in Water−Ethylene Glycol Mixed Solvents, *J. Phys. Chem. B.* 110 (2006) 8302–8306. https://doi.org/10.1021/jp060939s.
[23] Y. Wang, Y.X. Moo, C. Chen, P. Gunawan, R. Xu, Fast precipitation of uniform CaCO3 nanospheres and their transformation to hollow hydroxyapatite nanospheres, *J. Colloid Interface Sci*. 352 (2010) 393–400. https://doi.org/10.1016/j.jcis.2010.08.060.
[24] Y. Mori, T. Enomae, A. Isogai, Preparation of pure vaterite by simple mechanical mixing of two aqueous salt solutions, *Mater. Sci. Eng. C.* 29 (2009) 1409–1414. https://doi.org/10.1016/j.msec.2008.11.009.
[25] S. Niju, K.M. Meera Sheriffa Begum, N. Anantharaman, Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve clam shell, *Arab. J. Chem.* 9 (2016) 633–639. https://doi.org/10.1016/j.arabjc.2014.06.006.
[26] N.S. Yapo, B.G.H. Briton, S. Aw, L. Reinert, P. Drogui, K. Adouby, Bivalve shells (*Corbula trigona*) as a new adsorbent for the defluoridation of groundwater by adsorption-precipitation, *J. Environ. Sci. Health Part A.* 56 (2021) 694–704. doi.org/10.1080/10934529.2021.1917937.
[27] A.N. Mohd Faizal, N.R. Putra, M.A. Ahmad Zaini, Scylla Sp. Shell: a potential green adsorbent for wastewater treatment, *Toxin Rev.* (2022) https://doi.org/10.1080/15569543.2022.2039201.
[28] H.H. Kzar, O.D. Salahdin, L.A.B. Arenas, R.M.R. Parra, S. Aravindhan, F. Mohammed, M.J. Ansari, M.E. Al-Gazally, K.F. Uktamov, T.A. Hamza, A.K.O. Aldulaim, M.K. Abid, Solamen Vaillanti Mollusk Powder as an Efficient Biosorbent for Removing Cobalt Ions from Aqueous Solution: Kinetic and Equilibrium Studies, *Phys. Chem. Res.* 11 (2023) 159–169. https://doi.org/10.22036/pcr.2022.336422.2073.

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