

Development and optimization of hydroxyapatite/kaolin-based ceramic materials as potential adsorbents for water purification

Juliana O. Iji^{a,c,f}, Fatima B. Ibrahim^{a,c}, Abdullahi S. Argungu^a, David O. Obada^{b,c,d,e,*}

^a Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Zaria, Nigeria

^b Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria

^c Africa Centre of Excellence on New Pedagogies in Engineering Education, Ahmadu Bello University, Zaria, Nigeria

^d Mathematical Modelling and Intelligent Systems for Health and Environment Research Group, School of Science, Atlantic Technological University, Sligo, Ireland

^e Multifunctional Materials Laboratory, Shell Office Complex, Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria

^f Department of Water Resources and Environmental Engineering, University of Ilorin, Ilorin, Nigeria

ARTICLE INFO

Keywords:

Hydroxyapatite
Grey relational analysis
Porosity
Brittleness Index
Adsorption
Filtration
Ceramic materials

ABSTRACT

In this study, porous hydroxyapatite/kaolin-based ceramic (PHKC) materials were fabricated using beneficiated kaolin, starch as a pore former, and hydroxyapatite (HAp) as potential adsorbents for water purification. The effect of different raw materials content and sintering temperature on the physical, chemical, and mechanical properties of the ceramic materials was investigated, and grey relational analysis was used to optimize the process. A PHKC filter was produced using parameters from the grey relational analysis and the filter was used to treat tannery wastewater. The pH, electrical conductivity (EC), total dissolved solids (TDS), temperature, chromium, and turbidity of the raw tannery effluent and treated effluent were determined. The volumetric porosity of the PHKC materials ranged between 35 and 43% and this shows that all samples obtained in the study can be considered as porous materials. Surface area analysis (B.E.T) showed that the samples with pore formers had a greater number of small pores, and increasing the sintering temperature led to the reduction of the number of pores. The brittleness index of the ceramic materials were in the range of 0.19 and 0.46. Using the grey relational analysis, the sample with the highest grey relational grade was sample S8 (0.72), and the least was sample S3 (0.38). From the findings, it could be concluded that the ceramic samples (S3 and S8) have inherent properties for use as adsorbent materials in the purification of wastewater. From the adsorption experiments, the chromium removal rates of 67.91 %, 98.67%, and 98.74% were obtained for kaolin, kaolin + HAp, and kaolin + HAp + starch filters, respectively. The filter made from the optimum material composition of kaolin, HAp, and starch gave the maximum adsorption capacity of chromium (98.74%) at pH 7.12, and temperature of 25.23°C, while the turbidity removal was 97.07%.

1. Introduction

Environmental pollution remains a major health concern today (Suzuki et al., 2020). One form of pollution that has become a global issue is water pollution which is caused by both natural and human activities as highlighted by Mustapha et al. (2019). The amount and toxicity of industrial waste released into the environment vary depending on industrial processes (Varjani et al. 2020). During manufacturing, untreated effluents are often discharged into bodies of water, contributing to water pollution (Mustapha et al. 2020). Most industrial waste is water-based and released untreated or inadequately treated into waterways, leading to water pollution (Van Puijenbroek

et al., 2019). Medical, industrial, and agricultural sectors are all sources of contaminants released into water bodies, such as hormones, pharmaceuticals, personal care products, mining, electroplating, dyeing, tanning, textiles, herbicides, fertilizers, pesticides, and fungicides (Arif et al., 2020).

The industrial tanning process converts animal hides and skins into leather produce with coloured, highly foul-smelling wastewater that contains a variety of inorganic and organic pollutants (e.g., sulphides, chlorides, chromium complex collagens, and hydrogen sulphide) that threaten human life and must be addressed (Mustapha et al., 2020). According to statistics obtained globally, 300 million pieces of cowhide are processed in the leather markets each year resulting in an estimated

* Corresponding author.

E-mail address: obadavid4@gmail.com (D.O. Obada).

yearly tannery wastewater output of 300 million tons (Zhao and Chen, 2019). In the field of pollution control, more efforts are being put into the environmental remediation business (Zhang et al., 2022), with the focus shifting to the creation of new and improved technologies to eliminate air, soil, and water contaminants. Several methods such as adsorption have recently been established to treat wastewater in a green economically feasible and effective manner (Hubadillah et al., 2018). Adsorption is a common method for removing contaminants from liquids. The batch adsorption technique relies on the use of either modified or unmodified adsorbents controlled by parameters such as pH, concentration, contact or residence duration, adsorbent dosage, and temperature (Al-Essa and Khalili, 2018). Numerous techniques have been adopted for the treatment of tannery wastewater, grading from simple to advanced methods (Korpe and Rao, 2021). However, most of them exhibit some drawbacks such as the high cost of treatment, generating toxic sludge and occupying large spaces etc. The adsorption process is a convenient technique in terms of flexibility, cost, and simplicity, but the high cost of materials affect the use of the adsorption process for wastewater treatment in developing countries (Mustapha et al., 2021). Also, adsorbents have low density and high porosity, and their mechanical strength is usually low which hinders their large-scale application in a corrosive environment (Han et al., 2021).

In the treatment of wastewater, membrane technology has been established as the principal technique for the isolation of contaminants from polluted sources due to its great efficiency, excellent filtration capability and low energy consumption (Kumar et al., 2019). In the water industry, membrane technology is used to improve water quality for use, reuse, or discharge into the environment. Membranes may eject contaminants such as protozoa, bacteria, and ions ranging from finely porous to non-porous structures (Sharma et al., 2020). In some circumstances, the key advantages of membrane technology are a reduced number of processing steps, less energy usage, high separation efficiency, and improved quality of the finished product. Ceramic membrane technology for industrial wastewater treatment has lately gained popularity due to its superior features over polymeric membranes. When compared to polymeric membranes, ceramic foams or membranes have high mechanical strength, high chemical stability, (Kamarudin et al., 2021; Han et al., 2022), high porosity, strong adsorption capabilities, hierarchical-pore structure and good recyclability (Li et al., 2022). Nonetheless, the fabrication of ceramic membranes is generally made of alumina as the starting material which necessitates thermal treatment at high temperatures and cost of production (Hubadillah et al., 2020). The potential of ceramic membranes from naturally sourced materials such as ashes from agricultural wastes, animal bone wastes, and clays has attracted great attention for the fabrication of ceramic membranes (Hubadillah et al., 2017). In this regard, one of these materials is hydroxyapatite (HAp) ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which has shown remarkable adsorption efficiency in filtering wastewater (Foroutan et al., 2021).

HAp has received a lot of interest from many fields of research study due to its inherent properties and remarkable structure (Ibrahim et al., 2019; Osuchukwu et al., 2022a; Osuchukwu et al., 2022b; Obada et al., 2023b). HAp, a bio-ceramic-based material, may be synthesized from natural sources such as fish, cow, camel and sheep bones by calcining the bones at temperatures above 800 °C (Obada et al., 2022). HAp and its sources have been developed as an alternative adsorbent for the treatment of dye and heavy water contaminants in wastewater. This is due to some important properties which include high thermal stability, high ion exchange, low water solubility and high adsorption affinity for many heavy metals (Amenaghawon et al., 2022). HAp sourced from natural sources are available in sufficient numbers, benefit the environment through waste management and are cost-effective (Obada et al., 2023a). Selimin et al., (2022) synthesized natural HAp adsorbent from black tilapia fish for the removal of Cr(VI) in wastewater. The result shows that the Cr(VI) removal rate was at 60.43% after 60 min filtration time. However, due to the poor strength of HAp as a stand-alone material, several studies reinforced HAp with other

materials with high strength (Akartasse et al., 2022; Hokkanen et al., 2016; Huang et al., 2023; Lu et al., 2019). For example, Hokkanen et al. (2016) investigated the efficiency of HAp nanocomposite reinforced with nano-cellulose and bentonite in the removal of cadmium, nitrate ions, nickel, and phosphate. The result shows that the developed composite adsorbent was effective in ion adsorption with high adsorption capacities. Kaolin is another alternative ceramic material to produce ceramic adsorbents among all clays (Hedfi et al., 2016; Obada et al., 2016; Obada et al., 2017). Kaolin is a desirable substrate for producing ceramic adsorbents because of its mineralogical qualities, chemical composition, and particle size which makes it simple and possible to produce good membranes (Obada et al., 2017; Kamarudin et al., 2021). Kaolin gives the adsorbents low plasticity, high refractoriness, and hydrophilic properties, all of which are highly desirable for adsorbent characteristics (Kamarudin et al., 2021). Also, kaolin-based ceramics have high mechanical strength but low porosity since the particles are closely packed which limits its usage for industrial applications. To overcome this drawback, several studies incorporate pore formers (porogens) in ceramic adsorbents. For example, Obada et al., (2016) produced porous ceramics from kaolin using different materials like sawdust, Styrofoam and high-density polyethylene as the porogens. The authors reported that 67% porosity was obtained with 80 wt.% kaolin. Similarly, Efavi et al., (2012) developed ceramic bodies from kaolin sourced from two different locations and pores were created using millet, sawdust, charcoal, Styrofoam, rice, and charcoal as the pore formers. The results showed that the apparent porosity of the samples was within the range of 28% and 67%. From the reviewed literature, it was observed that several articles reported only the mechanical properties, thermal and chemical stability of the ceramic materials made from kaolin. However, Kaolin-based ceramics for water purification application were produced by Salami et al., (2022) using a factorial design of experiment. The filtration capacity of the produced ceramic was tested on its ability to remove heavy metals like lead (Pb), zinc (Zn), and many others. From the results obtained, the removal efficiency of the ceramic adsorbent without the pore former was less than 10% which was attributed to the unfinished adsorption process and the low affinity of the kaolin to some heavy metals (e.g., lead). Therefore, it is vital to incorporate materials with high adsorption affinity in kaolin-based materials to improve the removal efficiency of the ceramic adsorbents.

For the first time, optimized variants of PHKC materials were produced as potential adsorbents. The use of HAp and kaolin in the development of the adsorbents are in two folds. One of the reasons is that HAp cannot be used as the sole adsorbent material due to its brittleness, and low fracture toughness. However, kaolin has improved mechanical properties and mixing it with HAp can enhance the mechanical strength of the adsorbent. Secondly, kaolin has a limited ion exchange capacity which can influence the adsorbent performance. The inclusion of HAp in the matrix can increase the adsorption affinity. Hence, this study focused on the fabrication of PHKC adsorbents using beneficiated kaolin, starch as pore former and HAp. Next, the effect of sintering temperature on the physical and mechanical properties of the pelletized ceramic adsorbents was investigated. The optimum condition to produce the adsorbent used for the tannery wastewater treatment was determined using the grey relational analysis.

2. Materials and method

2.1. Materials

The materials used in this study are kaolin obtained from Kankara, Kastina State, HAp derived from bovine which was sourced from an Abattoir in Zaria, Nigeria, and starch (pore former) purchased from Sabon Gari Market, Zaria, Nigeria. The chemical composition of the raw materials (kaolin and HAp) in weight percent (wt.%) is as follows. Kankara kaolin (Obada et al., 2017): SiO_2 - 51.50%; Al_2O_3 - 39.24%; Fe_2O_3 -0.95%; TiO_2 -1.46%; MgO -0.47%; CaO -1.21%; Na_2O - 0.61%; K_2O -

Table 1
Taguchi Design Input and Response Parameters.

S/N	Input Parameters	Input Level		Response Parameters
		High	Low	
1.	Sintering Temperature(°C)	1000	800	Brittleness Index
2.	Pore former (wt.%)	10	0	Pore size/ Pore diameter
3.	HAp (wt.%)	30	10	Porosity (%)
4.	Kaolin (wt.%)	90	60	

1.80%; CuO- 0.02%; and LoI-15.01%. The chemical composition (elemental and oxides) of the HAp used in this study is detailed in the study by [Osuchukwu et al. \(2022c\)](#).

2.2. Preparation and beneficiation of kaolin

The debris in the collected clay sample was removed and thereafter dried at room temperature for three days. The removal of impurities was done by physical separation as described by [Obada et al., \(2016a; 2016b\)](#) then followed by a wet/soaking method. The sample was benefited by soaking the debris-free clay in a plastic container with de-ionized water for 48 h. The resultant slurry was plunged and screened through a sieve and then allowed to settle. The water was decanted, and the sample was air-dried. The obtained powder was then crushed using a mortar and pestle. Finally, the powder was sieved using a 100 µm mesh sieve to obtain a fine powder.

2.3. Preparation of cow bone powder

The waste bovine bones were boiled for 1 hour to remove attached tissues, fats, and macroscopic adhering impurities. Next, the bones were washed and rinsed severally with clean water to ensure the complete removal of bone marrow, attached meat, and other soft tissues. The washed bones were then dried in an oven at 100 °C for 24 h to remove the water moisture in them. The dried bones were carbonized until the fat was completely removed. The carbonized bones were then calcined in a muffle furnace at temperatures of 800 °C, 900 °C, and 1000 °C. The calcined animal bones were manually crushed and sieved using a 100 µm mesh size ([Obada et al., 2021](#)).

2.4. Preparation and fabrication of sintered specimens

The Taguchi design of experiments was employed as an optimization tool in this study, leading to a set of 18 different samples. The design from the Design Expert Software was modified so that the total

composition of the three raw materials brings to a total of 100 wt.%. The parameters used in this study with the response materials are given in [Table 1](#). The raw materials (Kaolin, HAp, and Starch) were mixed according to the formulation given in [Table 2](#) using water as a binder. Next, the blended powders were cold compacted in a designed stainless-steel mould by applying a compacting pressure of 10 MPa to obtain green cylindrical-shaped compacts of a diameter of 25 mm and 12 mm in height approximately.

The compacted samples were de-moulded and air-dried at room temperature (temperature of 27 °C, and humidity of 41%) for three days to obtain the desired strength. The samples were then subjected to thermal treatment using sintering temperatures of 800, 900, and 1000 °C. Three sintering regimes were used. Firstly, the calcination temperature was set up at 500 °C at a heating rate of 8 °C/min where all the porogen content would have burnt off. Next, the temperature was increased to 800, 900, and 1000 °C at a heating rate of 2 °C/min and a 2 h dwell time to fabricate the pellets for the physical and mechanical measurements ([Salami et al., 2022](#)). The response parameters that were considered are porosity, pore size, and brittleness index as shown in [Table 1](#). The thickness and the diameter of the fabricated porous ceramics are presented in [Table 2](#).

2.5. Characterization of the raw materials and the optimum sample

X-ray diffraction technique was used to identify the phases present in the raw materials. X-ray diffraction was conducted using an X-ray Diffractometer with a monochromatic Cu K_α radiation in a 2-theta range of 10-70°. The measurement was performed at a scanning rate of 4 min⁻¹ with a step size of 0.002° and the crystallite size was calculated using Scherrer's equation as stated in [Equation 1](#). The crystallinity is calculated using the ratio of the total area under the crystalline peaks and the total area of the pattern. An X-ray Diffractometer was used to elucidate the phase transformation after heat treatment. Fourier Transform Infrared Spectrophotometer (FTIR), Shimadzu, FTIR-8400s, was used to analyze the functional groups of the kaolin and HAp with a spectra range of 4000 – 400cm⁻¹.

$$B(2\theta) = \frac{K \lambda}{L \cos(\theta)} \quad (1)$$

Where: K= dimensionless shape factor (0.9), λ= X-ray wavelength, L = FWHM, and θ = Bragg angle.

Table 2
Formulations of the raw materials using the design of experiments.

Sample Code	Input Parameters				Thickness (mm)	Diameter (mm)
	Kaolin Content	HAp Content	Pore former content	Sintering Temperature		
S1	90	10	0	800	13.0	26.5
S2	70	20	10	900	15.0	26.5
S3	80	10	10	1000	15.0	26.0
S4	80	20	0	900	15.0	26.0
S5	70	30	0	1000	14.0	26.0
S6	60	30	10	800	15.0	27.0
S7	90	10	0	900	14.0	27.0
S8	90	10	0	1000	15.0	26.0
S9	70	20	10	800	15.0	27.0
S10	70	20	10	1000	14.5	26.1
S11	80	10	10	900	16.0	27.0
S12	80	10	10	800	16.0	26.5
S13	80	20	0	1000	15.0	25.5
S14	80	20	0	900	14.5	26.0
S15	70	30	0	800	13.5	26.5
S16	70	30	0	900	15.0	27.0
S17	60	30	10	1000	15.0	26.0
S18	60	30	10	900	15.0	26.5

2.6. Volumetric porosity measurement

The apparent porosity of the fabricated pellets was calculated using Equation 2 as stated by Bose and Daz, (2013). After removing the fabricated pellets from the furnace, the weight of the dry samples was measured and then soaked in water for 24 h. Next, the soaked samples were wiped with tissue paper to soak out excess water and the wet weight of the samples was measured. The porosity was calculated using the expression.

$$\text{Porosity} = \left(\frac{W_2 - W_1}{\rho \times V} \right) \quad (2)$$

Where: W_2 =Weight of the wet samples after soaking for 24 hours, W_1 =Weight of the dry samples, ρ = Density of water, V = Volume of the fabricated samples which was a function of the diameter and height of the samples.

2.7. Brunauer-Emmett-Teller (BET) analysis

BET-specific surface area, pore volume, and pore size of the fabricated pellets were determined using the Quantachrome NovaWin. The pellets were first dried in an argon stream in a way to obtain uniform weight. The pellets were further placed in liquid Nitrogen and the amount of adsorbed gas was measured. The outgas time of 3 h was considered for the process. Based on the amount of desorption and adsorption, the surface area, pore volume, and pore sizes were determined. The surface area of the sample was measured based on the BET equation (Equation 3) for multilayer and nitrogen isotherm.

$$\frac{1}{X \left[\left(\frac{P_0}{P} \right) - 1 \right]} = \frac{1}{X_m C} + \frac{C - 1}{X_m C} \left(\frac{P}{P_0} \right) \quad (3)$$

where:

X represents the weight of gas that is adsorbed at a relative pressure of P/P_0 , while X_m denotes the weight of the adsorbate forming a monolayer of surface coverage. The BET C constant, known as "C," is linked to the energy of adsorption in the initial adsorbed layer. Therefore, its value indicates the extent of the interactions between the adsorbent and the adsorbate.

2.8. Mechanical properties measurement

The hardness of the specimen was determined using Vickers' micro-hardness tester with a pyramid indenter and a load of 300 g and 10 seconds as the loading time. Next, the fracture toughness, K_{1c} , and the brittleness index were calculated using the equation adopted by Akpan et al., (2020). The fracture toughness, K_{1c} , $MPa^{1/2}$ was obtained using Equation 4 where a and l were both obtained from the micro indenter machine during the hardness test.

$$K_{1c} = 0.016 \times \left(\frac{c}{a} \right)^{-1.5} \times H_v \times (a)^{0.5} \quad (4)$$

where H_v is the Vickers hardness in MPa, a is the half diagonal length in mm, l is the crack length from the center of the indent to the crack tip in mm, $2c = 2(a + l)$ in mm

The brittleness index was calculated using Equation 5

$$\text{Brittle Index} = \frac{H_v}{K_{1c}} \quad (5)$$

2.9. Grey relational analysis steps

The grey relational analysis was performed to obtain the sample with the optimum parameters, and this was done using steps as described by Kazemian et al., (2021). The signal-to-noise ratio was calculated using the smaller-the-better for the responses using Equation 6 since minimization of the responses is needed for the various target outputs.

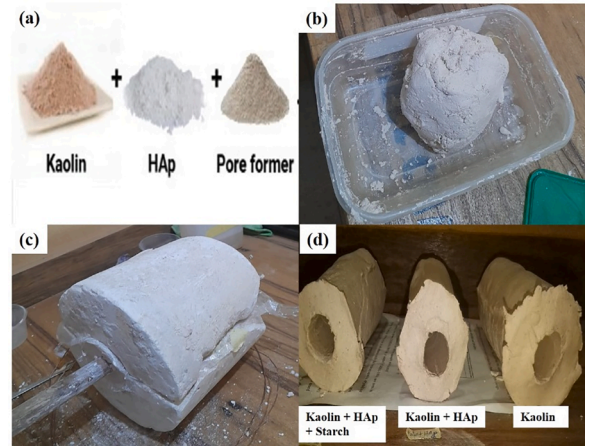


Plate 1. Process in the fabrication of ceramic adsorbents.

$$S/N \text{ ratio } (\eta) = -10 \log_{10} \left(\frac{1}{n} \sum_{i=1}^n y_{ij}^2 \right) \quad (6)$$

Then, Normalizing y_{ij} as Z_{ij} ($0 \leq Z_{ij} \leq 1$) of the data was done by using the formula in Equation 7 to reduce the variability and avoid the effect of adopting a different unit. It is necessary to normalize the original data before applying the grey relation theory since it affects the ranking.

$$Z_{i,j} = \frac{\max(y_{i,j=1,2,\dots,n}) - y_{i,j}}{\max(y_{i,j=1,2,\dots,n}) - \min(y_{i,j=1,2,\dots,n})} \quad (7)$$

(Used along with the S/N ratio for the larger the better)

The grey relational coefficient was determined from the normalized S/N ratio values using Equation 8.

$$\gamma(y_o(k)y_1(k)) = \frac{\Delta_{\min} + \xi \Delta_{\max}}{\Delta_{oj}(k) + \xi \Delta_{\max}} \quad (8)$$

Where:

- i $y_o(k)$ = reference sequence ($y_o(k) = 1, k=1,2,\dots,m$);
- ii $\Delta_{oj} = \|y_o(k) - y_j(k)\|$, the absolute value of the difference between $y_j(k)$ and $y_o(k)$
- iii $\Delta_{\min} = \min, \min \|y_o(k) - y_j(k)\|$, the smallest value of $y_j(k)$
- iv $\Delta_{\max} = \max, \max \|y_o(k) - y_j(k)\|$, the largest value of $y_j(k)$

ξ = is the distinguishing coefficient, which is defined in the range $0 \leq \xi \leq 1$

Equation 9 was used to generate the grey relational grade and the optimal factor was obtained.

$$\bar{\gamma} = \frac{1}{k} \sum_{i=1}^n \gamma_i \quad (9)$$

Where: $\bar{\gamma}$ = grey relational grade, and k = number of performance characteristics.

2.10. Production of the HAp/kaolin-based ceramic adsorbent

Different sets of batch-formulated samples composed of kaolin, HAp, and pore former (starch) were mixed with water and kneaded to eliminate lumps and trapped air bubbles and to ensure homogeneity. Samples S3 and S8 are ceramic bodies with (80 wt.% of kaolin + 10 wt.% of HAp + 10 wt.% of pore former) and (90 wt.% of kaolin + 10 wt.% of HAp), respectively, while kaolin is the control sample with no HAp or pore former (100% kaolin). Each mixture was then filled into a mold and

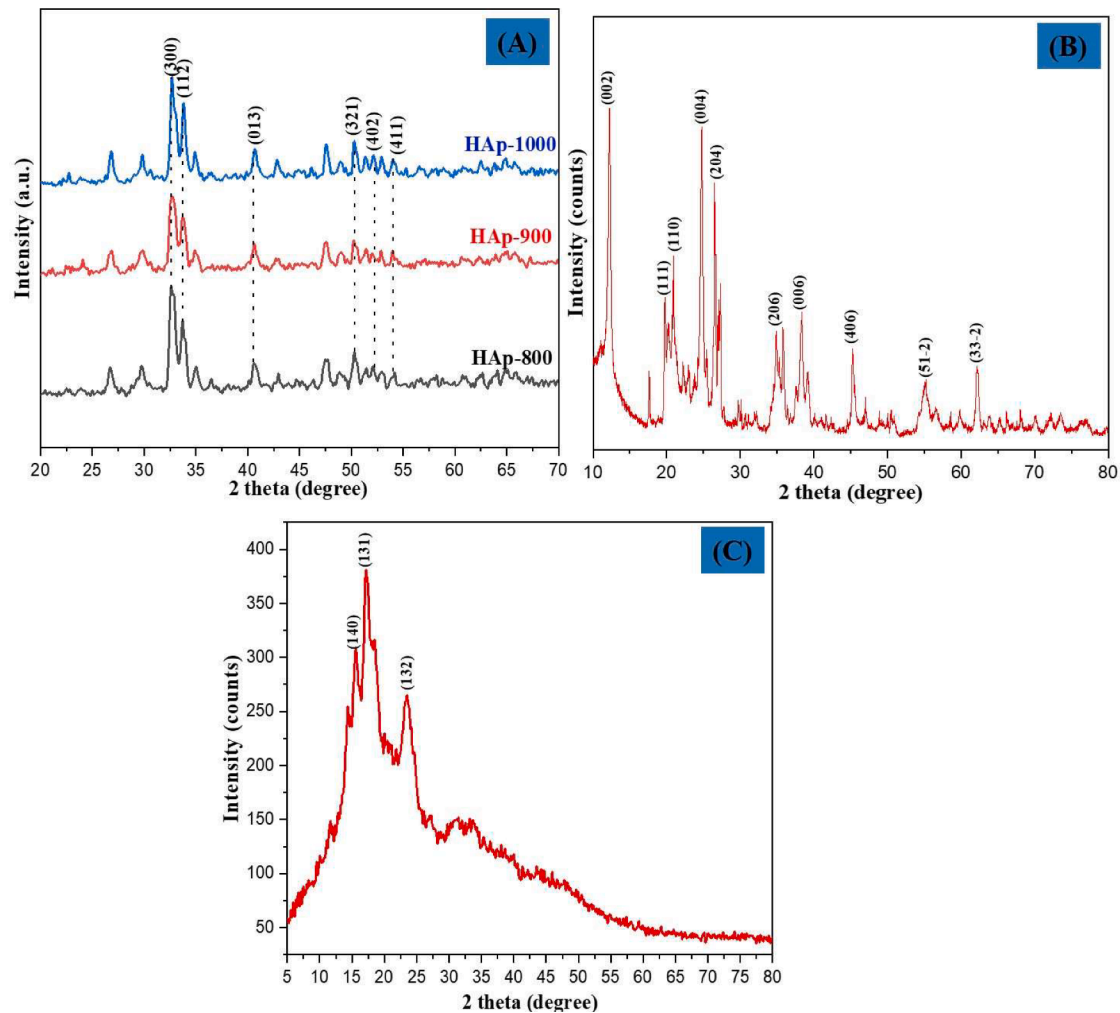


Fig. 1. XRD pattern: (A) HAp at different temperatures (B) Kaolin (C) Starch derived from corn.

pressed to the same level to ensure compactness and dimensional homogeneity. The as-prepared green body samples were removed from the mold and dried at room temperature (25 °C) on boards for three (3) days after which they were further dried at 100 °C to remove moisture as illustrated in Plate 1 (a-d). This increased their green strength and made them safe for subsequent handling. The dried batch-formulated green bodies were then sintered at 1000 °C for 2 h in an electric muffle furnace at a heating rate of 5 °C/ min. (Obada et al., 2016; Obada et al., 2020)

2.11. Water sampling

Tannery wastewater was collected from the Nigerian Institute of Leather and Science Technology- NILEST, Zaria, Nigeria. The wastewater sample was a mixture of all stages of the tanning process e.g. soaking, liming, deliming, bating, pickling, chrome tanning, and retaining. The wastewater sample was collected in clean plastic containers from the collecting tank, stored in a cooling set and transported to the laboratory for analysis. Sample collection was based on the techniques outlined by Feka et al., (2021).

2.11.1. Characteristics of the tannery wastewater effluent

The physical parameters including pH, electrical conductivity (EC), total dissolved solids (TDS), temperature, chromium, and turbidity of raw tannery effluent and treated effluent were measured. pH, temperature, TDS, and conductivity were measured in situ using a combined pH/T°/TDS and conductivity meter. In the laboratory, turbidity was measured using a turbidimeter. Concentrations of chromium present in

the effluent were estimated using an Atomic Absorption Spectroscopic machine (Shimadzu GF-AAS Model AA-6800) following digestion of the samples with nitric acid and hydrochloric acid mixer in the ratio 3:1. The procedure was carried out at a pre-determined wavelength (λ max) of 357.9 nm. These parameters were selected because they are deleterious to the receiving environment, and they were included in the discharge limit (Reda, 2016).

2.11.2. Treatment process

2.11.2.1. Coagulation treatment of wastewater samples. Aluminium Sulphate ($\text{Al}_2\text{SO}_4)_3$ also regarded as alum was used as the primary coagulant. Stock solutions of alum were prepared according to the APHA procedure for the enhancement of the coagulation process by dissolving 15 grams (Islam et al., 2011) of aluminium sulphate in one litre of distilled water. Therefore, one ml of this stock gives an alum solution of 15 mg/l. This study consists of batch experiments involving rapid mixing, slow mixing, and sedimentation using alum as a coagulant. The apparatus allowed four beakers to be agitated simultaneously. One litre of raw wastewater sample was poured into 4 beakers each and placed under a special multiple stirrer rig. The prepared solution of alum was added at concentrations of 75, 150, 225, 300, 375, 450, 525 and 600 mg/l. The coagulant concentrations were added simultaneously. The set-up was stirred thoroughly for 10 minutes with a glass rod to enable total dispersal of the coagulant. Samples were then flocculated for 30 minutes and allowed to stand in a quiescent condition for 24 h on a

Table 3

The average crystallite size and crystallinity of the hydroxyapatite.

Sample Name	Average crystallite size (nm)	Crystallinity (%)
HAp-800	11.73	56.1
HAp-900	13.06	61.6
HAp-1000	18.88	72.5

workbench for the flocculation and sedimentation process to take place. The supernatant was decanted and analyzed, and the optimum coagulant dosage was then obtained. The jar test experiment was carried out using standard methods. A laboratory jar test equipment manufactured by Peterson Candy International Limited, England was used to carry out the coagulation on the water samples (Ibrahim et al., 2014).

2.11.2.2. Filtration treatment of wastewater samples. The effluent sample with the optimum coagulant dosage was further treated using a the fabricated adsorbents. The supernatant liquid after the settling process was poured into a filter system for filtration. The water filter system consists of two containers, one placed on top of the other. Both containers are made of white transparent plastic buckets and each bucket has a capacity of 3L. The upper unit holds the ceramic adsorbent while the bottom container collects treated water that seeps down through the ceramic adsorbent. The Cr concentration of the filtered solution was determined by an Atomic Absorption Spectrophotometer. The ceramic adsorbent was washed with clean water prior to assembly, for sterilization and to remove any fine clay particles from the ceramic adsorbent. The ceramic adsorbent is cylindrically shaped with a height of 202 cm and a diameter of 50 cm wide. The ceramic adsorbents are made of kaolin, kaolin mixed with HAp, and kaolin mixed with HAp and starch, respectively. The used ceramic adsorbents were reused and regenerated through sterilization by boiling them (Sagara, 2000).

2.12. Statistical analysis

To determine the differences in means of the parameters, the significance of variations within effluent samples was examined with one-way analysis of variance (ANOVA) i.e., differences between coagulants within each test variable e.g., pH, turbidity, etc. The least significant difference (LSD) was done as a post-hoc analysis to observe these variations at $p < 0.05$ level of significance. The data analysis was carried out using IBM SPSS version 23.

3. Results

3.1. Analysis of raw materials

The X-ray diffraction patterns of the calcined HAp powder at different temperature is illustrated in Fig. 1(A). The phase identification and purity of the powders were confirmed with the XRD analysis. It is observed that the prominent reflections of HAp at 32.64° and 33.85° corresponding to the (300) and (112) miller planes are common to the hexagonal phase of HAp as reported by Obada et al., (2020) and matched with the ICDD no.: 96-1095. According to the spectrum, the different temperature regimes plays a significant role in the formation of HAp. The sample sintered at 800°C showed more broad peaks when compared with other samples which implies low crystallinity. However, increasing the sintering temperature, the peaks become narrower leading to an increase in the crystallinity. Further, the reduction in crystallinity leads to an increase in the average crystallite size (Table 3). It is also observed that an additional phase (pentacalcium tri (phosphate) hydroxide) was noticed at a temperature above 900°C . The XRD pattern of kaolin as presented in Fig. 1(B) shows two prominent reflections at $2\theta = 12.4^\circ$ and 24.9° corresponding to the (002) and (004) miller planes, respectively. The peaks are matched with the ICDD card number 96-154-4873 and are like the reflections reported by Obada et al., (2021). The result confirmed that kaolinite was the dominant phase in

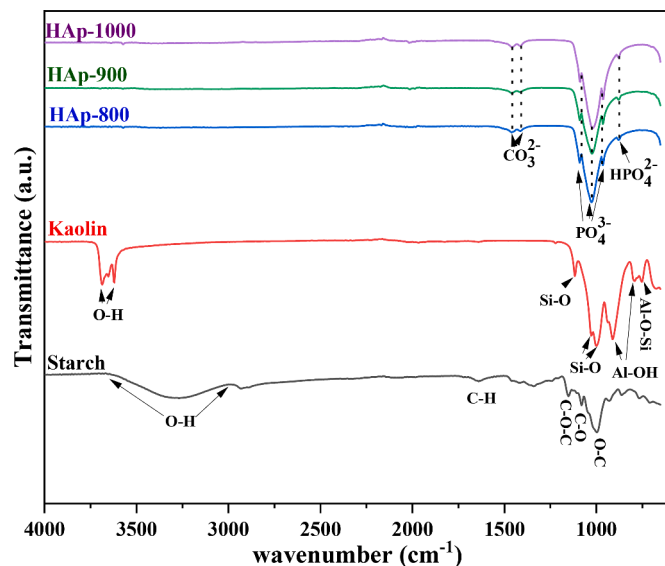


Fig. 2. FTIR spectra of the raw materials.

the pattern. The XRD pattern of the starch derived from corn also known as an A-type source of starch is illustrated in Fig. 1(C). From the pattern, there is a mixture of amorphous and crystalline features which is typical of the A-type crystalline structure of starch. The type A source of starch had major peaks at $2\theta = 12.58^\circ$ and 23.58° coupled with some low peaks at $2\theta = 27.36^\circ$. The peaks observed are like the A-type starch reported by Pozo et al., (2018) and Dome et al., (2020).

The FTIR spectra of the raw materials illustrated in Fig. 2 were recorded within the range of $4000\text{--}400\text{ cm}^{-1}$. The FTIR spectra of HAp (HAp-800, HAp-900, and HAp-1000) at different sintering regimes revealed that the functional groups that are present in calcium phosphate-based materials are PO_4^{3-} , HPO_4^{2-} and CaCO_3 (Obada et al., 2022). The formation of HAp was first observed through the broad and strong IR band around $1100\text{--}950\text{ cm}^{-1}$ and this can be attributed to the PO_4^{3-} asymmetric stretching. The presence of the carbonate functional group at 1457 and 1409 cm^{-1} could be attributed to the substitution of the OH in the HAp lattice or from the CO_2 in the atmosphere during sample preparation and handling. The effect of different sintering temperatures is pronounced with the increase or decrease in the intensities. For instance, the CaCO_3 band increases with the increase in temperature which shows that the CaCO_3 ion replaces the PO_4^{3-} ion in the HAp structure. The functional group present in the spectra shows a typical characteristic of HAp. For kaolin, the single bond region between $3700\text{--}3600\text{ cm}^{-1}$ shows the stretching at 3655 , and 3011 cm^{-1} which corresponds to the O-H groups and shows the presence of water content. Bands at 1020 and 1025 cm^{-1} are attributed to the Si-O stretching band. The bands at 746 cm^{-1} and 914 cm^{-1} represent the Al-O-Si bending vibration and Al-OH stretching in the kaolinite (Salami et al., 2022). The FTIR of the starch shows broadband within 3655 and 3011 cm^{-1} assigned to the stretching mode of the O-H group. The absorption peak at 1645 cm^{-1} corresponds to the intermolecular H-bond associated with the carboxyl group. The IR bands at 1152 , and 1080 cm^{-1} are assigned to C-O-C and C-O stretching, respectively.

3.2. Measurement of the volumetric porosity

For the fabrication of adsorbents, the volumetric porosity is an important property needed for optimization since it affects the performance. The adsorbent with high porosity leads to an increase in heavy metal or contaminant rejection and flux permeation. The calculated porosity of the fabricated adsorbent measured using Archimedes' method is illustrated in Fig. 3. It is observed that the porosity is between 35 and 43%. The result obtained in this study is closer to the porosity

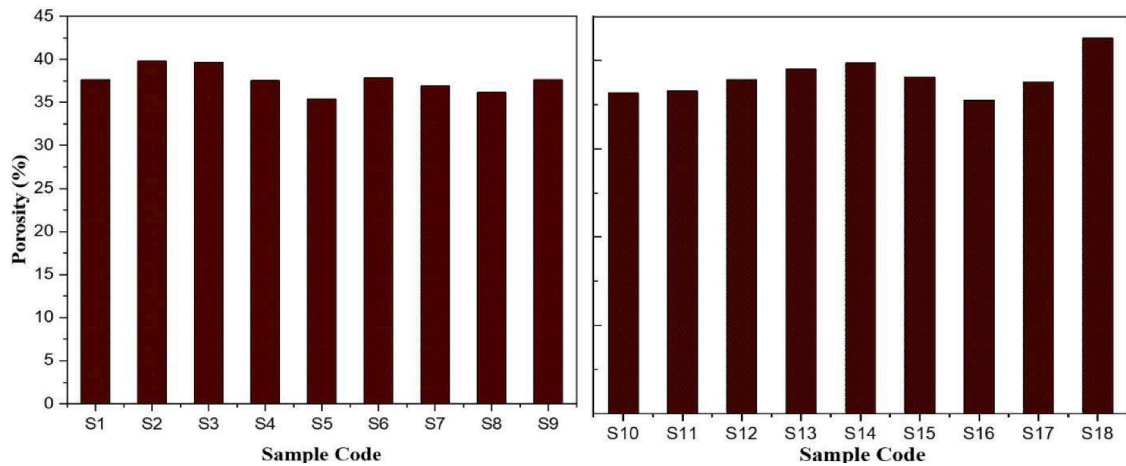


Fig. 3. Porosity of the fabricated samples.

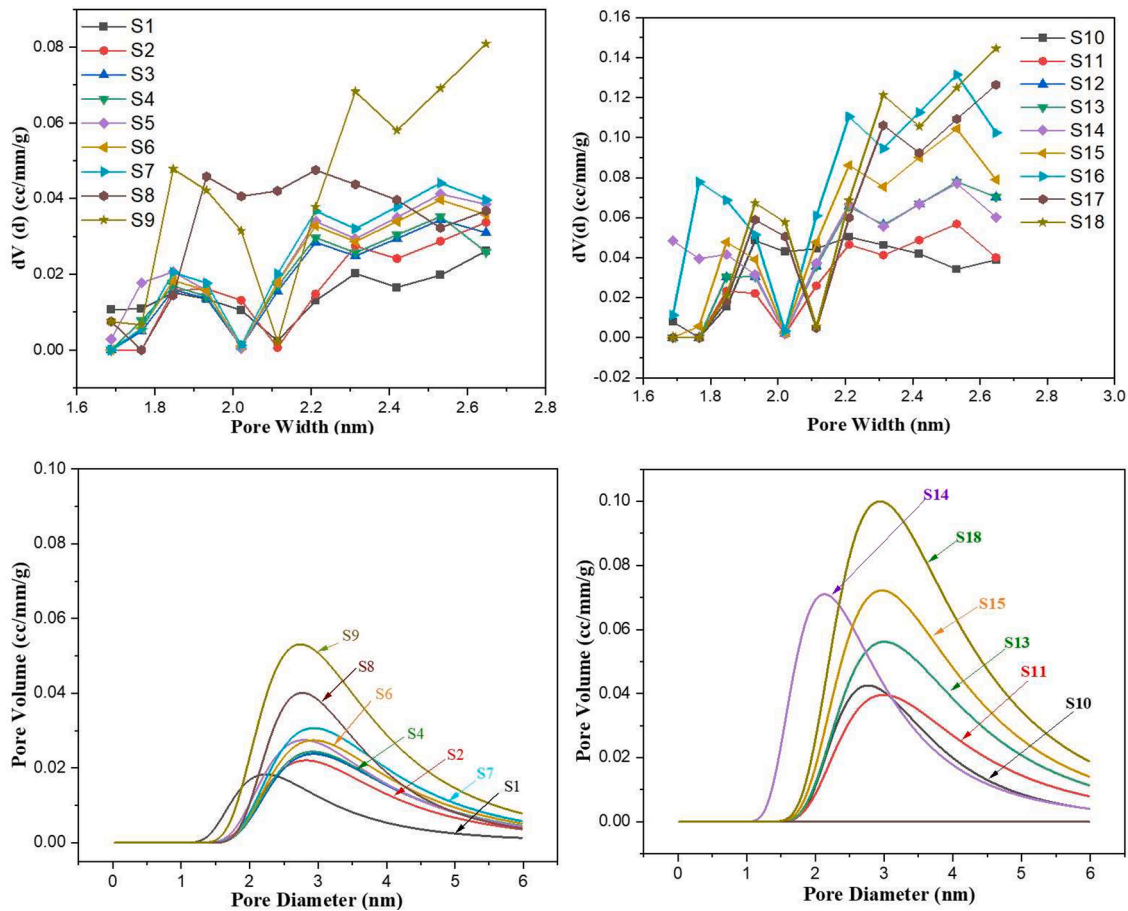


Fig. 4. (a): BJH pore size distribution curves of the fabricated samples. (b): Macropore size distribution of the fabricated samples.

reported by [Salami et al., \(2022\)](#), [Du et al., \(2022\)](#), and some commercial ceramic adsorbents where the porosity of the fabricated porous ceramic adsorbents is above 40%. According to [Malik et al., \(2020\)](#), ceramic materials are considered porous when the porosity is above 30%. Hence, all samples obtained in the study can be considered porous materials.

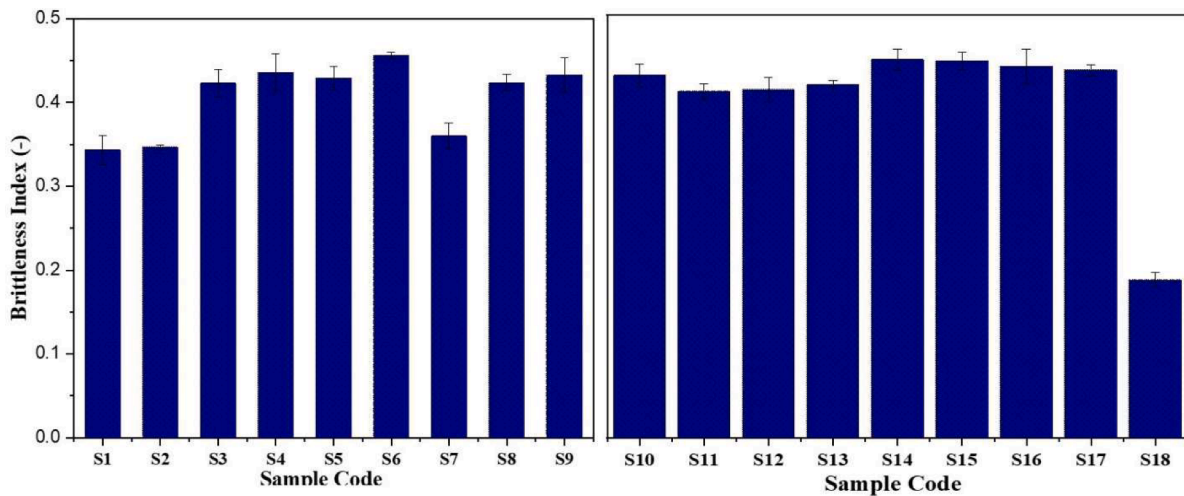
From the obtained porosity, it is observed that the input parameters affect the increase or decrease in the porosity of the fabricated adsorbents. For instance, the inclusion of the pore former (starch) increases the porosity significantly since the starch being a combustible material

might have burnt out leaving behind interconnected pores in the material. An example of the increase in porosity could be noticed in sample S16 with a porosity of 35.5%, and the inclusion of the pore former increases the porosity by approximately 17% as noticed in sample S18 (42.5%). In addition, a further increase in the sintering temperature above 900 °C led to a reduction of the porosity which is typical in ceramic materials. Sintering at high temperatures led to growth in the particles secondarily and reduction of the pores. Hence, it resulted in a significant decrease in the porosity accompanied by distinct densification ([Chen et al., 2021](#)). Sample S18 gave the highest porosity at 42.5%.

Table 4

Pore size, Pore volume, and the Surface Area of the fabricated membrane.

Sample Code	Kaolin Content	HAp Content	Pore former content	Sintering Temperature	Pore size (nm)	Pore volume (cc/g)	Surface area (m ² /g)
S1	90	10	0	800	2.079	0.029	61.815
S2	70	20	10	900	2.144	0.041	82.985
S3	80	10	10	1000	2.133	0.04	82.11
S4	80	20	0	900	2.132	0.042	85.23
S5	70	30	0	1000	2.118	0.049	98.437
S6	60	30	10	800	2.133	0.047	94.743
S7	90	10	0	900	2.123	0.052	106.277
S8	90	10	0	1000	1.853	0.071	125.564
S9	70	20	10	800	2.072	0.095	197.523
S10	70	20	10	1000	1.853	0.075	133.097
S11	80	10	10	900	2.113	0.065	131.782
S12	80	10	10	800	2.088	0.092	186.513
S13	80	20	0	1000	2.088	0.092	186.513
S14	80	20	0	900	2.108	0.099	204.967
S15	70	30	0	800	2.153	0.117	239.583
S16	70	30	0	900	2.101	0.156	320.063
S17	60	30	10	1000	2.122	0.149	304.434
S18	60	30	10	900	2.122	0.17	347.924

**Fig. 5.** Brittleness Index of the samples.

3.3. Brunauer-Emmett-Teller (B.E.T) analysis

The pore size, surface area, and pore volume were investigated by the B.E.T method using Nitrogen as the adsorbate at 77.3K bath temperature. The relation between the pore volume and the pore diameter was determined using the BJH method and it is presented in Figs. 4a & 4b, respectively. As shown in the plots, the samples with the pore former have a greater number of small pores. However, increasing the sintering temperature led to the reduction of the number of pores as observed with the increase in the area under the hysteresis loop. The reduction of pore size due to an increase in the sintering temperature might be attributed to the closing of open pores resulting in a larger number of closed pores.

The total pore volume, surface area, and mean mesoporous diameter are summarized in Table 4. It is observed that the material's surface area and the pore volume increase with the increase in HAp content on the base material (kaolin). In addition, the increase in the surface area led to the reduction of the pore size. It might mean that the HAp content closes some small pores within the parent material (kaolin). The results proved that the pore size, pore volume, and surface area can be controlled by choosing the appropriate HAp percentage and sintering temperature.

3.4. Brittleness index of the fabricated samples

Brittleness is an inherent feature and a common defect of ceramic materials. During production, micro defects on the ceramic surface are inevitable and form the source of cracks. It affects the reliability of the material to a large extent. It is important for the ceramic materials needed for the filtration process to have a low brittleness index. Fig. 5 illustrates the brittleness index of the fabricated samples. The brittleness values in this study are between 0.19 and 0.46 and S18 had the least brittleness. The low brittleness values obtained in the study could be attributed to the size of the HAp particles (Table 3). HAp might have created a weak interface structure that absorbs the external energy from the indentation. From the findings, it could be concluded that the ceramic materials fabricated are reliable and should be able to withstand external energy during handling or transporting with little or no crack formation. The brittleness value obtained in this study is very close to the values reported by Salami et al., (2022) where the brittleness index is less than 0.5.

3.5. Taguchi design of experiment analysis

As stated in section three (materials and method), four factors (sintering temperature, pore former content, HAp content, and the kaolin content) at different levels for each factor were examined using the

Table 5
ANOVA analysis for each response.

ANOVA Analysis: Porosity					
Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	22.56	7	3.22	1.04	0.4618
A-Sintering Temperature	4.10	2	2.05	0.6606	0.5377
B-Pore Former content	2.25	1	2.25	0.7258	0.4142
C-HAp content	6.13	2	3.07	0.9888	0.4056
D-Kaolin content	11.01	2	5.51	1.78	0.2188
Residual	31.00	10	3.10		
Cor Total	53.57	17			
ANOVA Analysis: Pore size					
Model	0.0698	9	0.0078	1.04	0.4857
A-Sintering Temperature	0.0299	2	0.0150	2.00	0.1975
B-Pore Former content	0.0012	1	0.0012	0.1670	0.6935
C-HAp content	0.0329	2	0.0165	2.20	0.1731
D-Kaolin content	0.0241	2	0.0121	1.61	0.2581
AB	0.0016	2	0.0008	0.1051	0.9014
Residual	0.0599	8	0.0075		
Cor Total	0.1296	17			
ANOVA Analysis: Brittleness Index					
Model	0.0658	13	0.0051	6.81	0.0388
A-Sintering Temperature	0.0138	2	0.0069	9.28	0.0314
B-Pore Former content	0.0001	1	0.0001	0.0753	0.7973
C-HAp content	0.0037	2	0.0018	2.47	0.2004
D-Kaolin content	0.0106	2	0.0053	7.14	0.0479
AD	0.0371	6	0.0062	8.33	0.0298
Residual	0.0030	4	0.0007		
Cor Total	0.0688	17			

Taguchi matrix resulting in the 18 runs. The level of the pore former, HAp, and kaolin in the matrix was modified to obtain a total of 100 wt.% for each run. The main effect of the factors on the responses was determined. The effect was studied using the analysis of variance (ANOVA). The ANOVA is aimed at investigating the factors from the design of the experiment that had statistical significance on the responses.

3.5.1. Effect of the factors on the Responses (porosity, pore size, and brittleness index)

The statistical significance of the responses can be noticed in the ANOVA table (Table 5). The model is termed significant when the P-value is less than 0.05, and values greater than 0.1 indicate that the terms in the model are not significant. From Table 5, it can be inferred

that the four factors had no significant effect on the porosity and the pore size since the P-values obtained are greater than 0.1. However, the P-value for the brittleness index is 0.0388, and this indicated that the model gave statistical significance. As observed in the ANOVA table for the porosity, the P-value for the sintering temperature, HAp content, and kaolin content is less than 0.05 which shows that the mentioned parameters had a significant effect on the porosity.

The ANOVA analysis also shows the significance of the model's adequate scale i.e., correlation coefficient (R^2) and the mathematical model needed to calculate the predicted values for the responses. The statistical correlation coefficients (R^2) measure the good fit in the linear regression models. A negative predicted R^2 denotes that the overall mean may give a better predictor for the responses while a higher order might give a better prediction. Negative R^2 values were obtained for the porosity and pore size which indicated that the predicted and actual might be a distance apart. It led to the scattering point around the regression line as shown in Fig. 6 while in Fig. 6(c), the predicted and actual are close to the regression line.

The mathematical models in Eqs. 10–12 are the final equation in terms of the coded factors. The model can be used to predict the responses at a given level for each factor. The equations can be used to identify the relative impact of the factor by comparing the factor coefficients (factors with higher coefficients had more impact than others). For instance, the coefficient of the kaolin content in equation 10 is much higher, meaning that the kaolin content had more impact on the porosity. This is in agreement with the ANOVA table since kaolin content gave the least P-value.

$$\text{Porosity} = +38.04 + 0.523 \times A + 0.3819 \times B + 0.0306 \times C + 2.2013 \times D \quad (10)$$

$$\text{Poresize} = +2.08 + 0.0574 \times A + 0.0090 \times B + 0.0846 \times C + 0.0293 \times D - 0.0068 \times A \times B \quad (11)$$

$$\text{BrittlenessIndex} = +0.3941 + 0.0316 \times A - 0.0019 \times B - 0.0261 \times C - 0.016 \times D - 0.0235 \times A \times D \quad (12)$$

Where:

A-Sintering Temperature
B-Pore Former content
C-HAp content
D-Kaolin content

3.6. Optimization of the process using taguchi grey relational analysis

The Taguchi method only optimizes a response performance while optimizing multiple responses is way more complex. Hence, this study uses Taguchi grey relational analysis on the orthogonal array for optimizing the responses since the analysis can indicate the

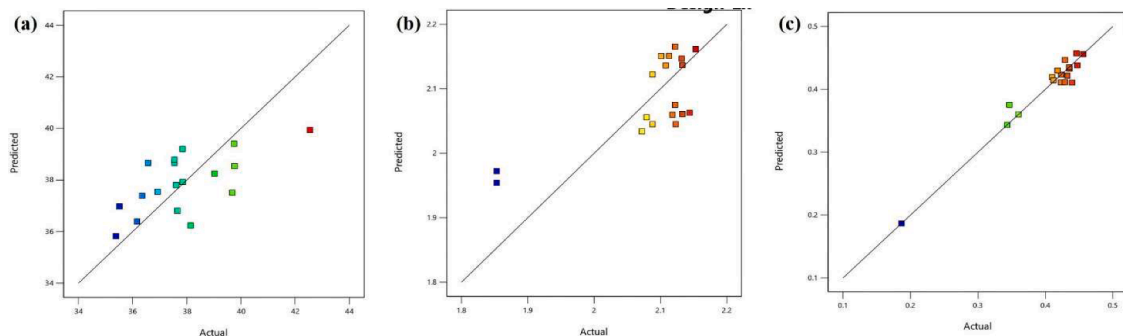
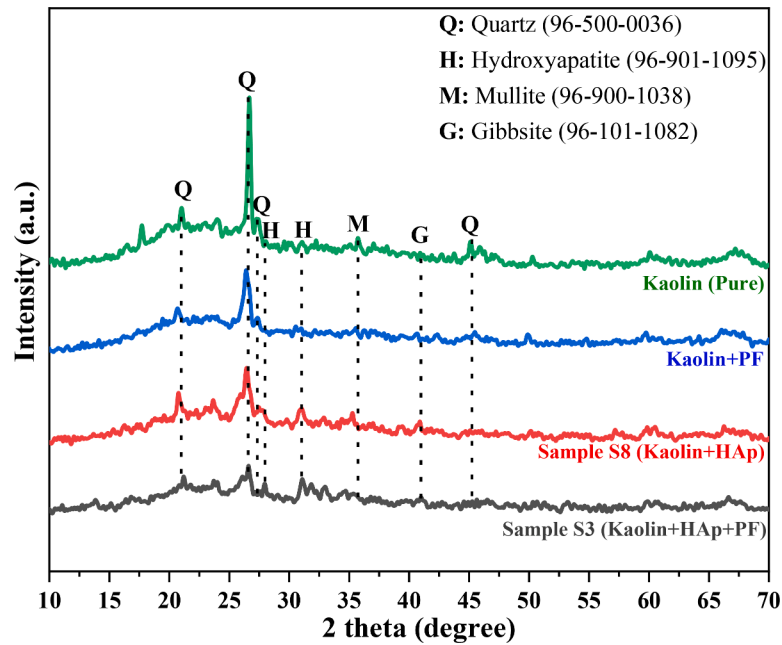


Fig. 6. Predicted vs Actual for the responses (a) porosity (b) pore size (c) brittleness Index.

Table 6

Grey Relational Analysis for the responses.

Runs	Experimental Responses			S/N ratio			Normalization			Grey Relational Co-efficient			Grey Relational Grade	Rank
	Porosity (%)	Pore size (nm)	Brittleness Index	Porosity (%)	Pore size (nm)	Brittleness Index	Porosity (%)	Pore size (nm)	Brittleness Index	Porosity (%)	Pore size (nm)	Brittleness Index		
S1	37.66	2.08	0.34	-31.52	-6.36	9.29	0.34	0.77	0.68	0.60	0.39	0.42	0.47	8
S2	39.77	2.14	0.35	-31.99	-6.62	9.20	0.63	0.97	0.69	0.44	0.34	0.42	0.40	16
S3	39.68	2.13	0.42	-31.97	-6.58	7.48	0.62	0.94	0.92	0.45	0.35	0.35	0.38	18
S4	37.54	2.13	0.44	-31.49	-6.58	7.22	0.32	0.93	0.95	0.61	0.35	0.35	0.43	12
S5	35.38	2.12	0.43	-30.98	-6.52	7.35	0.00	0.89	0.93	1.00	0.36	0.35	0.57	3
S6	37.84	2.13	0.46	-31.56	-6.58	6.82	0.36	0.94	1.00	0.58	0.35	0.33	0.42	13
S7	36.93	2.12	0.36	-31.35	-6.54	8.87	0.23	0.91	0.74	0.68	0.36	0.40	0.48	7
S8	36.16	1.85	0.42	-31.17	-5.36	7.47	0.12	0.00	0.92	0.81	1.00	0.35	0.72	1
S9	37.61	2.07	0.43	-31.51	-6.33	7.28	0.33	0.74	0.94	0.60	0.40	0.35	0.45	9
S10	36.35	1.85	0.43	-31.21	-5.36	7.36	0.15	0.00	0.93	0.77	1.00	0.35	0.71	2
S11	36.57	2.11	0.41	-31.26	-6.50	7.75	0.18	0.88	0.88	0.74	0.36	0.36	0.49	6
S12	37.85	2.09	0.41	-31.56	-6.39	7.71	0.37	0.80	0.89	0.58	0.39	0.36	0.44	10
S13	39.03	2.09	0.42	-31.83	-6.39	7.58	0.53	0.80	0.90	0.48	0.39	0.36	0.41	14
S14	39.75	2.11	0.45	-31.99	-6.48	6.99	0.63	0.86	0.98	0.44	0.37	0.34	0.38	17
S15	38.14	2.15	0.45	-31.63	-6.66	7.01	0.41	1.00	0.98	0.55	0.33	0.34	0.41	15
S16	35.51	2.10	0.44	-31.01	-6.45	7.14	0.02	0.84	0.96	0.96	0.37	0.34	0.56	5
S17	37.54	2.12	0.44	-31.49	-6.53	7.23	0.32	0.90	0.95	0.61	0.36	0.35	0.44	11
S18	42.55	2.12	0.19	-32.58	-6.53	14.58	1.00	0.90	0.00	0.33	0.36	1.00	0.56	4

**Fig. 7.** XRD patterns of samples S3, S8, and Kaolin with and without the pore former (PF).

interrelationships between the responses. Using Equations 5 to 8, the grey relational coefficient and grade for each experimental run and the optimization process are presented in Table 6. From the table, the sample with the highest grey relational grade is sample S8 (0.72) and the least is S3 (0.38). Therefore, the optimum samples are considered for further study (i.e., chemical characterization (XRD)).

Table 7

Crystallinity of the optimum samples, samples with and without the additives.

Sample code	Crystallinity (%)
S3	98.1
S8	98.8
Kaolin + Pore former	97.3
Kaolin	92.7

3.7. Characterization of the optimum sample

3.7.1. Structural analysis (x-ray diffraction)

The structural analysis of the samples was conducted using the X-ray diffraction techniques as illustrated in Fig. 7. The samples include S3 (kaolin + HAp + pore former), S8 (kaolin + HAp), kaolin + pore former, and kaolin, all sintered at 1000 °C based on the optimum parameters from the grey relational analysis. The major phase observed from the patterns is quartz and other phases include HAp, mullite, and gibbsite. Upon sintering the sample at 1000 °C, there is a reduction or loss of the peaks attributed to the kaolinite mineral due to bond disruption in the kaolin layer and possible phase transformation from kaolinite to quartz, mullite, and gibbsite (Malik et al., 2020; Obada et al., 2016). Further reduction in the prominent peak at 2-theta = 27° in samples S3 and S8 can be ascribed to hydroxylation, an oxidation reaction due to the loss of

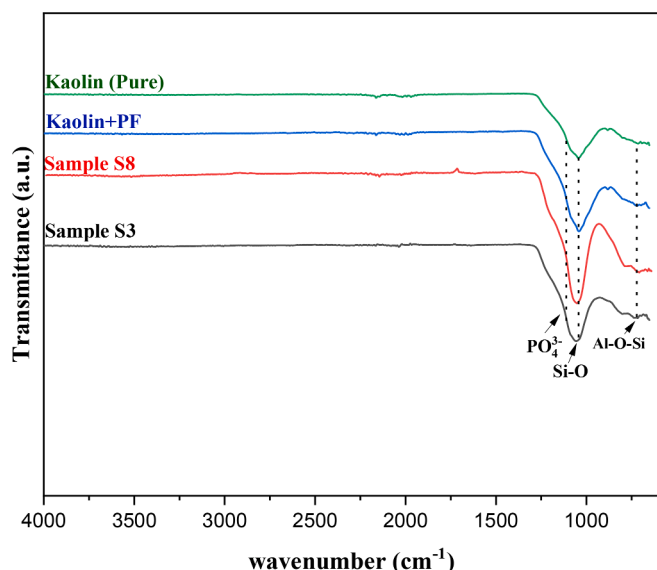


Fig. 8. FTIR spectra of samples S3, S8, Kaolin with and without the pore former (PF).

Table 8

Average concentration (mean $\pm$ SD, $n = 3$) values of wastewater quality parameter for raw tannery wastewater.

Parameters	Initial Content (Mean statistics)	FEPA (1991) Limits
pH	4.85 $\pm$ 0.006	6-9
Electrical Conductivity (μScm^{-1})	15.42 $\pm$ 0.066	1000
Total Dissolved Solids (mg^{-1})	41453.33 $\pm$ 6.667	2000
Temperature($^{\circ}\text{C}$)	28.23 $\pm$ 0.033	<40
Turbidity (NTU)	981.33 $\pm$ 0.667	NG
Chromium (mgL^{-1})	58264.33 $\pm$ 1371.289	1

Al^{2+} and Si^{2+} ions, and an increase in oxygen. There is a high tendency that the lost electron could have been replaced with the calcium and phosphate ion in the HAp. Further, the addition of HAp and the pore former improves the crystal structure of the samples as noticed in Table 7. Hence, it could be envisaged that the sample with HAp and the pore former might have good physicochemical properties and higher filtration efficiency since it has a better crystal structure.

3.7.2. FTIR analysis

The FTIR spectra of samples S3, S8, and kaolin with pore former and kaolin are presented in Fig. 8. From the spectra, the sharp and broad adsorption band at 1056 cm^{-1} is attributed to the Si-O stretching band. The functional groups observed are Si-O, PO_4^{3-} , and Al-O-Si. According to Obada et al. (2022), this confirms the presence of HAp in the sample S3 and S8 and the transformation of the kaolin to quartz and gibbsite as noticed from the XRD analysis in Fig. 7. The broadening of the

phosphate and Si-O band depends on the compositional weight present in the mixture. For instance, sample S8 had a high content of kaolin which results in the broadening of the Si-O band.

3.8. Characterization of tannery effluents before and after treatment

Characteristics of the raw tannery effluent before treatment with the coagulant are shown in Table 8 and compared to the Federal Environmental Protection Agency (FEPA, 1991) interim guidelines and standards for industrial effluent. The colour appearance of the untreated effluent was found to be dark blue. This indicates the presence of a highly coloured compound contained in the effluent capable of environmental pollution. The original colour of the effluent turned light blue after coagulation/ flocculation, which indicates the effectiveness of the coagulant (alum). Three different kaolin-based adsorbents were used to assess filtration efficiency, and the result showed the effective performance of the filters in removing colour and odour from the tannery effluent. Clear effluent was observed after filtration with the three adsorbents. The effluent appearance showed a clear light brownish colour. The odour had an obnoxious smell in the untreated effluent but an objectionable odour was observed after filtration using kaolin-based adsorbents. The results obtained are in agreement with Islam et al., (2011), who reported light blue, bluish green, and dark appearance for tannery effluents of tannery; Nourisepehr et al., (2005), who reported the colour of tanning house effluent as dark blue due to inorganic chemicals like chromium used during processing, Rouf et al. (2013) who reported the colour of tannery effluent of various leather industries of the point sources as dark, navy blue, blackish blue and violet with a pungent odour and, Chowdhury et al., (2013) who reported the colour of filtered tannery effluent as light brown. The colour of the untreated tannery effluent indicates the presence of coloured compounds and does not allow penetration of sunlight required for photosynthesis by aquatic plants.

Comparison of the tannery wastewater parameters to FEPA standard on discharge for all classes of industries (Table 8) shows that the effluent parameters were above the FEPA standards for total dissolved solids (41453.33mg/l) and chromium (58264.33mg/l). The effect of dissolved solids in water is that it directly affects the aesthetic value (odour and colour) of the water by increasing turbidity. A high level of chromium implies that the effluent is contaminated by heavy metal and therefore toxic. Turbidity was high with a mean value of 981.33NTU. High turbidity of the effluent could be a result of suspended matter, organic and inorganic matter present in the effluent. The pH of the raw tannery effluent was 4.85 which was an acidic condition. A comparison of the initial condition of the tannery effluent with FEPA also shows that EC (15.42 $\mu\text{S}/\text{cm}$) and temperature (28.23 $^{\circ}\text{C}$) values fall within the discharge limit set by FEPA for industrial effluents to be discharged into the water body.

3.8.1. Optimization of coagulant dose

The effect of coagulant (alum) dose on the different parameters (pH, EC, TDS, temperature, turbidity and chromium) are shown in Table 9. It shows that optimum removal of turbidity 686.67 ± 1.764 NTU (30.03%)

Table 9

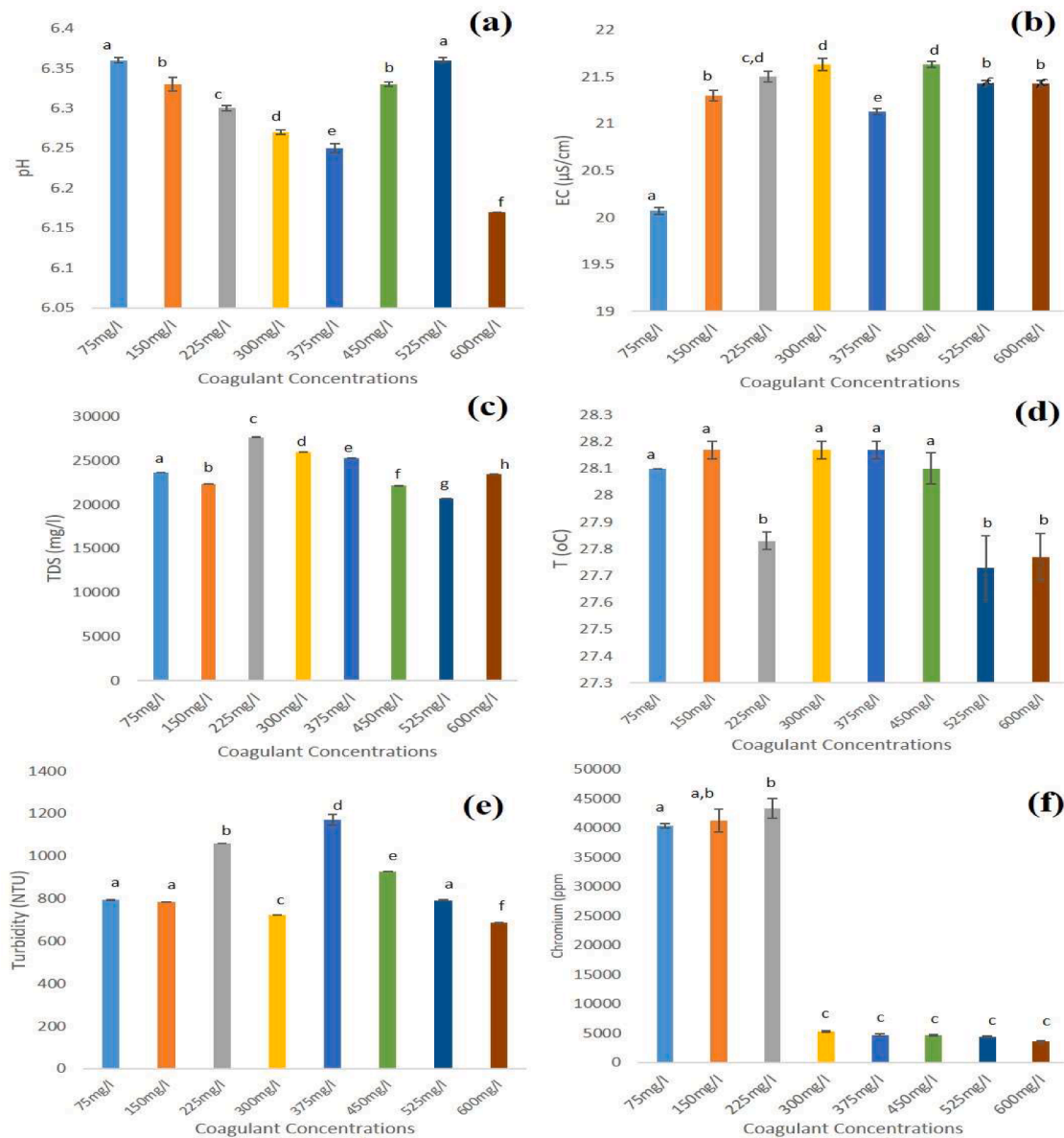
Mean values of characteristics of alum treatment on tannery effluent.

Treatment	pH	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/l)	T ($^{\circ}\text{C}$)	Turbidity (NTU)	Chromium (mg/l)
75 mg/l	6.36 $\pm$ 0.003	20.07 $\pm$ 0.033	23640.00 $\pm$ 11.547	28.10 $\pm$ 0.000	793.33 $\pm$ 0.667	40369.13 $\pm$ 353.933
150 mg/l	6.33 $\pm$ 0.009	21.30 $\pm$ 0.058	22346.67 $\pm$ 6.667	28.17 $\pm$ 0.033	784.67 $\pm$ 0.667	41233.73 $\pm$ 1970.800
225 mg/l	6.30 $\pm$ 0.003	21.50 $\pm$ 0.058	27653.33 $\pm$ 6.667	27.83 $\pm$ 0.033	1060.67 $\pm$ 0.667	43375.80 $\pm$ 1646.472
300 mg/l	6.27 $\pm$ 0.003	21.63 $\pm$ 0.067	25940.00 $\pm$ 0.000	28.17 $\pm$ 0.033	724.00 $\pm$ 1.155	5281.27 $\pm$ 145.493
375 mg/l	6.25 $\pm$ 0.006	21.13 $\pm$ 0.033	25293.33 $\pm$ 17.638	28.17 $\pm$ 0.033	1170.00 $\pm$ 25.007	4687.20 $\pm$ 242.637
450mg/l	6.33 $\pm$ 0.003	21.63 $\pm$ 0.033	22133.33 $\pm$ 13.333	28.10 $\pm$ 0.058	927.33 $\pm$ 0.667	4678.30 $\pm$ 133.551
525 mg/l	6.36 $\pm$ 0.003	21.43 $\pm$ 0.033	20666.67 $\pm$ 6.667	27.73 $\pm$ 0.120	792.67 $\pm$ 2.667	4323.07 $\pm$ 110.516
600 mg/l	6.17 $\pm$ 0.000	21.43 $\pm$ 0.033	23486.67 $\pm$ 17.638	27.77 $\pm$ 0.088	686.67 $\pm$ 1.764	3528.07 $\pm$ 247.278
FEPA	6-9	1000	2000	<40	NG	1

Table 10

Mean values of parameters of kaolin based filters treatment on tannery effluent.

Adsorbents	pH	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/l)	T ($^{\circ}\text{C}$)	Turbidity (NTU)	Chromium (mg/l)
Kaolin	7.15 ± 0.066	8.85 ± 0.319	6463.33 ± 447.599	25.43 ± 0.273	34.80 ± 2.413	1132.27 ± 86.995
Kaolin + Hydroxyapatite	7.19 ± 0.020	10.89 ± 0.506	7596.67 ± 262.827	24.90 ± 0.000	34.43 ± 2.520	46.97 ± 20.905
Kaolin + Hydroxyapatite + Starch	7.12 ± 0.012	8.60 ± 0.886	5323.33 ± 268.597	25.23 ± 0.167	20.10 ± 0.551	44.33 ± 14.122
FEPA	6-9	1000	2000	<40	NG	1

**Fig. 9.** Plots of comparison for effect of coagulant dose on (a) pH (b) EC (c) TDS (d) Temperature (e) Turbidity (f) Chromium.

and chromium $3528.07 \pm 247.278 \text{ mg}/\text{l}$ (93.90%) were obtained in 600 mg/L coagulant (alum) dose. A similar observation was made by Naumczyk and Rusiniak (2005), who reported that a 600 mg/L dose of FeCl_3 showed the best removal efficiency for most parameters at pH 6.35. The results of the study revealed that low coagulation performance was observed at lower coagulant doses. The study also observed that the pH values (6.17– 6.36), EC values (20.07– 21.63 $\mu\text{S}/\text{cm}$), and temperature values (27.17– 28.17 $^{\circ}\text{C}$) of the alum-treated effluent for all coagulant doses fall within discharge limit set by FEPA for industrial effluents to be discharged into water body. The study observed that the alum treated effluent parameters were above the FEPA standards for total

dissolved solids (20666.67– 27653.33 mg/l) and chromium (3528.07– 43375.80 mg/l).

3.8.2. Adsorption tests

After coagulation with optimum alum dosage (600 mg/l), the tannery effluent was filtered using the kaolin-based adsorbents. The mean performance of the three adsorbents (kaolin, kaolin + HAp, kaolin + HAp + starch) on the different parameters (pH, EC, TDS, temperature, turbidity and chromium) are as shown in Table 10. The results show the chromium removal rate of kaolin, kaolin + HAp, and kaolin + HAp + starch adsorbents as 67.91 %, 98.67%, and 98.74%, respectively. The

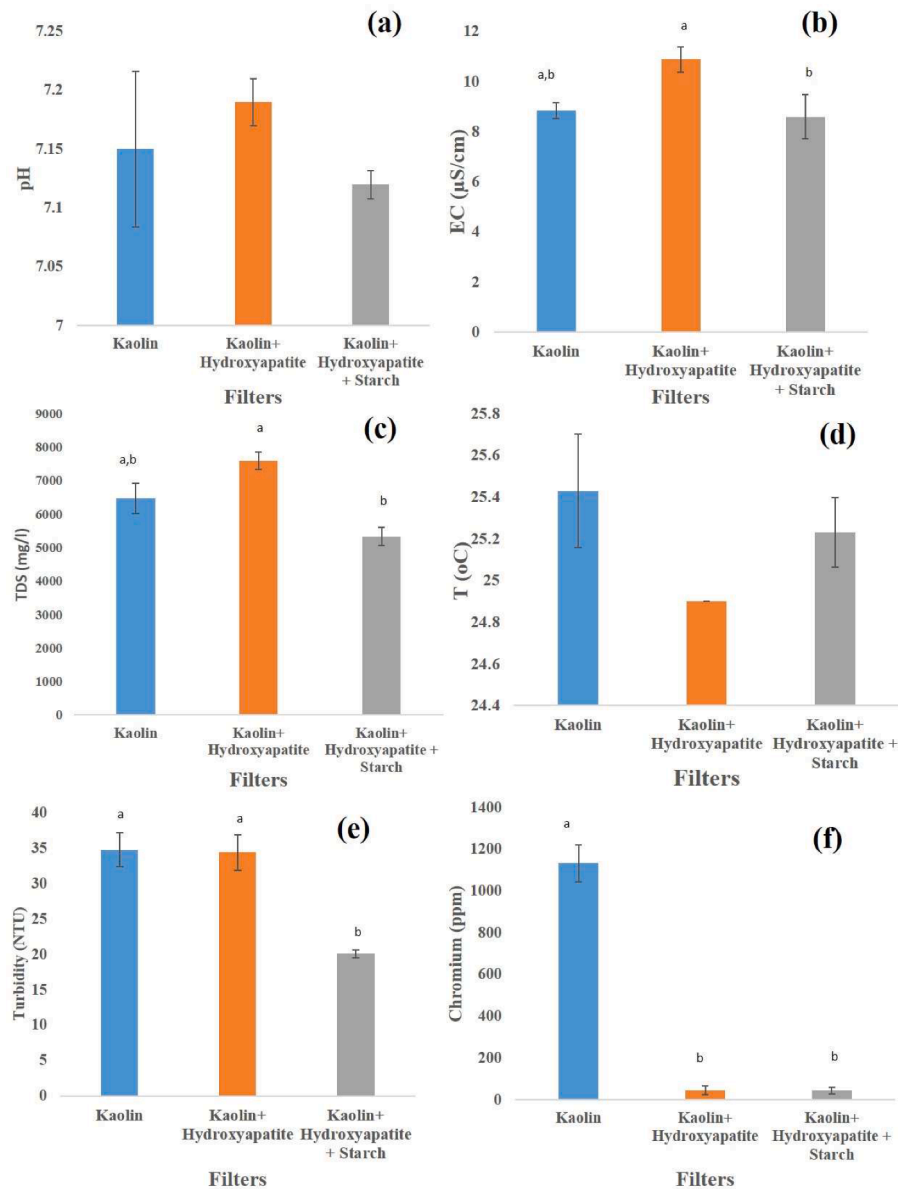


Fig. 10. Plots of comparison for ceramic adsorbents on (a) pH (b) EC (c) TDS (d) Temperature (e) Turbidity (f) Chromium.

maximum adsorption capacity of chromium was 98.74% at pH 7.12, and a temperature of 25.23°C when the turbidity removal is 97.07%. This optimum removal of chromium was achieved by the adsorbent which composed of kaolin + HAP + starch. The study results observed that after the adsorption experiments, the pH of the treated effluents increased from 6 to 7. Kaolin-based adsorption experiments revealed that chromium removal capabilities depended on the composition of the individual adsorbents. The addition of pore former increased the porosity thereby enhancing the adsorption process while the inclusion of HAP aided the efficient removal of chromium. Non-inclusion of HAP could be the reason for low filtration performance in the kaolin adsorbent since HAP is known for its ion exchange capacity.

3.9. Comparative analysis of the effect of coagulant dose on effluent parameters

The post hoc comparison of the mean test was used to compare the coagulant doses with the parameters and adsorbent performance. Fig. 9 shows the comparison of coagulant concentration with pH, EC, TDS, temperature, turbidity, and chromium parameters. For pH, a

concentration of 75 mg/l dosage did not show any difference in comparison to 525 mg/l dosage, but it was different from all other dosages. This means that the concentration of 75 mg/l gave the same pH result as 525 mg/l. Concentrations of 150 mg/l and 450 mg/l had the same pH level. However, 225 mg/l, 300 mg/l, 375 mg/l, and 600 mg/l had significant differences from one another and the others. For chromium, a concentration of 75 mg/l dosage was not different from 150 mg/l dosage, but it was different from 225 mg/l dosage. However, 150 mg/l was not different from 75 mg/l and 225 mg/l, which implies that the concentration of 150 mg/l gave the same result as 75 mg/l and 225 mg/l. There was a significant difference when the concentration increased to 300 mg/l, and this did not change until it reached 600 mg/l, which means they were within the same chromium level. The significant drastic change occurred at 225 mg/l when moving to 300 mg/l. At 75 mg/l, the turbidity was about 800 NTU, and there was a significant increase at 225 mg/l, which led to a decrease at 300 mg/l and another significant increase at 375 mg/l. However, 75 mg/l and 525 mg/l had the same turbidity level. The peak turbidity level was at 375 mg/l, and there was a sharp decline at 300 mg/l, followed by a sharp rise at 375 mg/l, after which it started to decline significantly. All values with

different superscript alphabets show a difference in means.

3.10. Comparative analysis of the effect of kaolin-based adsorbents on effluent parameters

Fig. 10 displays a comparison of the effects of ceramic filters on various parameters, including pH, EC, TDS, temperature, turbidity, and chromium. The post hoc comparison of means test was utilized for this analysis. The results demonstrate that there were no significant differences in pH or temperature for any of the adsorbents. This suggests that the adsorbents did not impact the pH or temperature of the filtered effluent. However, for EC and TDS, only the kaolin + HAp and kaolin + HAp + starch adsorbents showed a significant difference. Nonetheless, kaolin + HAp and kaolin + HAp + starch adsorbents were not different from the kaolin filter alone. Essentially, the kaolin adsorbent did not show any significant difference from the other two filters, but the other two filters showed a difference from each other. For turbidity, there was no significant difference between kaolin and kaolin + HAp filters ($p > 0.05$). However, kaolin + HAp + starch adsorbent showed a significant difference from both kaolin and kaolin + HAp filters ($p < 0.05$). In terms of chromium, there was a significant difference between kaolin when compared to kaolin + HAp and kaolin + HAp + starch ($p < 0.05$). However, there was no significant difference between kaolin + HAp and Kaolin + HAp + starch adsorbents ($p > 0.05$). The statistical analysis was performed using ANOVA (Analysis of Variance). The post hoc analysis helped to reveal the differences between the means. These charts show the means of the parameters level with the coagulant/adsorbents.

4. Conclusion

In this study, adsorbents were fabricated using beneficiated kaolin, starch as a pore former, and HAp. We investigated the impact of sintering temperature and different raw material content on the physical, chemical, and mechanical properties of the pelletized ceramic adsorbents. We identified the optimal conditions for producing the adsorbents by utilizing the parameters from the Grey relational analysis. The fabricated HAp/Kaolin-based ceramic adsorbent was used to filter tannery wastewater and the pH, electrical conductivity (EC), total dissolved solids (TDS), temperature, chromium, and turbidity of raw tannery effluent, and treated effluent were determined. The volumetric porosity of the porous kaolin/HAp ceramic adsorbent was between 35% and 45%. From the B.E.T analysis, we concluded that the samples with the pore formers have a greater number of small pores, and increasing the sintering temperature led to the reduction of the number of pores. Using the grey relational analysis, we found that the sample with the highest grey relational grade is sample S8 (0.72) and the least is S3 (0.38). Based on our findings, we concluded that the ceramic adsorbents (S3 and S8) have good physicochemical properties and higher filtration efficiency due to their superior crystalline characteristics. The average concentration of the effluent parameters before filtration was above the FEPA standards for total dissolved solids (41453.33 mg/l), chromium (58264.33 mg/l), and turbidity (981.33NTU). Low coagulation performance at lower coagulant doses was observed. For the adsorption test, the chromium removal rate of kaolin, kaolin + HAp, and kaolin + HAp + starch adsorbents is 67.91%, 98.67%, and 98.74%, respectively. The maximum adsorption capacity of chromium was obtained with the adsorbent made from kaolin, HAp, and starch at pH 7.12 and a temperature of 25.23 °C when the turbidity removal is 97.07%.

CRediT authorship contribution statement

Juliana O. Iji: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Fatima B. Ibrahim:** Formal analysis, Methodology, Supervision, Conceptualization. **Abdullahi S. Argungu:** Supervision. **David O.**

Obada: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing, Supervision.

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.

Data availability

Data will be made available on request.

Acknowledgement

The authors thank the Africa Centre of Excellence on New Pedagogies in Engineering Education, Ahmadu Bello University, Zaria, Nigeria for providing support to conduct this study. The authors also thank Engrs. Kazeem A. Salami and Ayodeji N. Oyediji of the Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria, and Dr Bidemi K. Okeshina of the Department of Medical Physiology, College of Medicine and Health Sciences, University of Rwanda, Rwanda, for their valuable contributions to the experimental sections of the manuscript. The award received by Juliana O. Iji during the Student Innovation Research Award (SIRA) Ceremony in the Gambia is also acknowledged. The SIRA award was facilitated by the Association of African Universities (AAU), the Regional Facilitating Unit (RFU) for the African Centres of Excellence for Development Impact (ACE Impact) project, with support from the World Bank (WB).

References

- Akartasse, N., Azzaoui, K., Mejdoubi, E., Elansari, L.L., Hammouti, B., Sijaj, M., Rhazi, L., 2022. Chitosan-Hydroxyapatite bio-based composite in film Form: Synthesis and application in wastewater. *Polymers* 14 (20), 4265.
- Akpan, E.S., Dauda, M., Kuburi, L.S., Obada, D.O., Bansod, N.D., Dodoo-Arhin, D., 2020. Hydroxyapatite Ceramics Prepared from two natural Sources by Direct thermal Conversion: from material processing to mechanical measurements. *Materials today Proceedings*. <https://doi.org/10.1016/j.matpr.2020.06.391>.
- Al-Essa, K., Khalili, F., 2018. Heavy metals adsorption from aqueous solutions onto unmodified and modified Jordanian kaolinite clay: batch and column techniques. *Am. J. Appl. Chem.* 6 (1), 25–34.
- Amenaghawon, A.N., Anyalewechi, C.L., Darmokoesomo, H., Kusuma, H.S., 2022. Hydroxyapatite-based adsorbents: Applications in sequestering heavy metals and dyes. *Journal of Environmental Management* 302, 113989.
- Arif, A., Malik, M.F., Liaqat, S., Aslam, A., Mumtaz, K., Afzal, A., Javed, R., 2020. 3. Water pollution and industries. *Pure and Applied Biology (PAB)* 9 (4), 2214–2224.
- Bose, S., Das, C., 2013. Preparation and Characterization of Low Cost Tubular Ceramic Support Membranes using Sawdust as a Pore-Former. *Materials Letters* 110, 152–155.
- Chen, Y., Wang, N., Ola, O., Xia, Y., Zhu, Y., 2021. Porous ceramics: Light in weight but heavy in energy and environment technologies. *Materials Science and Engineering: R: Reports* 143, 100589.
- Chowdhury, M., Mostafa, M.G., Biswas, T.K., Saha, A.H., 2013. Treatment of Leather Effluents by Filtration and Coagulation process. *Water Resources and Industry* 3, 11–22.
- Dome, K., Podgorbunskikh, E., Bychkov, A., Lomovsky, O., 2020. Changes in the Crystallinity Degree of Starch Having Different Types of Crystal Structure after Mechanical Pretreatment. *Polymers* 12 (3), 641. <https://doi.org/10.3390/polym12030641>.
- Du, J., Xiao, X., Ai, D., Liu, J., Qiu, L., Chen, Y., Wang, L., 2022. Fabrication, Characterization and Drainage Capacity of Single-Channel Porous Alumina Ceramic Membrane Tube. *Membranes* 12 (4), 390.
- Efavi, J.K., Damoah, L., Bensah, D.Y., Arhin, D.D., Tetteh, D., 2012. Development of porous ceramic bodies from kaolin deposits for industrial applications. *Appl. Clay Sci.* 65, 31–36.
- Feka, D.P., Habila, A.J., Francis, K., Habila, J.D., Bammai, M.Y., 2021. Synthesis, characterization and application of a bio-derived ZnO nano-powder from spinacia oleracea leaf extract for the removal of BOD and COD from tannery wastewater. *Chemistry of the Total Environment* 1 (1), 1–8.
- FEPA, A., 1991. Guidelines and Standards for Environmental Pollution Control in Nigeria. Federal Environmental Protection Agency (FEPA), Lagos, Nigeria.
- Foroutan, R., Peighambari, S.J., Hosseini, S.S., Akbari, A., Ramavandi, B., 2021. Hydroxyapatite biomaterial production from chicken (femur and beak) and fishbone

- waste through a chemical less method for Cd²⁺ removal from shipbuilding wastewater. *Journal of Hazardous Materials* 413, 125428.
- Hedfi, I., Hamdi, N., Rodriguez, M.A., Srasra, E., 2016. Development of a low cost micro-porous ceramic membrane from kaolin and Alumina, using the lignite as porosity agent. *Ceramics International* 42, 5089–5093.
- Hokkanen, S., Bhatnagar, A., Repo, E., Lou, S., Sillanpää, M., 2016. Calcium hydroxyapatite microfibrillated cellulose composite as a potential adsorbent for the removal of Cr (VI) from aqueous solution. *Chemical Engineering Journal* 283, 445–452.
- Huang, J., Liu, T., Zhang, Y., Hu, P., 2023. Reinforced adsorption mechanism of fluorine ions by calcium-depleted hydroxyapatite and application in the raffinate from the vanadium industry. *Chemical Engineering Journal* 452, 139379.
- Hubadillah, S.K., Othman, M.H.D., Harun, Z., Ismail, A.F., Rahman, M.A., Jaafar, J., Jamil, S.M., Mohtor, N.H., 2017. Superhydrophilic, low cost kaolin-based hollow fibre membranes for efficient oily-wastewater separation. *Mater. Lett.* 191, 119–122.
- Hubadillah, S.K., Othman, M.H.D., Ismail, A.F., Rahman, M.A., Jaafar, J., Iwamoto, Y., Honda, S., Dzahir, M.I.H.M., Yusop, M.Z.M., 2018. Fabrication of low cost, green silica based ceramic hollow fibre membrane prepared from waste rice husk for water filtration application. *Ceram. Int.* 44, 10498–10509.
- Han, L., Li, X., Li, F., Zhang, H., Li, G., Jia, Q., Zhang, S., 2022. Superhydrophilic/air-superoleophobic diatomite porous ceramics for highly-efficient separation of oil-in-water emulsion. *Journal of Environmental Chemical Engineering* 10 (5), 108483.
- Han, L., Khalil, A.M., Wang, J., Chen, Y., Li, F., Chang, H., Zhang, S., 2021. Graphene-boron nitride composite aerogel: A high efficiency adsorbent for ciprofloxacin removal from water. *Separation and Purification Technology* 278, 119605.
- Hubadillah, S.K., Othman, M.H.D., Tai, Z.S., Jamalludin, M.R., Yusuf, N.K., Ahmad, A., Harun, Z., 2020. Novel hydroxyapatite-based bio-ceramic hollow fiber membrane derived from waste cow bone for textile wastewater treatment. *Chemical Engineering Journal* 379, 122396.
- Ibrahim, F.B., Iji, J., Ismail, A., 2014. Evaluation of the Use of Moringa Oleifera Seed Extract and Maize Starch as Coagulant Aids to Aluminium Sulphate in Water Treatment. In: *Proceedings of the Materials Science and Technology Society of Nigeria (MSN) Zaria Chapter*, pp. 67–106.
- Ibrahim, M., Labaki, M., Giraudon, J., Lamonier, J. (2019). Hydroxyapatite, a multifunctional material for air, water and soil pollution control: A review. Manuscript version available under the Elsevier user license <https://www.elsevier.com/open-access/userlicense/1.0/>.
- Islam, K.M.N., Misbahuzzaman, K., Majumder, A.K., Chakrabarty, M., 2011. Efficiency of different coagulants combination for the treatment of tannery effluents: A case study of Bangladesh. *African Journal of Environmental Science and Technology* 5 (6), 409–419.
- Kamarudin, S.N., Jamalludin, M.R., Rasman, S.N.S., Hubadillah, S.K., Pauzan, M.A.B., Othman, M.H.D., 2021. Fabrication and characterization of composite hollow fibre membrane derived from hydroxyapatite cow bone and kaolin. *IOP Conf. Series: Materials Science and Engineering* 1142, 012011. <https://doi.org/10.1088/1757-899X/1142/1/012011>.
- Kazemian, A., Parcheforosh, A., Salari, A., Ma, T., 2021. Optimization of a novel photovoltaic thermal module in series with a solar collector using Taguchi based grey relational analysis. *Solar Energy* 215, 492–507.
- Korpe, S., Rao, P.V., 2021. Application of advanced oxidation processes and cavitation techniques for treatment of tannery wastewater—A review. *Journal of Environmental Chemical Engineering* 9 (3), 105234.
- Kumar, V., Sandhu, P.P., Ahluwalia, V., Mishra, B.B., Yadav, S.K., 2019. Improved upstream processing for detoxification and recovery of xytilol produced from corn cob. *Bioresour. Technol.* 291, 121931 <https://doi.org/10.1016/j.biortech.2019.121931>.
- Li, X., Han, L., Huang, Z., Li, Z., Li, F., Duan, H., Zhang, S., 2022. A robust air superhydrophilic/superoleophobic diatomite porous ceramic for high-performance continuous separation of oil-in-water emulsion. *Chemosphere* 303, 134756.
- Lu, J., Sun, C., Yang, K., Wang, K., Jiang, Y., Tusiime, R., Yu, M., 2019. Properties of polylactic acid reinforced by hydroxyapatite modified nanocellulose. *Polymers* 11 (6), 1009.
- Malik, N., Bulasara, V.K., Basu, S., 2020. Preparation of novel porous ceramic microfiltration membranes from fly ash, kaolin and dolomite mixtures. *Ceramics International* 46 (5), 6889–6898.
- Mustapha, S., Ndamitso, M.M., Abdulkareem, A.S., Tijani, J.O., Mohammed, A.K., Shuaib, D.T. (2019). Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater. *Heliyon* (5) e02923. doi:10.1016/j.heliyon.2019.e02923.
- Mustapha, S., Oladejo, T.J., Muhammed, N.M., Saka, A.A., Oluwabunmi, A.A., Abdulkabir, M., Joel, O.O., 2021. Fabrication of porous ceramic pot filters for adsorptive removal of pollutants in tannery wastewater. *Scientific African* (11), e00705. <https://doi.org/10.1016/j.sciaf.2021.e00705>.
- Mustapha, S., Tijani, J.O., Ndamitso, M.M., Abdulkareem, A.S., Shuaib, D.T., Mohammed, A.K., Sumaila, 2020. The Role of Kaolin and Kaolin/Zno Nano-adsorbents in Adsorption Studies for Tannery Wastewater Treatment. *Scientific Reports/Nature research* 10 (13068), 1–22.
- Naumczyk, J., Rusiniak, M., 2005. Physicochemical and chemical purification of tannery wastewaters. *Polish Journal of Environmental Studies* 14 (6), 789–797.
- Nourisepehr, M., Nasser, S., Mazaheri, A.M., Yaghmaian, K., 2005. Chromium Bio-removal From Tannery Industries Effluent by *Aspergillus Oryzae*. *Iran. J. Environ. Health. Sci. Eng.* 2 (4), 273–279.
- Obada, D.O., Dodoo-Arhin, D., Dauda, M., Anafi, F.O., Ahmed, A.S., Ajayi, O.A., Samotu, I.A., 2016a. Physical and Mechanical Properties of Porous Kaolin Based Ceramics at different temperatures. *West Indian Journal of Engineering* 39 (1).
- Obada, D.O., Aliyu, A., Kuta, U.M., Lisiyas, A., Ogenyi, V.F., Aquatar, M.O., Adam, I., 2022. Trends in the development of hydroxyapatite from natural sources for biomedical applications. *WIT Transactions on Ecology and the Environment* 257, 199–210.
- Obada, D.O., Dauda, E.T., Abifarin, J.K., Dodoo-Arhin, D., Bansod, N.D., 2020. Mechanical properties of natural hydroxyapatite using low cold compaction pressure: Effect of sintering temperature. *Materials Chemistry and Physics* 239, 122099.
- Obada, D.O., Osseni, S.A., Sina, H., Oyedeji, A.N., Salami, K.A., Okafor, E., Dauda, E.T., 2023a. Hydroxyapatite materials-synthesis routes, mechanical behavior, theoretical insights, and artificial intelligence models: a review. *Journal of the Australian Ceramic Society* 1–32.
- Obada, D.O., Osseni, S.A., Sina, H., Salami, K.A., Oyedeji, A.N., Dodoo-Arhin, D., Dauda, E.T., 2021. Fabrication of novel kaolin-reinforced hydroxyapatite scaffolds with robust compressive strengths for bone regeneration. *Applied Clay Science* 215, 106298.
- Obada, D.O., Dodoo-Arhin, D., Dauda, M., Anafi, F.O., Ahmed, A.S., Ajayi, O.A., 2016b. Potentials of fabricating porous ceramic bodies from kaolin for catalytic substrate applications. *Appl. Clay Sci.* 132, 194–204.
- Obada, D.O., Dodoo-Arhin, D., Dauda, M., Anafi, F.O., Ahmed, A.S., Ajayi, O.A., 2017. The impact of kaolin dehydroxylation on the porosity and mechanical integrity of kaolin based ceramics using different pore formers. *Results in physics* 7, 2718–2727.
- Osuchukwu, O.A., Salihi, A., Abdullahi, I., Obada, D.O., Abolade, S.A., Akande, A., Csaki, S., 2022a. Structural and nano-mechanical characteristics of a novel mixture of natural hydroxyapatite materials: Insights from ab-initio calculations and experiments. *Materials Letters* 326, 132977.
- Obada, D.O., Salami, K.A., Alabi, A.A., Oyedeji, A.N., Csaki, S., Hulan, T., Meher, A.K., 2023b. Mechanical behaviour of porous kaolin-based ceramics for potential catalysts support applications. *Journal of the Korean Ceramic Society* 60 (1), 99–112.
- Osuchukwu, O.A., Salihi, A., Abdullahi, I., Obada, D.O., 2022b. Synthesis and characterization of sol-gel derived hydroxyapatite from a novel mix of two natural biowastes and their potentials for biomedical applications. *Materials Today: Proceedings* 62, 4182–4187.
- Osuchukwu, O.A., Salihi, A., Abdullahi, I., Obada, D.O., 2022c. Experimental data on the characterization of hydroxyapatite produced from a novel mixture of biowastes. *Data in Brief* 42, 108305.
- Pozo, C., Rodríguez-Llamazares, S., Bouza, R., Barral, L., Castaño, J., Müller, N., Restrepo, I., 2018. Study of the structural order of native starch granules using combined FTIR and XRD analysis. *Journal of Polymer Research* 25 (12), 1–8.
- Reda, A.H., 2016. Physico-chemical characterization of tannery effluent and its impact on the nearby river. *Journal of Environmental Chemistry and Ecotoxicology* 8 (6), 44–50.
- Rouf, M.A., Islam, M.S., Haq, M.Z., Ahmed, N., Rabeya, T., 2013. Characterization of effluents of leather industries in Hazaribagh area of Dhaka city. *Bangladesh J. Sci. Ind. Res.* 48 (3), 155–166.
- Sagara, J., Study of filtration for point-of-use drinking water treatment in Nepal, 2000. MSc Thesis submitted to the Department of Civil and Environmental Engineering, Massachusetts Institute of Technology.
- Salami, K.A., Obada, D.O., Alabi, A.A., Csaki, S., Oyedeji, A.N., 2022. Utilization of sawdust as a pore-former in the fabrication of ceramic adsorbents for water purification. *Journal of the Australian Ceramic Society* 58 (4), 1297–1309.
- Selmin, M.A., Latif, A.F.A., Lee, C.W., Muhamad, M.S., Basri, H., Lee, T.C., 2022. Adsorption efficiency of hydroxyapatite synthesised from black tilapia fish scales for chromium (VI) removal. *Materials Today: Proceedings* 57, 1142–1146.
- Sharma, P.R., Sharma, S.K., Lindström, T., Hsiao, B.S., 2020. Nanocellulose-enabled membranes for water purification: perspectives. *Advanced Sustainable Systems* 4 (5), 1900114.
- Suzuki, T., Hidaka, T., Kumagai, Y., Yamamoto, M., 2020. Environmental Pollutants and the Immune Response. *Nature Immunology* (21), 1486–1495. <https://doi.org/10.1038/s41590-020-0802-6>.
- Varjani, S., Joshi, R., Srivastava, V.K., Ngo, H.H., Guo, W., 2020. Treatment of wastewater from petroleum industry: current practices and perspectives. *Environmental Science and Pollution Research* 27, 27172–27180.
- Van Puijenbroek, P.J.T.M., Beusen, A.H.W., Bouwman, A.F., 2019. Global nitrogen and phosphorus in urban waste water based on the Shared Socio-economic pathways. *Journal of environmental management* 231, 446–456.
- Zhang, W., Pasquini, M., Li, Y., 2022. Microplastic and Nanoplastic Pollution: Characterization, Transport, Fate, and Remediation Strategies. *Frontiers of Environmental Science and Engineering* 16 (1), 12.
- Zhao, C., Chen, W., 2019. A review for Tannery Wastewater treatment: some thoughts under stricter discharge requirements. *Environmental Science and Pollution Research* 26 (25), 26102–26111. <https://doi.org/10.1007/s11356-019-05699-6>.