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Performance Assessment of Coagulation and Ceramic Filtration of Tannery Effluent Using Hydroxyapatite/Kaolin-Based Materials

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ABSTRACT

Tannery effluent remains a pressing environmental concern due to its complex composition and presence of hazardous contaminants. In this study, an approach employing chemical coagulation followed by filtration using hydroxyapatite (HAp)/kaolin-based ceramic materials was applied to treat tannery effluent. Aluminium sulphate served as primary coagulant and was introduced to the effluent at varying concentrations (75, 150, 225, 300, 375, 450, 525, and 600 mg/L). Samples were subjected to rapid mixing (10 mins), slow mixing (30 mins), and allowed to settle for 24 hrs. Post-coagulation, supernatant was filtered using three types of ceramic filters fabricated from: (i) pure kaolin, (ii) kaolin combined with HAp, and (iii) kaolin blended with HAp and starch. The performance of each filter was evaluated based on chromium removal efficiency and turbidity reduction. The kaolin, kaolin + HAp, and kaolin + HAp + starch filters achieved chromium removal efficiencies of 75.75%, 81.36%, and 84.03%, respectively. The optimum chromium removal (84.03% at pH 6.93, temperature of 24.9°C, with a corresponding turbidity reduction of 45.44%) was obtained using the kaolin + HAp + Starch filter. However, the treated effluent still exceeded regulatory limits for chromium in effluent, as established by required standards at 1 mg/L and U.S. Environmental Protection Agency (EPA) at 0.02 mg/L. The kaolin/HAp/starch filter, which demonstrated an optimal flow rate of 29.17 mL/h, gave the most effective contaminant removal. These findings suggest that while HAp/kaolin-based ceramic filters show considerable promise for chromium removal in tannery wastewater, their performance must be further enhanced.

Keywords: Coagulation, Tannery Effluent, Kaolin, Hydroxyapatite, Ceramic Filtration

1.0 INTRODUCTION

Several industries have emerged, one of the industries that has significantly contributed to the growth of nations and the global economy is leather industry (Silveira et al. 2023). However, the sector faces major environmental challenges due to inadequate waste management practices (Zhao et al., 2022). Tannery effluents are highly complex, containing a wide range of pollutants such as hairs, acids, proteins, chlorides, tannins, chromium salts, alkalis, dyes, sulphides, solvents, and auxiliaries. Moreover, the tanning process is known for its intensive water usage and high volumes of wastewater output. These pollutants result from the complex chemical processes involved in converting raw hides into finished leather products.

Multiple studies have highlighted the toxicity, genotoxicity, and environmental threats posed by untreated tannery wastewater (Devi et al., 2023; Eid et al., 2023, Nigam et al., 2023). Given its hazardous physicochemical characteristics, untreated tannery effluent poses serious risks to both human health and ecosystems, thus necessitating immediate and effective remediation strategies. While various pollution control technologies have been introduced, including recycling of tanning agents, enzymatic unhairing, and cleaner

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production techniques, comprehensive treatment of tannery wastewater remains a challenge in many parts of the world (Zhao et al., 2022). The increasing stringency of environmental protection regulations has forced the leather tanning industry to explore alternative treatment methods that are not only effective and environmentally sustainable but also commercially viable (Zhao and Chen, 2019).

Tannery wastewater treatment typically involves three major stages (primary, secondary, and tertiary) (Díaz-Garduño et al., 2017). Primary treatment includes physical and chemical processes designed to remove suspended solids and reduce organic load. Coagulation and flocculation, using aluminium-based coagulants such as sodium aluminate, aluminium chloride, and aluminium sulfate, are frequently employed to eliminate dyes and solid contaminants (Zhou and Chen, 2019; Mcyotto et al., 2021). These processes are vital not only for initial contaminant reduction but also for preventing fouling in subsequent filtration stages (Aragaw and Angerasa, 2019).

Secondary treatment are effective in treating tannery wastewater, but several drawbacks are associated with their use, such as high operating, time-consuming (Bhardwaj et al., 2023).

However, secondary treatment alone often proves insufficient in removing nutrients like phosphorus and nitrogen, prompting the need for advanced tertiary treatment (Ahmed et al., 2016). Tertiary methods, particularly membrane-based filtration, are effective for fine purification but are prone to fouling due to residual organics and bio-colloids from earlier treatment stages (Chaipetch et al., 2021). Among membrane technologies, ceramic membranes have attracted significant attention due to their high impurity rejection rates, mechanical durability, thermal stability, and recyclability (Iji et al., 2023; Salami et al., 2023). Nonetheless, their high production costs, mainly due to the use of alumina and energy-intensive manufacturing, remain a barrier to widespread adoption.

Recent research has increasingly focused on developing ceramic membranes from low-cost, naturally derived materials such as clay, agro-wastes, and animal bones (Hubabdillah et al., 2017). For instance, Hubabdillah et al. (2020) demonstrated the effectiveness of hydroxyapatite-based ceramic membranes from cow bones in removing turbidity, color, Chemical Oxygen Demand (COD), and heavy metals with high efficiency. Similarly, Kamarudin et al. (2021) and Iji et al. (2023) fabricated membranes using combinations of hydroxyapatite, kaolin and starch, achieving substantial pollutant removal and strong adsorption capacities in tannery effluent treatment. In light of these developments, this study was designed to evaluate an integrated approach to tannery wastewater treatment by combining chemical coagulation with natural-material-based ceramic membrane filtration. Specifically, the study aimed to assess the effect of varying alum concentrations on key physicochemical parameters of tannery effluent, including pH, conductivity, total dissolved solids (TDS), turbidity, chromium concentration, biological oxygen demand (BOD) and chemical oxygen demand (COD).

The underlying hypothesis of the study was that increasing the concentration of alum as a coagulant would significantly enhance the reduction of pollutants in the primary treatment stage. Furthermore, it was hypothesized that ceramic filters composed of kaolin, hydroxyapatite and starch would outperform those made from pure kaolin or kaolin/HAp blends due to their higher porosity and adsorption capacity. The study also posited that the combination of coagulation and ceramic filtration would provide a more effective and sustainable solution for treating tannery wastewater than either method alone.

2.0 MATERIALS AND METHOD

2.1 Materials

The kaolin was gathered from the Kankara deposit in Katsina State, Nigeria, and the cow bones, which are the source of HAp were obtained from the Abbatoir in Zango, Zaria, Kaduna State, Nigeria. The starch, serving as the pore former, was obtained from Sabon Gari Market in Zaria, Kaduna State. Tannery effluent was collected from the Nigerian Institute of Leather and Science Technology- NILEST, Zaria, Nigeria. The effluent sample was a mixture of wastewater from all stages of the tanning process e.g. soaking, liming, deliming, bating, pickling, chrome tanning and retaining. The effluent sample was collected in clean plastic containers from the collection 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).

2.2 Characteristics of the tannery wastewater effluent

The parameters including pH, electrical conductivity (EC), total dissolved solids (TDS), temperature, turbidity, biological oxygen demand in 5 days at 20

°c (BOD_5), chemical oxygen demand (COD) of raw tannery effluent and treated effluents were determined. Other parameters including heavy metals of untreated and treated effluents were analyzed. These parameters were selected because of deleterious nature of untreated effluent to the receiving environment (Reda, 2016). 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. BOD_5 and COD were determined according to standard methods (APHA, 1998). Concentrations of Chromium present in the effluent was obtained 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 to 1. The procedure was carried out at a pre-determined wavelength (λ max) of 357.9 nm. All chemicals and reagents used were of analytical grade and the experiments were carried out multiple times to minimize analytical error. The results were then analysed and compared with the wastewater discharge standards set by the Environmental Protection Agency (EPA) 2021and Federal Environmental Protection Agency (FEPA) 2023 in Nigeria.

2.3 Kaolin Preparation and Beneficiation

The clay samples collected underwent a process where debris was removed and then left to dry naturally for three days. The removal of impurities was followed by a method outlined by Aroke et al. (2013), involving physical separation and subsequent soaking. The clay was immersed in de-ionized water for 48 hours in a plastic container. The resulting mixture was then filtered through a 100 μm mesh sieve and allowed to settle, after which the water was decanted, and the sample air-dried. The dried clay was crushed using a mortar and pestle, and the resulting powder was sieved through a 100 μm mesh sieve to achieve a fine consistency, as described by Mustapha et al. (2019).

2.4 Extraction of Hydroxyapatite from Animal Bone

Waste Cow Bones were boiled in hot water at 100°c for an hour to eliminate attached tissues, fats, and visible impurities. Subsequently, the bones underwent multiple washing and then rinsed with distilled water to ensure the complete removal of attached meat and soft tissues. Afterwards, the cleaned bones were dried in an oven at 100°c for 24 hours to remove moisture. The dried bones were then subjected to carbonization until all fat was removed. Following carbonization, the carbonized bones were calcined in a muffle furnace at temperatures of 800°c, 900°c, and 1000°c. The thermally decomposed samples were then allowed to cool at room temperature following the procedure of Barakat et al., (2009), to obtain fine HAp powder. Finally, the powders were sieved to separate off particle sizes above 100 μm (Khoo et al., 2015).

2.5 Production of the Hap/kaolin-based ceramic filter

Various sets of batch-formulated samples consisting of kaolin, hydroxyapatite, and a pore former (starch), were mixed with water and kneaded to ensure uniformity, eliminate lumps and trapped air bubbles. A sample devoid of hydroxyapatite and pore former (100 wt.% of kaolin) served as the control, while other samples comprised 80 wt.% of kaolin + 10 wt.% of HAp + 10 wt.% of pore former (optimum sample obtained from Iji et al., 2023), and 90 wt.% of kaolin + 10 wt.% of HAp. Each mixture was filled into a mould to the same level to ensure consistency and uniformity and pressed to achieve compactness. The resulting green body samples were taken out of the mould and air-dried at room temperature (25°c) for three days, followed by further drying at 100°c to ensure total moisture removal, enhancing their green strength and making them safe for subsequent handling. Cross sectional view through fabricated porous ceramic kaolin-based filter is as shown in Figure 1.

Subsequently, the dried batch-formulated green bodies were sintered at 1000°c for 2 hours in an electric muffle furnace, with a heating rate of 5°c/min (Obada et al., 2016).

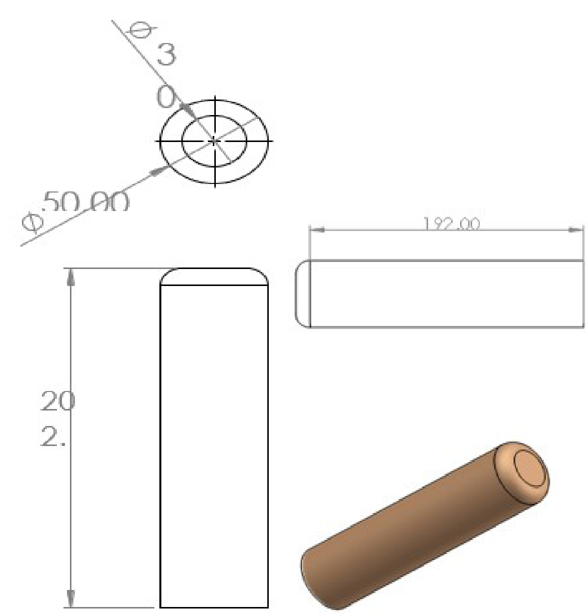


Fig 1: Cross sectional view through fabricated porous ceramic kaolin-based filter

2.6 Treatment Process

2.6.1 Coagulation treatment of wastewater samples

To prepare the alum solution, 15 grams of aluminium sulphate was dissolved in one litre of distilled water. This resulted in a concentration of 15 mg/L in the alum solution. The research involved batch experiments comprising rapid mixing, slow mixing, and sedimentation processes, all employing alum as the coagulant. A Jar test machine capable of agitating four beakers simultaneously was utilized. Each beaker was filled with one litre of raw wastewater sample and positioned under specialized multiple stirrer rig. Various concentrations of alum (75, 150, 225, 300, 375, 450, 525, and 600 mg/L) were added to the samples simultaneously. Stirring was conducted rapidly for 10 minutes using metallic stirrers to ensure complete dispersal of the coagulant. Subsequently, the samples were left to flocculate for 30 minutes and then allowed to stand undisturbed for 24 hours on a workbench to facilitate the flocculation and sedimentation processes respectively (Maliki et al., 2019). Afterwards, the supernatant was decanted and analysed to determine the optimum coagulant dosage.

2.6.2 Flow rate Calculation

The upper transparent plastic buckets were filled halfway with pre-treated tannery effluent sample and the flow rate of the water was determined by measuring the quantity of water filtered after 24 hours. This was conducted in accordance with the method used by Dies (2003) as represented in Equation 1.

$$\text{Flowrate} = \frac{\textit{Volume of water measured at time T (mL)}}{\textit{Elapsed time,T,from start of test (hours)}} \quad (1)$$

2.6.3 Filtration treatment of wastewater samples

The effluent sample with the optimum coagulant dosage was further treated using the fabricated low-cost porous ceramic kaolin-based water filters. The supernatant liquid after the settling process was poured into a filter medium for filtration. A water filter system was set up using the fabricated ceramic filters to achieve optimum removal of pollutants such as turbidity, total dissolved solids and heavy metal. 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 had a capacity of 3L. The upper unit holds the ceramic filter while the bottom container collects treated effluent that seeps down through the ceramic filter (Figure 2). The Cr concentration of the filtered solution was determined using an Atomic Absorption Spectrophotometer. The ceramic filter was washed with distilled water before being assembled, to remove any fine clay particles from the ceramic filter. This ceramic filter candle is cylindrically shaped with a height of 202mm and a diameter of 50mm wide. The ceramic filters are made of only kaolin, kaolin mixed with hydroxyapatite and kaolin mixed with hydroxyapatite and starch respectively. The used ceramic filters were regenerated through sterilization by boiling them (Sagara, 2000), then brushing them lightly with a soft brush before been reused.

Figure 2: Filtration setup for the pre-treated tannery effluent

2.6.4 Determination of Filtration Performance

The effectiveness of the ceramic filter for heavy metal removal from tannery wastewater was determined by obtaining the heavy metal removal efficiency (%). The experimental setup is shown in Figure 3. The actual heavy metal concentration of the effluent was measured before filtration and after filtration using Atomic Absorption Spectroscopic (AAS). The removal efficiency was then calculated using Equation 2 as adopted by Muhamad et al., (2018).

$$\textbf{Removal efficiency (\%)} = \frac{C_{BF} - C_{AF}}{C_{BF}} \times 100 \quad (2)$$

Where C_{AF}, and C_{BF} are concentrations after and before filtration respectively.

Percentage reduction in turbidity was also used to determine the efficiency of the coagulant and ceramic kaolin-based filter. The turbidity of unfiltered and filtered effluent was determined using a turbidimeter (WGZ-B Turbidimeter). The percentage turbidity reduction was calculated using the expression in Equation 3 as stated by Bulta and Micheal, (2019).

$$\textbf{Turbidity (\%)} = \frac{\textit{Turbidity of the contaminated water} - \textit{Turbidity of th}}{\textit{Turbidity of the contaminated water}} \times 100 \quad (3)$$

2.6.5 Statistical analysis

To discern disparities in parameter means among effluent samples, one-way analysis of variance (ANOVA) was employed to assess the significance of variations, specifically focusing on differences between coagulant doses within each test variable such as pH and turbidity. Post-hoc analysis utilizing the least significant difference (LSD) method was conducted to examine these variations at a significance level of $p < 0.05$. The data analyses were performed using IBM SPSS version 23

3.0 Results and Discussion

3.1 Characterization of tannery effluents before and after treatment

Table 1 displays the characteristics of the untreated tannery effluent. Comparative analysis with the Federal Environmental Protection Agency (FEPA) interim guidelines and standards for industrial effluent (1991) and Environmental Protection Agency (EPA) revealed a substantial pollution load in the effluent. The untreated effluent exhibited a dark blue colouration, indicating the presence of highly coloured compounds capable of environmental pollution. Following coagulation/flocculation, the original effluent colour lightened to light blue, underscoring the efficacy of the coagulant (alum). Furthermore, the study assessed the filtration efficiency using three different kaolin-based filters, which demonstrated effective removal of colour and odour from the tannery effluent. Notably, clear effluent was observed in post-filtration with the three filters, displaying a clear light brownish hue. While the untreated effluent emitted an obnoxious odour, filtration with kaolin-based filters resulted in an objectionable odour. These findings aligned with previous studies, such as Islam et al. (2011), who reported light blue, bluish-green, and dark appearances in tannery effluents in Bangladesh. Nourisepher et al. (2005) described the colour of tanning house effluent as dark blue due to the presence of inorganic chemicals like chromium used during processing.

Additionally, Rouf et al. (2013) documented various colours (dark, navy blue, blackish blue, and violet) and pungent odours in tannery effluents from different leather industries. Chowdhury et al. (2013) reported the colour of filtered tannery effluent as light brown. The dark colouration of untreated tannery effluent signifies the presence of coloured compounds, hindering sunlight penetration necessary for aquatic plant photosynthesis.

Table 1: Average concentration (mean ± SD) values of wastewater quality parameters for raw tannery wastewater

Parameters	Initial Content (Mean statistic)	FEPA (1991) Standard	EPA Standard
pH	5.31±0.012	6-9	6-9
Electrical Conductivity (μScm^{-1})	17.39±0.007	1000	1500
Total Dissolved Solids (mgL^{-1})	14553.33±26.667	2000	1000
Temperature(^0C)	24.77±0.133	<40	<30
Turbidity (NTU)	315.33±3.712	NG	NG
Chromium (mgL^{-1})	562.08±10.202	1	0.2
BOD_5 (mgL^{-1})	80.00±0.000	50	50
COD (mgL^{-1})	3866.67±66.667	500	250

It is evident in Table 1 that certain effluent parameters exceeded the FEPA and EPA discharge standards. Notably, Total Dissolved Solids (TDS) measured as 14553.33 mg/L and Chromium at 562.08 mg/L surpassed the discharge standards. Elevated levels of dissolved solids in water directly impact its aesthetic qualities, such as odour and colour, by increasing turbidity. The presence of high chromium levels indicates contamination by heavy metals, rendering the effluent toxic. Turbidity was notably high, with a mean value of 315.33 NTU, possibly due to the presence of suspended matter, as well as organic, and inorganic substances in the effluent. According to Reda (2016), pH determination is crucial as it influences other physicochemical parameters and the availability of metal ions in water and wastewater. The untreated effluent exhibited an average pH value of 5.31, indicative of acidic conditions, falling below the FEPA standard range of 6-9 for industrial effluents discharged into water bodies. However, Electrical Conductivity (EC) at 17.39 µS/cm and temperature at 24.77°C fell within the discharge limits set by FEPA and EPA for industrial effluents discharged into water bodies.

3.2 Optimization of alum dose as a coagulant

3.2.1 Effect of alum on effluent's pH, EC, TDS and Turbidity

The mean pH result for the tannery effluent before treatment with alum was 5.31±0.012, which is not the ideal pH range for effluent discharge as given by FEPA. The pH of the tannery effluent was almost constant before and after treatment because it was acidic before and after the coagulant was added. From the result obtained as shown in Table 2, alum dosages of 75 to 600 mg/L did not have much effect on the pH. Therefore, treatment with alum did not have a significant effect on the pH value of tannery effluent. No additional step was required to adjust the pH value after the treatment. The mean conductivity for the tannery effluent before treatment with alum was 17.39±0.007 µS/cm. After the treatment, conductivity remained fairly constant. According to the standard from FEPA, levels up to 1000 µS/cm are acceptable in wastewater. Hence, conductivity values for treated tannery wastewater with a different dose of alum (75–600 mg/L) are acceptable for wastewater discharge standards.

High TDS indicates presence of contaminants in wastewater with maximum of 2000 mg/L set by FEPA. The result obtained in Table 2 showed that the TDS in tannery effluent after treatment with alum decreased across for all dosages used with optimum removal of 13820.00±11.547 mg/L at 450 mg/L concentration of alum dosage. However, this still exceeded the standard level set by FEPA. It is necessary to treat the wastewater further to reduce excess TDS before discharge to mitigate the negative impacts on the environment. Tannery wastewater treatment processes using alum as a coagulant have proved to be effective in turbidity removal. When alum was added to the sample and followed by rapid stirring, it was distributed to all parts of the liquid. It destabilized the colloidal particles present in water and then interacted with the negatively charged particles causing turbidity in water (Lea, 2010). From Table 2, the lowest (optimum) value of turbidity was obtained at 450 mg/L of alum dose with an average turbidity value of 23.33±1.333 NTU which implies 92.60% of turbidity removal. The results show that the optimum dose of alum as a coagulant was influenced by the level of the initial turbidity of the effluent sample. On exceeding the alum optimum dosage (450mg/L), turbidity was increased because all colloids have been neutralized and precipitated with an optimum dosage, so the excess coagulants will cause turbidity in water as there was no more interaction with oppositely charged colloidal particles (Mangale, 2012).

3.2.2 Effect of alum on effluent Chromium, BOD and COD

The Chromium concentration of the raw tannery effluent was 562.08±10.202 mg/L. When treated with alum as a coagulant, the concentration decreased gradually until optimum removal of 50.92% was achieved at 450 mg/L of alum dose. A gradual increase in concentration was then observed at 525 mg/L and 600 mg/L alum dosage. However, the optimum Chromium concentration of 275.87±11.099 mg/L obtained does not meet the wastewater discharge requirement set by FEPA. The BOD for the raw tannery effluent was 80.00±0.000 mg/L and varied across alum dosages. For instance, Alum doses of 75 mg/L, 150 mg/L, 225 mg/L, and 300 mg/L exhibited a decrease in BOD values while 600 mg/L dosage showed an increase in BOD value as shown in Table 2. Alum doses of 375 mg/L, 450 mg/L and 525 mg/L had the same BOD values (53.33±3.333 mg/L) which was the optimum BOD value obtained. However, this value is slightly above 50 mg/L recommended by FEPA and EPA for wastewater discharge. Therefore, the BOD values obtained do not meet the wastewater discharge requirement set by FEPA and EPA.

The COD test result indicates the amount of water-dissolved oxygen consumed by the contaminants, during two hours of decomposition from a solution of boiling potassium dichromate (Prasad & Rao, 2016). The higher the chemical oxygen demand, the higher the amount of pollution in the test sample. The COD for the raw tannery effluent was measured to be 3866.67±66.667 mg/L. After treatments, there was a significant decrease in COD at 75 mg/L dose of Alum being the optimum. However, the COD values obtained do not meet the wastewater discharge requirement set by FEPA and EPA. This conforms to the findings of Marco et al., (2016); that the jar experiments provided evidence that the coagulation process could not provide sufficient COD removal efficiency in wastewater treatment even at an alum dose of 450 mg/L. Based on results analysed, it essential to further treat the tannery effluent to reduce excess Chromium, BOD and COD before discharge to mitigate the negative impacts on the environment.

Table 2: Mean values of characteristics of alum treatment on tannery effluent

Treatment	pH	EC (µS/cm)	TDS (mg/L)	T (^oC)	Turbidity (NTU)	Chromium (mg/L)	BOD_5 (mg/L)	COD (mg/L)
75 mg/L	5.41±0.003	17.55±0.009	14500.00±23.094	26.17±0.067	67.33±0.667	524.52±9.552	70.00±0.000	2100.00±57.735
150 mg/L	5.26±0.019	18.08±0.007	14326.67±17.638	25.63±0.120	62.00±1.155	420.47±3.433	63.33±3.333	2466.67±66.667
225 mg/L	5.28±0.003	17.96±0.018	14260.00±11.547	25.43±0.088	55.33±1.333	373.90±6.682	60.00±0.000	3100.00±57.735
300 mg/L	5.27±0.006	18.19±0.007	14100.00±11.547	25.63±0.120	40.67±0.667	327.65±13.771	56.67±3.333	2166.67±33.333
375 mg/L	5.27±0.003	17.82±0.003	14046.67±17.638	25.50±0.058	33.33±0.667	291.42±1.139	53.33±3.333	2600.00±57.735
450mg/L	5.28±0.006	17.82±0.000	13820.00±11.547	25.47±0.067	23.33±1.333	275.87±11.099	53.33±3.333	2466.67±120.185
525 mg/L	5.23±0.006	17.77±0.003	14253.33±6.667	25.50±0.058	35.33±0.667	277.37±12.055	53.33±3.333	2633.33±66.667
600 mg/L	5.23±0.006	17.94±0.007	14013.33±6.667	25.67±0.088	38.67±0.667	445.25±15.265	56.67±3.333	2466.67±185.592
FEPA	6-9	1000	2000	<40	NG	1	50	500
EPA	6-9	1500	1000	<30	NG	0.2	50	250

3.3 Filtration tests

3.3.1 Flow rate analysis

The flow rate test results for the ceramic filters produced are summarized in Table 3. The average values obtained vary between 6.39 ml/h and 29.17 ml/h for the filters. The Kaolin + Hydroxyapatite + Starch filter (made from a combination of 80:10:10) was considered most suitable for producing a porous ceramic filter. It recorded a low flow rate but optimum removal efficiency of heavy metal was achieved. The Kaolin filter and Kaolin + Hydroxyapatite filters (without the pore former) both recorded lower flow rates which implies low porosity.

Table 3 Flow rate analysis

Filters	Flowrate (mL/hr)			
	1	2	3	Average
Kaolin	7.50	5.42	6.25	6.39
Kaolin + Hydroxyapatite	16.67	17.5	15.42	16.53
Kaolin + Hydroxyapatite + Starch	29.17	27.08	31.25	29.17

3.3.2 Filtration analysis

After coagulation with optimum alum dosage (450 mg/L), the tannery effluent was filtered using kaolin-based filters. The mean performance of the three filters (kaolin, kaolin + HAp, kaolin + Hap + starch) on the different parameters (pH, EC, TDS, Temperature, Turbidity, Chromium, BOD and COD) is shown in Table 4. The result showed that kaolin, kaolin + HAp, and kaolin + HAp + starch filter removal of chromium by 75.75%, 81.36%, and 84.03% respectively. The maximum adsorption capacity of chromium was 84.03% at pH 6.93, temperature 24.90°C when the turbidity removal was 45.44%. This optimum removal of chromium was achieved by the filter which was composed of kaolin + HAp + Starch. It was observed that after the adsorption experiment, pH of the treated effluents increased from 5 to 7 while COD remained high post filtration (1100mg/L), this suggests organic pollutants were not effectively removed by the ceramic filter. Kaolin-based filtration experiments revealed that chromium removal capabilities depended on the composition of the individual filters. The addition of pore former assists the fabrication of high-porosity ceramics, thereby enhancing the filtration process. With the use of HAp, an efficient removal of chromium was achieved. The lack of HAp could be the reason for low filtration performance in the kaolin filter since HAp is known for its ion exchange capacity.

Filter clogging was observed after 24-hour filtration of the effluent. Therefore, filters were regenerated by washing the ceramic filters with distilled water and scrubbing with a soft brush. The parameters considered for kaolin-based filter treatment on tannery effluent are as shown in Table 4

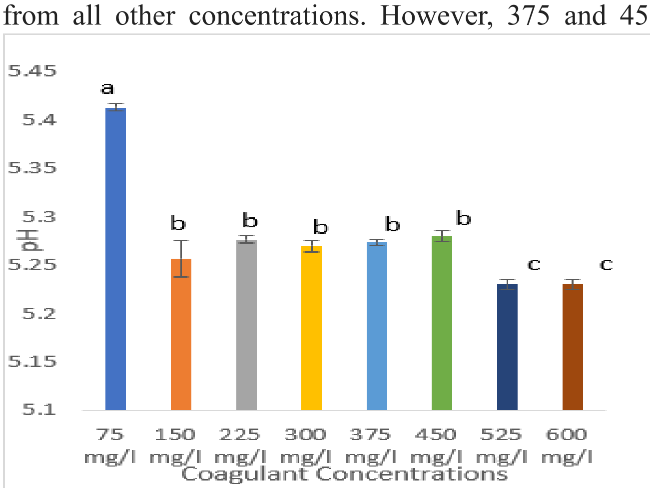
Table 4: Mean values of parameters of kaolin-based filter treatment on tannery effluent

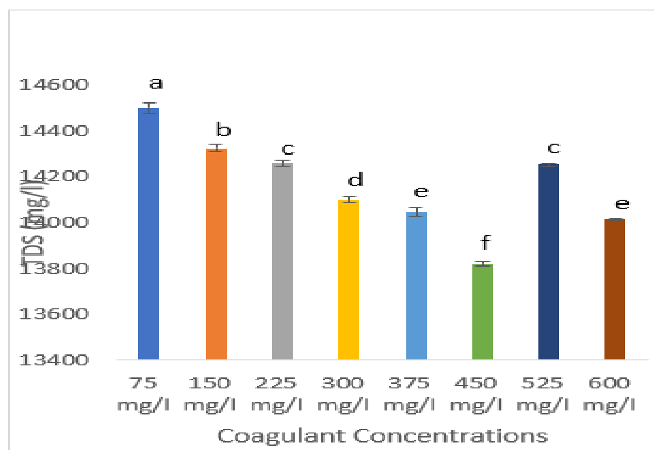
Filters	pH	EC (µS/cm)	TDS (mg/L)	T (°C)	Turbidity (NTU)	Chromium (mg/L)	BOD (mg/L)	COD (mg/L)
Kaolin	6.79±0.181	15.36± 0.101	11470.00±373.229	24.90±0.000	20.00±0.577	66.89±7.480	43.33±3.333	1600.00±100.000
Kaolin + Hydroxyapatite	7.00±0.003	14.18± 0.090	11026.67±64.893	24.83±0.033	18.33±0.882	51.42±7.879	40.00±0.000	1300.00±100.000
Kaolin + Hydroxyapatite + Starch	6.93±0.000	10.58±0.379	8570.00±30.551	24.90±0.100	12.73±0.167	44.05±3.841	40.00±0.000	1100.00±100.000
FEPA	6-9	1000	2000	<40	NG	1	50	500

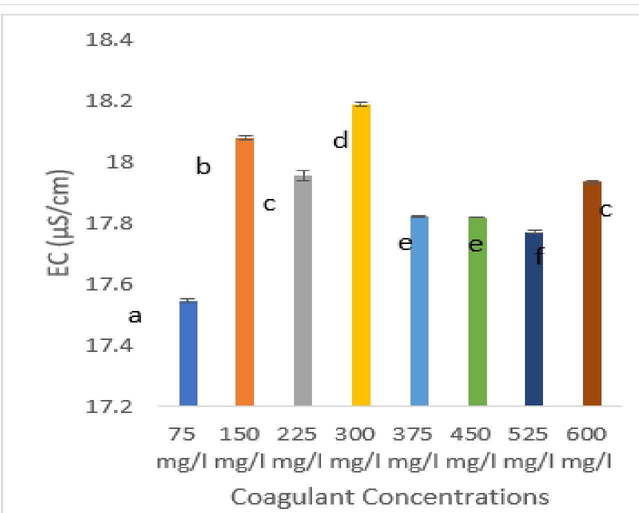
3.4 Comparison analysis of the effect of coagulant dose on effluent parameters

The post hoc comparison of means test was used to compare the parameters with the coagulant dosages and the performance of the filters. The action of coagulant concentration compared with the parameters are shown in Figs 4(a, b, c, d) for pH, EC, TDS, Temperature, and Figs 5(a, b, c, d) for Turbidity, Chromium, BOD and COD respectively. For pH in Figure 4(a), the concentration of 75 mg/L dosage significantly differs from 150 mg/L at $p < 0.05$. However, there is no significant difference between 150 mg/L, 225 mg/L, 300 mg/L, 375 mg/L and 450 mg/L which implies they have the same effect on pH. A significant reduction was observed at 525 mg/L dosage which is not significantly different from 600 mg/L. pH was maximum at a concentration of 75 mg/L dosage which is significantly different from all other concentrations.

At 75 mg/L, EC was at its lowest and significantly differs from all concentrations (see Figure 4b). There is a significant increase at 150 mg/L and differs significantly from all other concentrations. However, 375 and 450 mg/L dosages had the same EC level. There was a decline in EC at a concentration of 525 mg/L of alum, afterwards, it rises significantly at 600 mg/L. All the alum dosages that have different superscript alphabets show differences in means. In Figure 4(c), TDS is maximum at a concentration of 75 mg/L dosages which significantly differs from other concentrations at a p-value less than 0.05. TDS reduced significantly from the concentration of 75 mg/L to 450 mg/L concentration which had the least TDS value. However, there was a significant increase at 525 mg/L and then a significant decrease at 600 mg/L. There is no significant difference between the performance of 225 and 525 mg/L dosages. Similarly, no significant difference was observed between 375 and 600 mg/L which implies they have the same TDS level. At 75 mg/L, temperature was maximum and there was a significant decrease at 150 mg/L (see Figure 4d). However, 150 mg/L is not significantly different from all other dosages.







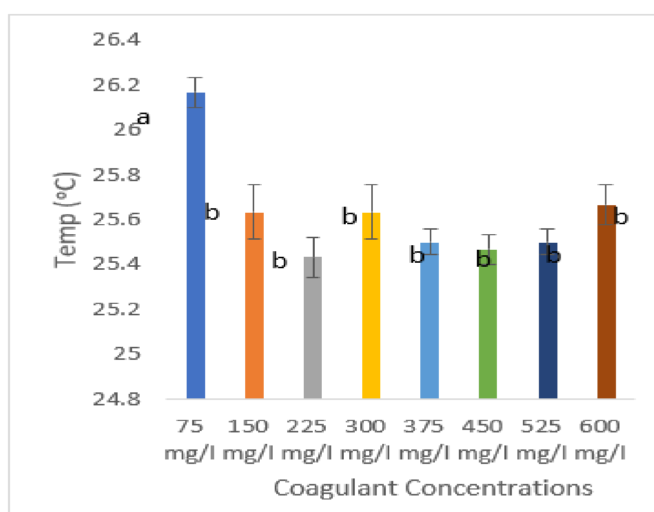


Figure 4: Comparison of the effect of coagulant dose on (a) pH (b) EC (c) TDS (d) Temperature

At a coagulant dose of 75 mg/L, maximum turbidity was about 80 NTU and significantly differs from all other dosages (see Figure 5a). There was a significant decrease at 150 mg/L with the least turbidity observed at 450 mg/L, which significantly differs from all other dosages. At 75 mg/L, chromium was maximum and significantly differs from all other dosages (see Figure 5b). It was observed that 150 and 600 mg/L had the same chromium level. For the BOD removal, the trend at different dosages is presented in Figure 5c with best performance occurred at coagulant concentrations of 375, 450 and 525 mg/L. Trend analysis of COD at different concentrations (Figure 5d) showed that the concentrations of 75 and 300 mg/L are significantly different from others being the lowest and highest occurred at concentration of 225 mg/L.

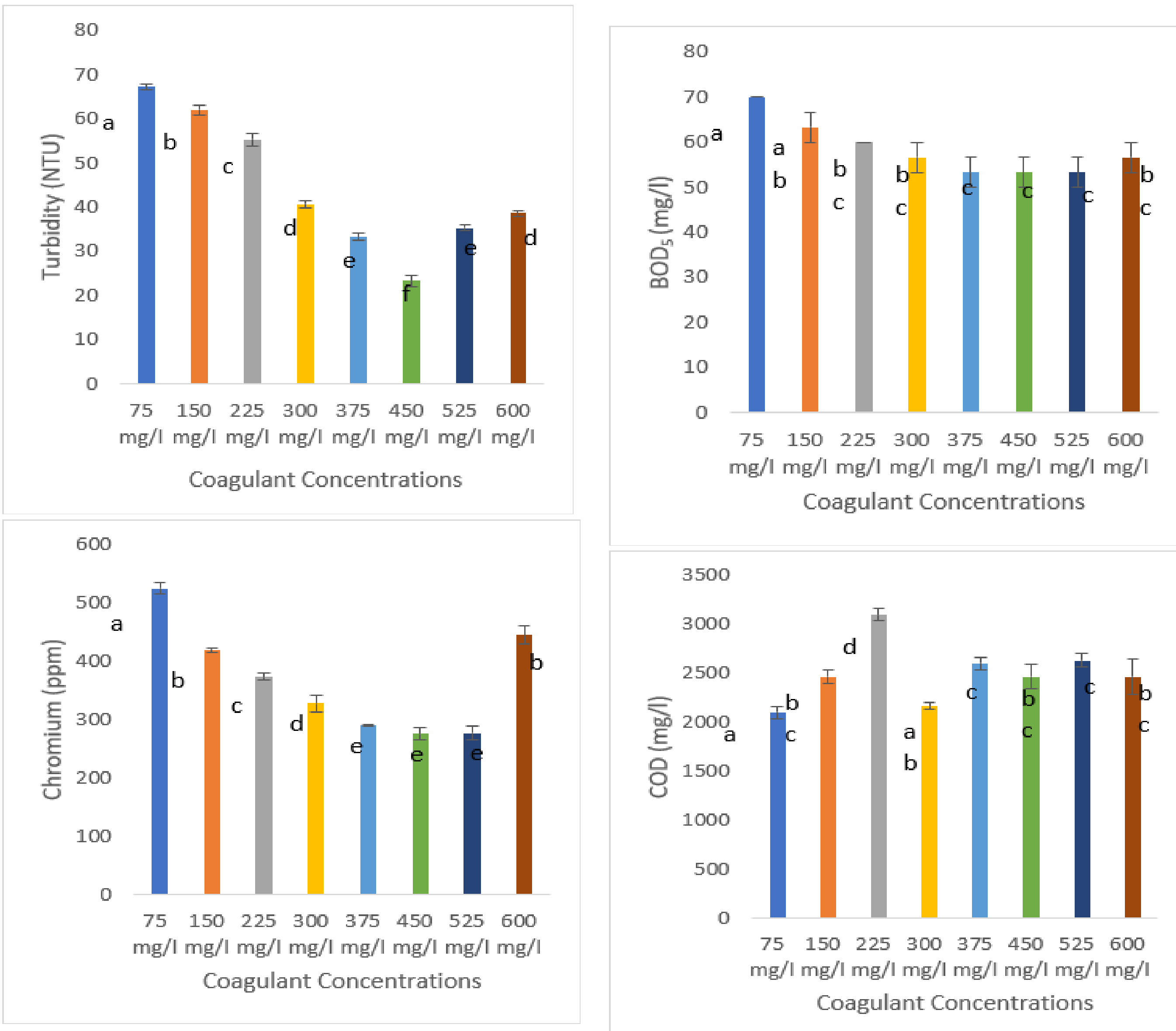


Figure 5: Comparison of the effect of coagulant dose on (a) Turbidity (b) Chromium (c) BOD (d) COD

3.5 Comparison analysis of the effect of kaolin-based filters on effluent parameters

The post hoc comparison of means test was used to compare the effluent parameters with the three ceramic filter types.

The performance of the ceramic filters with respect to the effluent parameters is shown in Figures 6-7 for pH, EC, TDS, Temperature, Turbidity and Chromium respectively.

For pH, there are no significant differences between the filters at an alpha level of 0.05 (see Figure 6a). This implies that the composition of the filters did not affect the pH of the filtered effluent. For EC, there is a significant difference between all the filters because they share different superscripts (see Figure 6b). This implies that the means differ when compared using ANOVA. For TDS, there is no significant difference between the kaolin filter and the kaolin + HAp filter because they share the same superscript (see Figure 6c). However, they are both significantly different from the kaolin + HAp + Starch filter. This implies that the means differ when compared using ANOVA. In temperature, there is no superscript which implies there is no significant difference between all the filters (see Figure 6d). Also, the temperatures of the filtered effluent are not affected by the filters.

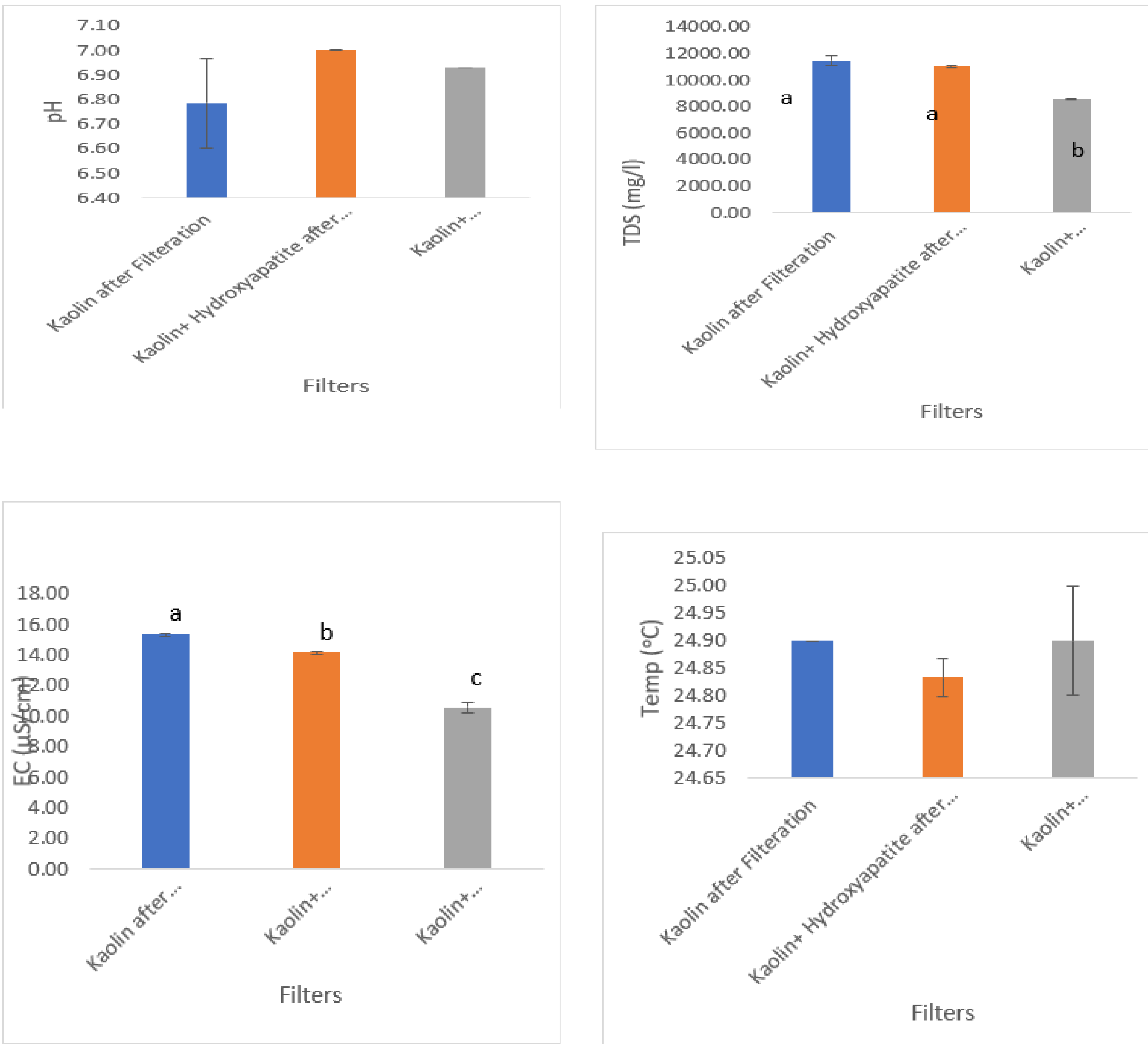


Figure 6: Comparison of ceramic filters' effect on (a) pH (b) EC (c) TDS (d) Temperature

For turbidity, there is no significant difference between the kaolin filter and the kaolin + HAp filter but the kaolin + HAp + Starch filter significantly differs from both ((see Figure 7a). However, chromium had no superscript which implies that there was no significant difference between all the filters at an alpha level of 0.05 (see Figure 7b). The statistical analysis was done using ANOVA (Analysis of Variance). The post-doc analysis helped to show the differences between the means. These charts represent the means of the parameters level with the parameters/ filters. BOD also had no superscripts which implies that there was no significant difference in BOD removal between all these filters at an alpha level of 0.05 (see Figure 7c). For COD, there is no significant difference between the kaolin filter and the kaolin + HAp filter but the kaolin + HAp + Starch filter significantly differs from both (see Figure 7d).

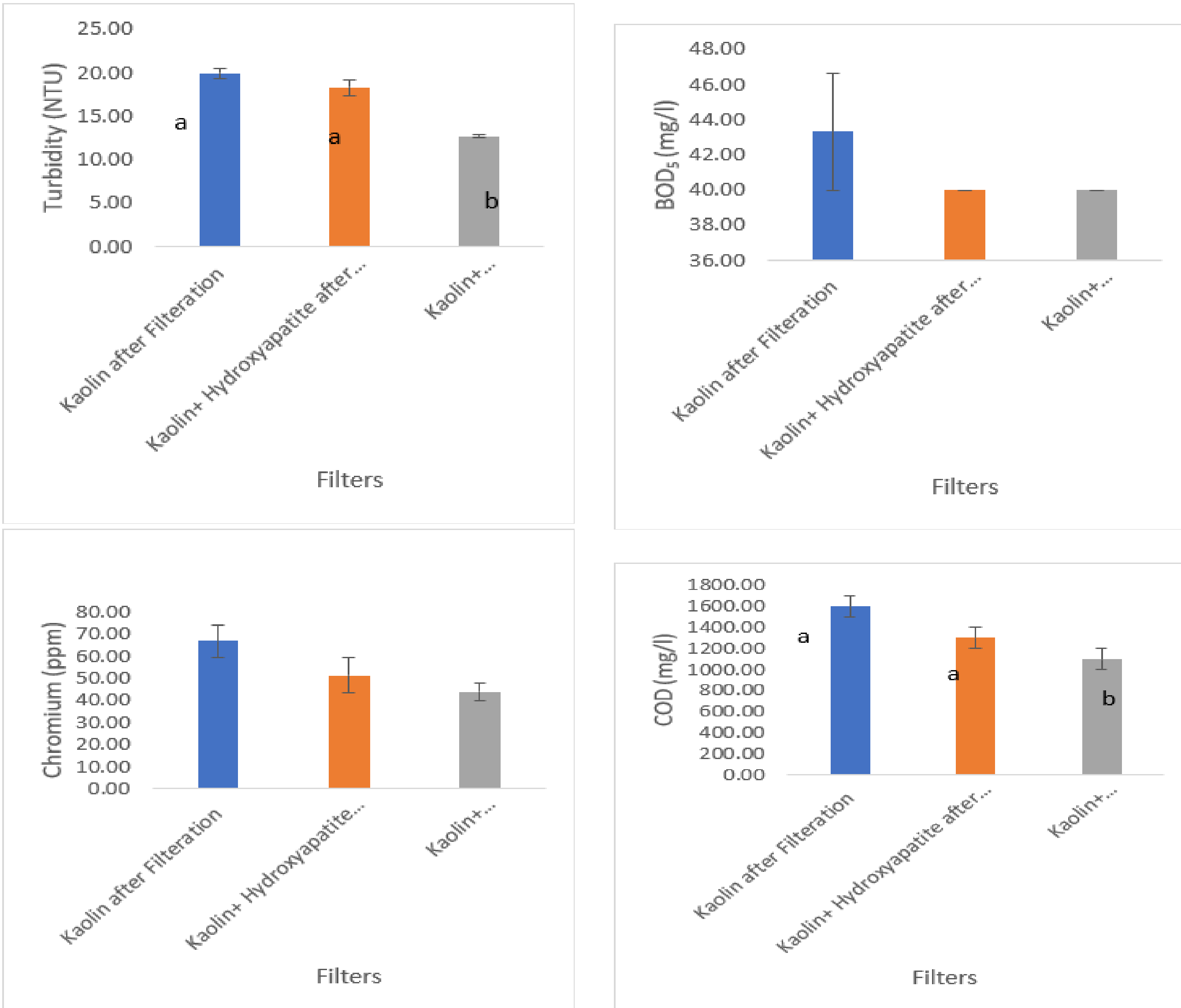


Figure 7: Comparison of ceramic filters' effect on (a) Turbidity (b) Chromium (c) BOD (d) COD

4.0 Conclusion

In this research study, a porous hydroxyapatite/kaolin-based ceramic filter was fabricated using beneficiated kaolin, starch as pore former and hydroxyapatite (extracted from cow bone). This study contributes to the development of environmentally sustainable technologies for industrial wastewater treatment, with particular emphasis on the tannery sector. The findings have potential implications for the broader application of natural-material-based membrane technologies in the management of complex industrial effluents. The pH of the tannery effluent was almost the same before and after treatment because it remained acidic before and after treatment with coagulant and was still not within the acceptable range of 6-9 according to FEPA and EPA. Therefore, treatment with alum did not have a significant effect on the pH value of the tannery effluent. The optimum electrical conductivity for the raw tannery effluent increased after treatment with alum. Hence, the addition of alum increased the electrical conductivity of the tannery effluent and was still within acceptable limits for wastewater discharge according to FEPA and EPA standards. The TDS concentration in tannery effluent after treatment with alum decreased significantly for all the dosages used. The maximum TDS measured was 13820.00±11.547 (5.04% removal) at 450 mg/L concentration of alum dosage but still exceeded the TDS maximum concentration level of 2000 mg/L and 1000 mg/L set by FEPA and EPA respectively. The turbidity was removed up to 92.60% after treatment with alum optimum alum dose of 450 mg/L. Therefore, an alum dosage of 450 mg/L was selected for the adsorption experiment. After treatment with alum, BOD and COD increased for some dosages while it reduced in others. Optimum BOD and COD percentage removal obtained at the optimum alum dosage of 450 mg/L was 50.00% and 36.21% respectively. The BOD and COD values obtained after treatment did not meet the wastewater discharge requirement set by FEPA and EPA. A hybrid system containing Kaolin/HAp filtration with biological treatment/ ion exchange could help bridge the gap in chromium and COD removal.

Treatment with alum achieved optimum chromium removal of 50.92% at 450 mg/L alum dosage. Percentage Chromium removal of 92.60% (275.87±11.099 mg/L) was achieved at the optimum alum dosage of 450 mg/L. However, the chromium concentration level obtained did not meet the wastewater discharge requirement of 1 mg/L set by FEPA. Heavy metal removal efficiency of the fabricated filters in tannery wastewater filtration was studied through adsorption using an optimum alum dose of 450 mg/L. The result showed kaolin, kaolin + HAp and kaolin + HAp + starch filter removal of chromium by 75.75 %, 81.36%, and 84.03% respectively. The maximum adsorption capacity of chromium was recorded as 84.03% (44.05 mg/L) at pH 6.93, a temperature of 24.90 ^{o}C while the turbidity removal was 45.44%. However, the chromium concentration level obtained after filtration did not meet the wastewater discharge requirement of 1 mg/L and 0.02mg/L set by FEPA and EPA respectively. This optimum chromium removal was achieved by the Kaolin + Hydroxyapatite + Starch filter (made from a combination of 80:10:10) with an optimum flow rate of 29.17 mL/h. Hydroxyapatite/kaolin-based filtration experiments revealed that chromium removal capabilities depended on the composition of the individual filters. The addition of pore former assists the fabrication of high-porosity ceramics, thereby enhancing the filtration process. By the use of HAp, a fair removal of chromium was achieved. The lack of HAp could be the reason for low filtration performance in the kaolin filter since HAp is known for its ion exchange capacity. In this research, it was observed from the filter experiments that in all three filter systems, the filtration process alone did not treat water to an acceptable level of wastewater discharge standard set by FEPA and EPA guidelines in terms of TDS, COD and Chromium. However, only the pH, EC, Temperature and BOD met the wastewater discharge standard set by FEPA and EPA.

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