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Application of synthesized Fish Scale Chito-Protein (FSC) for the treatment of abattoir wastewater: Coagulation-flocculation kinetics and equilibrium modeling

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ABSTRACT

This work explores the use of chito-protein synthesized from fish scale as a bio-coagulant in Abattoir wastewater (AW) treatment. The effect of settling time, pH, adsorbent dosage, and temperature of coagulation on Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), turbidity, and Color from the AW sample were studied. The kinetic study was carried out using four process equilibrium models which are Langmuir, Freundlich, Frumkin, and Tempkin to investigate the mechanism of the reaction. SEM and FTIR spectral analyses were used to evaluate the surface morphology and chemical composition of the bio-coagulant. A low pH, 3 g of dosage in 250 mL vessel, settling period of 30 to 35 min, and temperatures of 323 K for all parameters resulted in the most efficient pollutant elimination. Turbidity, however, had an optimal temperature of 313 K. The result of the study shows that Langmuir model provided the best fit from the equilibrium models compared to Freundlich, Frumkin, and Temkin's models. The experimental data suited the Elovich, Pseudo-first, and Second order kinetic models' analysis and the high values of the regression coefficient of 0.90 supported the idea of perikinetic as the governing mechanism of coag-flocculation in the study. It can be inferred from this study that fish scale as a bio-coagulant provides a significant resource for abattoir wastewater treatment.

Introduction

Wastewater from food processing companies has caused a serious environmental threat in Nigeria, as it has in most developing countries of the world [1]. The environmental impact of abattoir wastewater (AW) and operations has become a major concern, and research to solve this critical issue is both current and urgent for most developing countries [2].

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Wastewater treatment technology is still in its infancy in most developing countries; as a result, it is regarded as a critical area of research for the region's environmental sustainability [3]. Wastewater contains a variety of pollutants that, if allowed to build up in bodies of water and agricultural land, will have serious negative consequences for the environment, human health, and aquatic life. According to studies, massive amounts of AW are produced daily in Nigeria's municipal abattoirs, and several researchers believe that unregulated AW discharge into streams and waterbodies will pose a major environmental threat sooner rather than later [4–6].

Many conventional and non-conventional methods have been developed in wastewater treatment; which includes ion exchange, solvent extraction, reverse osmosis, evaporation, and nano-ultra filtration [7]. These techniques require complex equipment, and highly skilled personnel for maintenance, and in addition are not affordable for most developing countries [8]. A simple, affordable, and adaptable technology that will ensure adequate treatment of AW is critical to the environmental sustainability of developing countries. Coagulation and flocculation technique has received wide investigation among researchers and is asserted to be cost-effective, less complex, and environmentally friendly. A study by Oke [9] on the technical feasibility of coagulation in comparison to the conventional techniques reported that the operational costs of wastewater treatment depend on the characteristics of the initial wastewater, and the concentration of coagulant used for treatment. It is therefore essential to adapt the regional peculiarities of wastewater characteristics and the nature of available raw material in the treatment process. The feasibility of wastewater treatment technology is largely dependent on the availability of raw materials. The availability of fish scale as a resource material (though discarded and regarded as waste) in the region is critical in achieving a circular economy. The chitin obtained from the scales of fish could be used in a variety of applications especially when transformed into the more useful compound chitosan.

Coagulation is a crucial step in the treatment of both domestic and industrial wastewater. It's also one of the most important physicochemical processes in water and wastewater treatment, and it can be done chemically or electrically [10]. Identification of the mechanism involved in the process is critical; therefore, a thorough study of equilibrium kinetics is required to determine the controlling mechanism of coag-flocculation for optimal bio-coagulant utilization. Although several studies have investigated the use of fish scale for wastewater treatment [11,12], no study to the best of the authors' knowledge has applied fish scale nano-material to abattoir wastewater predominant in the study area. The kinetics and equilibrium modeling of the coagulation mechanism is also entirely new for the study area, despite being critical for environmental control of the enormous wastewater produced from various municipal abattoirs daily. Credible information on the reaction mechanism of the pollutant with the bio-coagulant is therefore essential in the optimum utilization of the coagulant forming the basis for this study.

Previous researchers [13] studied the kinetics and mathematical modeling for the removal of color from aqueous solution using *Moringa oleifera.* natural coagulant from dye, while another author [14] used *Sesamum indicum* seeds extract. Both studies, however, used an extract from edible biomass. Although there are many works in literature and significant contributions on the coagulation mechanism using *Moringa olerifera* as bio-coagulant by several researchers [13,15,16]. There are scarce studies on the mechanism of pollutant removal using fish scale bio-coagulant extract, insufficient details in this area make this study an important knowledge gap that needs to be filled. This research aims to use waste as a resource, resulting in less waste in the environment and less competition for the use of food in waste management processes, which is an important step toward achieving a circular economy. Water security is one of the priority areas of the first ten years of Africa's agenda 2063 with the aspiration based on inclusive growth and sustainable development [17]. The current study contributes to the use of affordable and adaptable technology that will ensure proper and adequate treatment of major wastewater (abattoir) usually obtained from meat processing in Africa.

The novelty of this research is a low-cost technology for abattoir wastewater treatment that is critical towards the development of wastewater management for the study area and most developing countries, using a local substrate (fish scale) that is considered waste by many people in the local community. This study used waste material as a resource, resulting in waste reduction in the environment and less competition in the use of food for waste management processes; this is an important step toward achieving a circular economy.

Materials and methods

Material source and extraction

The Abattoir wastewater used for this study was collected from Amansea municipal slaughterhouse in the Anambra state of Nigeria, while the fish scale was collected from Otuocha market in Anambra East, Anambra State of Nigeria. For the extraction of the bio-coagulant, about 1000 g raw samples of the fish scale were washed and thereafter sundried. An industrial grinding machine was used to ground the sample and sieved using a mesh size of 0.6 mm to maintain a constant surface area of 3.5% (w/v), we have described the extraction and preparation of bio-coagulants in detail in previous research [1].

Material characterization studies

To evaluate the surface morphological make-up of the polymeric coagulants, the Scanning Electron Microscopy (SEM) technique, was employed, this is a powerful tool for analyzing the. morphological features of a material. The SEM image was applied to reveal the surface texture and morphology of the bio-coagulant precursors and the synthesized coagulants, the SEM (Phenom Prox. model) was used for the study. The chemical composition of extracted polymers was also determined using X-ray fluorescence (XRF) analysis**.**

Bio-Coagulation experimental variables and procedure

Coagulation experiments were carried out using a jar-test procedure to investigate the effect of settling time, pH, adsorbent dosage, and temperature of coagulation on Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), turbidity, andcolor from the abattoir water sample. The pH of the solution is an important operating factor influencing performance in most wastewater treatment processes, especially in the coagulation process. It affects the surface charge of the coagulant and also affects the stabilization of the suspension. Based on this, the study of the effect of pH was done to determine the optimum pH level in the AW treatment process. The pH was varied from 2 to 10, while the temperature was varied at 303 K, 313 K, and 323 K. The dosage similarly varied from 1 g to 5 g, the variation is similar to previous studies on bio-coagulant [14,16,18].

Application of equilibrium models

The study used four equilibrium models: Langmuir, Freundlich, Frumkin, and Tempkin. According to Pannier, Soltmann [19], the Langmuir equilibrium model is based on the assumption that there is monolayer adsorption, without the interaction effect between the adsorbed molecules.

$$\text{Langmuir : Non}-\text{linear} : q_e = \frac{q_o b c_e}{1 + b c_e};\ \text{Linear;}\ \frac{C_e}{q_e} = \frac{1}{q_o} c_e + \frac{1}{b q_o} \tag{1}$$

$$\text{Freundlich : Non}-\text{linear;}\ q_e = K_f C_e^{1/n};\ \text{Linear;}\ \log\ k_f + \frac{1}{n}\log C_e \tag{2}$$

$$\text{Frumkin : Non}-\text{linear;}\ q_e = A + B\ \ln\frac{C_e}{q_e}\ \text{Linear;}\ q_e vs \ln\frac{C_e}{q_e} \tag{3}$$

$$\text{Tempkin : Non}-\text{linear}\ q_e = \frac{RT}{\beta_t}\ln k_p C_e\ \text{Linear;}\ q_e = \frac{RT}{\beta_t}\ln k_p + \frac{RT}{\beta_t}\ln C \tag{4}$$

Where: q_e = the equilibrium adsorption capacity (mg/g).
Q_0 = the maximum monolayer coverage capacity (mg/g) and
K_L = Langmuir isotherm constant (L/mg)
b = Langmuir isotherm constant
C_e = Equilibrium contaminant concentration (mg/L)
K_f = Freundlich isotherm constant (mg/g)
A and B = Frumkin isotherm constant
n = The number of observations in the experimental study
R = Universal gas constant (8.314 J/mol/K)
T = Temperature at 298 K b_T = Temkin isotherm constant

In Eq. (1-4), q_e is the biosorption capacity at equilibrium (mg/g), q_m is the maximum theoretical biosorption capacity (mg/g), b is the equilibrium biosorption constant correlated to the affinity between sorbent and sorbate (l/mg) and C_e is the equilibrium concentration of metal ion (mg/l).

Kinetic models/mechanism of pollutant removal

The adsorption kinetic reveals the solute uptake rate of the reaction. It is one of the important characteristics in defining the efficiency of adsorption [20]. The kinetic models are also used to investigate the mechanism of adsorption and the potential rate-controlling steps such as mass transport and chemical reaction processes [21].

Adsorption kinetic models were applied to test the experimental data and to investigate the adsorption kinetics of the adsorbate in the coag-adsorption process. The linear and non-linear forms of the Pseudo first order, Pseudo second order, and Elovich model were used to study the kinetics of pollutant removal from the AW. Eq. (5)-10 shows the model equations

$$\text{Pseudo}-\text{first}-\text{order} = q_t = q_e[1 - \exp(-k_1 t)] \tag{5}$$

Eq. (5) is linearized to obtain Eq. (6) below:

$$\text{Pseudo}-\text{first}-\text{order} =\ \log(q_e - q_t) = \log q_e - \left(\frac{K_s t}{2.303}\right) \tag{6}$$

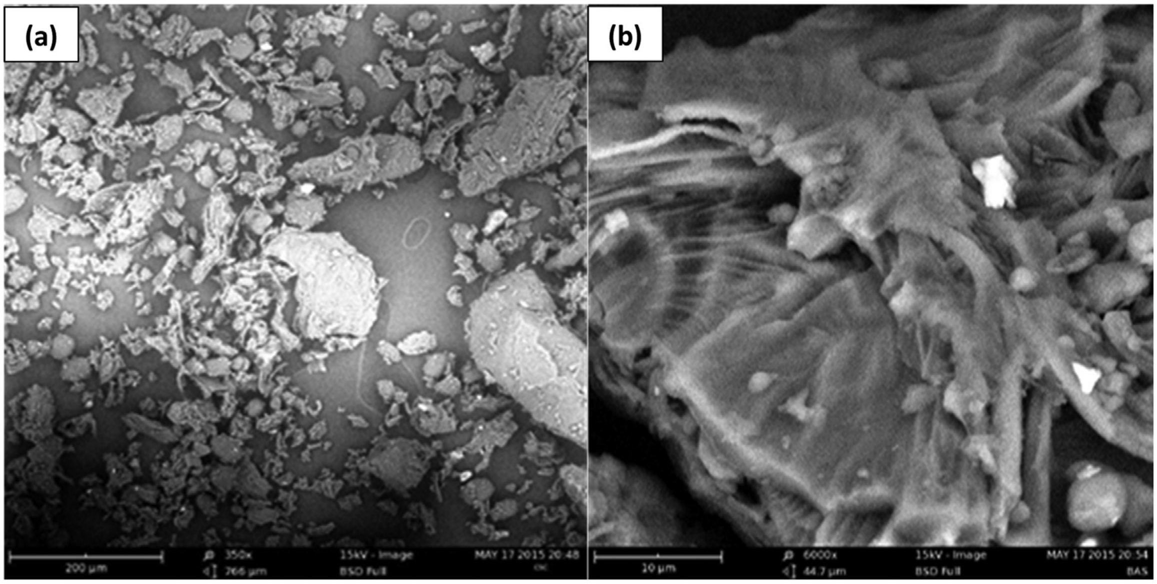

Fig. 1. SEM image of the bio-coagulant before (a) and after (b) the experiment.

For the Pseudo-second-order, the equation is given by:

$$\text{Pseudo} - \text{second} - \text{order} \quad = \frac{k_{2q_e^{2t}}}{1+\ k_2 q_e t} \tag{7}$$

The linearized equation of (7) is given by:

$$\text{Pseudo} - \text{second} - \text{order} = {}^{t}/_{q_t} = \frac{1}{K^2 q_e^2} + \frac{t}{q_e} q_t \tag{8}$$

Elovich equation is stated below:

$$qt = \left(\frac{1}{\beta}\right)\ln(1+\alpha_1\ \beta t) \tag{9}$$

While the linearized form of Eq. (9) is given as

$$qt = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right) lnt\ q_t \tag{10}$$

The removal efficiency was determined using the equation below:

$$\text{Pollutant Removal } (\%) = \frac{P_p - P_a}{P_p} \tag{11}$$

Where P_p is the value of the pollutant before treatment, and P_a is the value of the pollutant after treatment.

Results

Characterization of the bio-coagulant

The results of the SEM studies for the morphology of the bio-coagulant precursors before and after the experiment is presented in Fig. 1 (a-b). SEM image indicates that the morphology of the bio-coagulant precursors is mainly characterized by smooth surfaces with seemingly compact structures and the appearance of tiny homogenous pores. However, following the processing of these precursor materials into coagulants, modifications in surface morphologies from being smooth to rough with irregular ridges were observed. Similarly, heterogeneous and prominent interstitial cavities could be observed within their matrices. These pores which are numerically larger than those previously existent on the different precursor materials could have existed as a result of the extraction step and subsequent concentration of the crude coagulant. According to a study by Sun, Zhou [22], irregular granule structures are desirable characteristics of any coagulant with regards to adsorbing and connecting colloidal particles which further enhances the sedimentation of flocs. Table 1 shows the predominant functional groups and elemental composition of the bio-coagulant. X-ray Fluorescence microscopy (XRF) analysis of the fish scale was conducted to identify the material's changes in the surface functional group.

Table 1
Predominant functional groups and XRF result.

S/N	Peak (cm^{-1})		Differences	Assignment	XRF	Compounds
	FSF	FSC				
1	793.9931	773.6992	20.29	Out–of–plane C – H bending	Al_2O_3	20.135
2	1372.581	1348.451	24.13	SO_2 asymmetric band	CaO	11.192
3	–	1657.751	–	NO_2 asymmetric stretching	SiO_2	12.018
4	1862.719	–		C = O stretching	Fe_2O_3	6.529
5	2017.211	2013.944	3.28	Metal carbonyl C = O	P_2O_5	2.471
6	–	2207.94	–		Na_2O	2.905
7	2501.807	2648.799	146.99	Phosphoric acid and Ester O – H	K_2O	7.734
7	2833.771	2840.921	7.15	C – H stretching of aldehyde	MgO	2.796
8	3176.483	–	–	O – H stretching of carboxylic acid	TiO_2	0.617
9	3453.237	–	–	N – H stretching	Al_2O_3/CaO	1.799
10	–	3551.365	–	Si-OH stretching	CaO/SiO_2	0.931
11	–	3777.665	–			

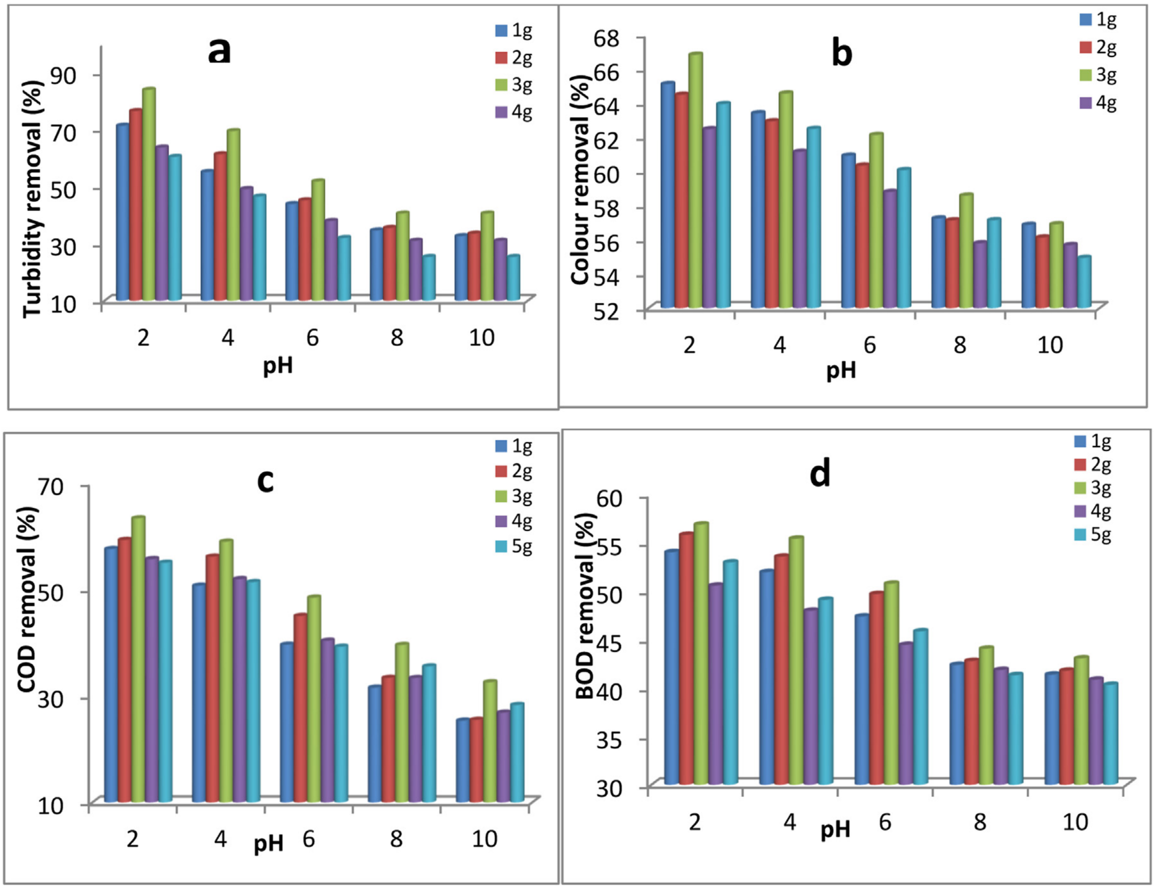

Fig. 2. The effect of pH on removal efficiency of wastewater.

The sample was prepared in powder form and carried out as described by Khursheed, Singh [23]. The functional groups on the surface of the fish scale coagulant were determined at the spectral range of 600 to 4000 cm^{-1} at a resolution of 4 cm^{-1}, scan number 32, and a scan speed of 30 s. The presence of peaks at 3176, 3551, and 3777 cm^{-1} are attached to bond O–H stretch in phenol and alcohols. The peaks at 2501 and 2648 cm^{-1} corresponded to the bonded –OH groups.

Results of the elemental composition of the bio-coagulant indicate its predominantly composed of Al_2O_3, CaO, and SiO_2. The high content of alumina and silica in the bio-coagulant is attributed to the natural composition of fish scales. Studies have reported that high alumina content is an important chemical property of materials that sustain surface matrices [1,24]. High silica and calcium oxide content helped to improve the weight of the bio-coagulant, which enhanced floc formation and particle sedimentation during the coagulation process. The results obtained here indicate the potential of the bio-coagulant in particle removal processes.

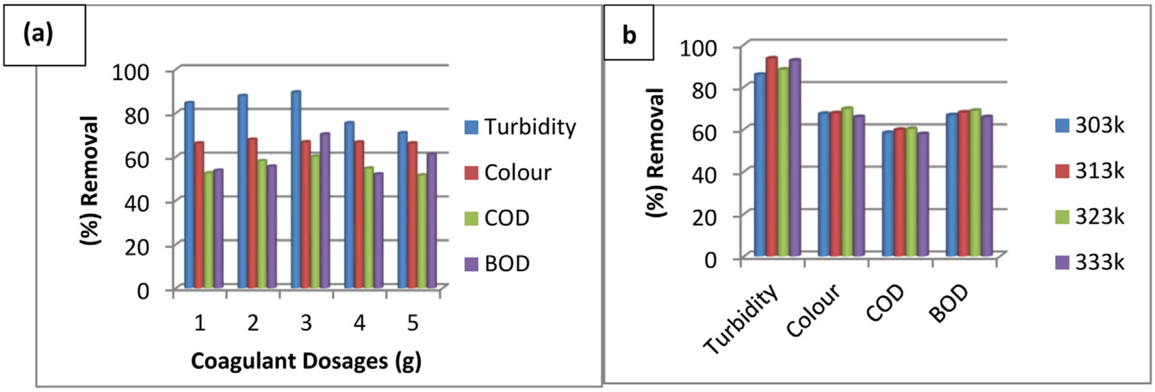

Fig. 3. Influence of (a) coagulant dosages and (b) temperature on variable removal.

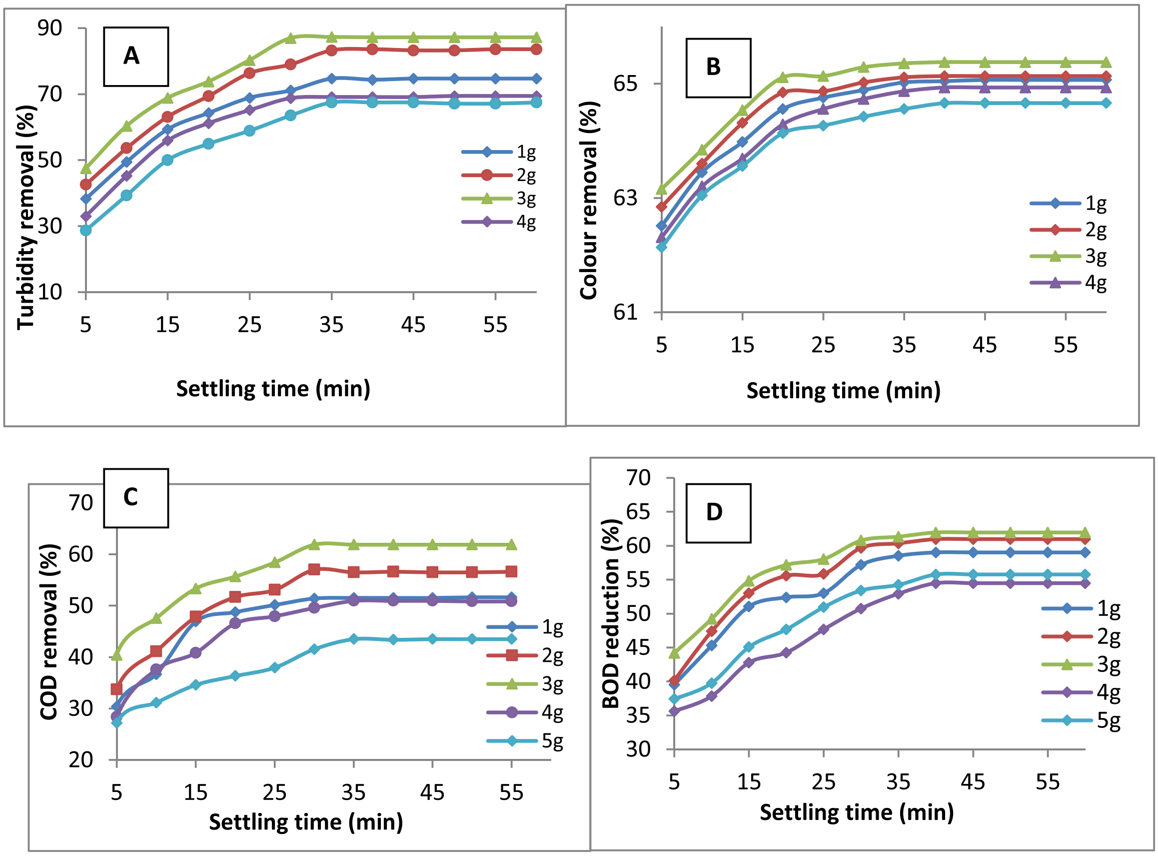

Fig. 4. Effect of settling time on the (a) Turbidity (b) Colour (c) COD (d) BOD.

Effect of the variables on the removal efficiency

The effect of the various parameters on the wastewater contaminant removal efficiency was assessed and the result is outlined below:

Effect of pH on wastewater contaminant removal efficiency

Graphs showing the effects of pH on the various wastewater parameter removal are shown in Fig. 2. In the treatment of abattoir wastewater in Fig. 2a, an optimum turbidity removal efficiency of 83.85% was obtained at a pH of 2 using a coagulant dosage of 3 g; while, in the treatments with pH of 4, 6, 8, and 10 as represented in the Fig. 2a, there was a

Table 2
Estimated Isotherm models parameters and constants at different temperature.

Parameters	Langmuir Model				Freundlich Model		
Linear	303 K	313 K	323 K	Linear	303 K	313 K	323 K
K_L (l/g)	0.026	0.032	0.054	K_F (mg/g)	9.71	3.81	1.14
Q_m (mg/g)	34.72	34.25	44.25	N	1.88	0.76	1.06
R^2	0.96	0.93	0.95	R^2	0.88	0.87	0.89
R_L	0.056	0.071	0.053				
Non-linear				Non- linear			
K_L (l/g)	0.028	0.12	0.043	K_F (mg/g)	11.94	4.75	8.23
Q_m (mg/g)	41.00	39.95	59.45	N	3.92	2.65	1.88
R^2	0.94	0.96	0.98	R^2	0.88	0.83	0.76
χ^2	0.099	0.022	0.86	χ^2	1.78	0.18	0.76
SSE	3.084	0.38	1.13	SSE	1.99	2.61	1.19
R_L	0.083	0.034	0.12				
	Frumkin Model				Tempkin Model		
Linear	303 K	313 K	323 K	Linear	303 K	313 K	323 K
A	72.11	53.68	45.20	K_T (l/g)	1.32	1.32	1.34
B	83.15	106.46	94.91	b (KJ/mol)	7.359	6.05	9.93
R^2	0.90	0.81	0.82	R^2	0.89	0.92	0.85
Non-linear				Non-linear			
A	132.71	58.80	52.04	K_T (l/g)	0.05	1.81	1.59
B	109.05	73.60	101.81	b (KJ/mol)	45.34	61.60	10.90
R^2	0.93	0.75	0.77	R^2	0.73	0.81	0.78
χ^2	3.94	7.40	5.40	χ^2	6.04	21.14	1.75
SSE	4.47	3.08	8.96	SSE	5.59	13.03	9.88

Q_m—Langmuir constant related to monolayer coagulation capacity (mg/g); K_L, K_F, K_T—isotherm constants for Langmuir, Freundlich, and Temkin (l/g; mg/g, l/g); n—Freundlich constant (dimension less); SSE-Sum of square error, R-coefficient of determination, χ^2-chi-square, the Temkin constant (b) is related to the sorption heat (KJ/mol).

decrease in turbidity removal when the pH increases. There was a general decrease in removal efficiency of turbidity for all the dosages with an increment in pH, after the highest efficient removal of 3 g, 2 g dosage for all the pH variation represented the second highest turbidity removal efficiency. These show that turbidity removal increased with a decrease in the initial solution pH value [13].

It can be seen in Fig. 2b that color removal efficiency increases with a decrease in pH for all the dosages, an optimum pH value of 2 was observed with the highest color removal efficiencies of 66.89%, this is followed by 65.43% removal efficiency for the pH of 4. The optimal value recorded for chemical oxygen demand (COD) removal is 63.3% as shown in Fig. 2c. Summarily, the findings of this study imply that COD removal is more effective when the solution is in an acidic medium. The effect of pH on biochemical oxygen demand (BOD) reduction is presented in Fig. 2d. An optimum pH value of 2 is seen as the highest BOD reduction efficiency at 56.89%.

Effect of dosage and temperature on wastewater contaminant removal efficiency

The impact of coagulant dosage on the contaminant removal is presented in Fig. 3a, it could be seen that a higher coagulant dose does not favor the removal of suspended particles from the abattoir wastewater. The minimum effect on the particle removal process was observed at the coagulant dosage of 5 g, while the highest effect on the system was observed at the 3 g dosage. The result presented in Fig. 3a depicts that there is no major difference in coagulant dosages on the color removal efficiency, it reveals that the removal efficiency ranged between 66 and 67%. The effects of coagulant dosages on COD removal efficiency indicate that with the decrease of coagulant dosage below the optimum value of 3 g, the removal efficiencies decreased, and similarly with an increase in the dosage value, there was a decrease in removal efficiency, the BOD has a similar trend with the COD.

Fig. 3b presents the effect of temperature on the coagulation of turbidity, color, COD, and BOD. The effect of temperature was investigated in the range of 303 K, 313 K, 323 K, and 333 K. The result revealed that an increase in temperature to the optimum value resulted in higher removal efficiency, the temperature affects the solubility of biological coagulants and the rate of formation of products. Fig, 2b trend also reveals that there is no significant difference between the temperature of 313 K and 323 K generally, however, a slight decline in removal efficiency is observed from 323 K to 333 K for color, COD, and BOD, while an optimum temperature of 323 K was observed for them. Turbidity however had an optimum temperature of 313 K.

Effect of settling time on contaminant removal efficiency

Fig. 4 explains at a glance the influence of settling time on turbidity removal efficiency (%). It can be seen that a coagulant dosage of 3 g gave the best turbidity removal efficiency. However, beyond 30 min, no significant change in the contaminant

Table 3
Coagulation of kinetic parameters for Turbidity, BOD, COD and Colour removal.

Turbidity removal Parameters	1 g	2 g	3 g	4 g	5 g
K_m(g.min)	0.0001	0.0002	0.0002	7.00E-05	6.00E-05
R^2	0.92	0.91	0.92	0.94	0.94
ßBr(g.min)	0.0002	0.0004	0.0004	0.00014	0.00012
$\tau_{1/2}$(min)	54	27	32	54	60
r	5.54E-05	0.000110829	0.000110829	3.88E-05	3.32E-05
(-r)	1.00E-04N_t^2	2.00E-04N_t^2	2.00E-04N_t^2	7.00E-04N_t^2	6.00E-04N_t^2
ε_p	2.00E+16	4.00E+16	4.00E+16	1.40E+16	1.20E+16
K_R	5.00E-21	5.00E-21	5.00E-21	5.00E-21	5.00E-21
D'	3.59E-18	1.79E-18	1.79E-18	5.12E-18	5.98E-18
B	0.0012	0.00233	0.00233	0.000816	0.000699
α	2	2	2	2	2
BOD removal					
K_m(g.min)	3.00E-05	3.00E-05	3.00E-05	6.00E-05	6.00E-05
R^2	0.83	0.81	0.83	0.95	0.95
ßBr(g.min)	0.00006	0.00006	0.00006	0.00006	0.00006
$\tau_{1/2}$(min)	253	260	273	220	213.33
r	1.66E-05	1.66E-05	1.66E-05	1.66E-05	1.66E-05
(-r)	3.00E-05N_t^2	3.00E-05N_t^2	3.00E-05N_t^2	3.00E-05N_t^2	3.00E-05N_t^2
ε_p	6.00E+15	6.00E+15	6.00E+15	6.00E+15	6.00E+15
K_R	5.00E-21	5.00E-21	5.00E-21	5.00E-21	5.00E-21
D'	1.20E-17	1.20E-17	1.20E-17	1.20E-17	1.20E-17
B	0.00035	0.00035	0.00035	0.00035	0.00035
α	2	2	2	2	2
COD removal					
K_m(g.min)	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
R^2	0.83	0.81	0.83	0.95	0.95
ßBr(g.min)	0.00004	0.00004	0.00004	0.00004	0.00004
$\tau_{1/2}$(min)	270	280	300	240	230
r	1.11E-05	1.11E-05	1.11E-05	1.11E-05	1.11E-05
(-r)	2.00E-05N_t^2	2.00E-05N_t^2	2.00E-05N_t^2	2.00E-05N_t^2	2.00E-05N_t^2
ε_p	4.00E+15	4.00E+15	4.00E+15	4.00E+15	4.00E+15
K_R	5.00E-21	5.00E-21	5.00E-21	5.00E-21	5.00E-21
D'	1.79E-17	1.79E-17	1.79E-17	1.79E-17	1.79E-17
B	0.00023	0.00023	0.00023	0.00023	0.00023
α	2	2	2	2	2
Color removal					
K_m(g.min)	2.00E-05	3.00E-05	2.00E-05	3.00E-05	3.00E-05
R^2	0.78	0.75	0.77	0.94	0.94
ßBr(g.min)	0.00004	0.00006	0.00004	0.00006	0.00006
$\tau_{1/2}$(min)	133	90	132	84.6	84
r	1.11E-05	1.66E-05	1.11E-05	1.66E-05	1.66E-05
(-r)	2.00E-05N_t^2	3.00E-05N_t^2	2.00E-05N_t^2	3.00E-05N_t^2	3.00E-05N_t^2
ε_p	4.00E+15	6.00E+15	4.00E+15	6.00E+15	6.00E+15
K_R	5.00E-21	5.00E-21	5.00E-21	5.00E-21	5.00E-21
D'	1.79E-17	1.20E-17	1.79E-17	1.20E-17	1.20E-17
B	2.33E-05	3.50E-05	2.33E-05	3.50E-05	3.50E-05
α	2	2	2	2	2

removal was observed for all the pollutants, therefore, the optimum settling time for the study was set at 30 min. The highest degree of coagulation was witnessed within the first 35 min. Then, between settling time of 5 – 30 min, a rapid percentage removal of contaminant was observed after which the removal efficiency reduced gradually until it attained equilibrium. Hence, an equilibrium time of ≥ 35 min was observed for the AW as depicted in (Fig. 4a-d) for a total settling time of 60 min, the result of this study is comparable with other studies [25]**.** In considering the impact effect of settling time, floc formation involves both interactions of coagulant hydroxide precipitate following hydrolyze reaction and contact with particles. This leads to a decrease in the concentration of particles that coincides with the growth of aggregates.

Equilibrium models

The equilibrium study was analyzed using four isotherms' models (Langmuir, Freundlich, Frumkin, and Temkin model). Figure SM1, SM2, SM3, and SM4 shows the isotherm representation of Langmuir, Freundlich, Frumkin, and Temkin models at temperature ranges of 303 K, 313 K and 323 K. For the studied temperatures of 303 K, 313 K, and 323 K, the linear and nonlinear model parameters were estimated from slopes and intercepts of respective plots. The models along with regression statistical analyses (coefficient of determination, R^2, Chi-square, $\chi^{2,}$ and sum of square error, SSE) have been shown in Table 2 below.

Table 4
Characterization results of the wastewater samples before and after coagulation.

S/N	Parameter	Unit	Before Coagulation	After Coagulation	WHO Standard
1.	BOD_5	mg/L	470	27	30
2.	COD	mg/L	692	23	NS
3.	TSS	mg/L	343.6	26	30.00
4.	Turbidity	NTU	310	23	
5.	pH	–	6.8	7.3	6.6–8.56
6.	color	mg/L	210.2	51.01	–
7.	Total hardness	mg/L	80	15	500.00
8	TDS	mg/L	215.7	41	50.00
9.	TS	mg/L	559.3	64	500
10.	sulfate	mg/L	12.63	1.42	–
11.	Lead	mg/L	0.5	0.00	0.1
12.	Iron	mg/L	4.790	0.07	0.3
13.	Magnesium	mg/L	58.64	1.02	75
14.	Potassium	mg/L	8.10	1.39	–

Note: NTU - nephelometric turbidity unit, TDS - total dissolved solids, TSS - total suspended solids, COD - chemical oxygen demand, BOD - biochemical oxygen demand and NS-not stated.

Table 5
Comparative analysis of this study with previous studies .

S/N	Coagulant	Wastewater	% Removal Turbidity	% Removal COD	% Removal BOD	% Removal Color	Reference
1.	FBC	Abattoir wastewater	92.58	96.68	94.26	75.73	This Study
2.	*Opuntia ficus-indica*	Dairy soiled water	99	84	–	–	[26]
3.	Alum	Tannery wastewater	99.7	53.3	–	–	[27]
4.	Snail shell biomass	Abattoir wastewater	93.33	92.0	93.70		[28]
5.	*Moringa oleifera*	Crystal Ponceau 6R dye	–	–	–	93.8	[13]
6.	*Maerua decumbent*	paint industry wastewater	99.2	78.6	–	–	[29]
7.	Orange peel	Dairy wastewater	96	–	–	–	[18]

Coagulation-Flocculation kinetic model

Three kinetic models were used to estimate the pollutant removal namely; Pseudo - first – order; Pseudo - Second – order and Elovich model have been shown in Figure SM5 and the kinetic model parameters are tabulated in Table 3. The kinetic study determines the extent of utilization of the adsorption capacity of the coagulant sample to time. The linear equation, the R^2, K_m, and collision efficiency parameters are reported in Table 3. The collision efficiency relates to the kinetic energy requirement which is needed to overcome the electrostatic energy barrier. Thus, high ε_p implies a high kinetic energy requirement for overcoming the electrostatic energy barrier. Also, the rate equation (-r) which accounts for the rate of depletion of particle concentration was evaluated in terms of K values and reaction order obtained were also presented in Table 3 for the wastewater and coagulant study.

Comparing the abattoir wastewater before and after coagulation with the standard regulations

The characteristics of the abattoir wastewater before and after treatment with the coagulant is compared with World Health Organization (WHO) regulatory standard (Table 4), this was done to put removals efficiency achieved in the context of expected water quality. Before treatment, the abattoir wastewater contains high levels of heavy metals and BOD, COD, and TSS and is above the threshold limit. In addition, a significant decrease in turbidity value after the treatment of wastewater samples indicates the presence of an efficient coagulation process [1].

Comparison with previous studies

To assess the removal efficiency of the pollutant, Eq. (11) was used to calculate the removal efficiency. Table 5 shows the removal efficiency recorded in this study in comparison with previous research work. The Turbidity was 310 NTU before treatment and 23 after treatment, accordingly, 692 mg/L, 470 mg/L, and 210.2 of COD, BOD, and color were recorded before treatment, and 23 mg/L, 27 mg/L, and 51.01 mg/L after treatment respectively. According to Table 5, this study compares favorably to previous studies on percentage turbidity removal because the efficiency is greater than 90%. Chemical oxygen demand (COD) removal appears to perform better in this study than in previous studies; however, BOD and color removal efficiency appear to perform less well in this study than in previous studies. The variation in percentage efficiency could be justified based on the wastewater characteristics and the type of coagulant used for the study.

Conclusion

The effectiveness of chito-protein synthesized from fish scale as a bio-coagulant in abattoir wastewater (AW) treatment was investigated in this study. Coagulation experiments were conducted using a jar-test procedure to investigate the effect of settling time, pH, adsorbent dosage, and coagulation temperature on BOD, COD, turbidity, and color in the AW sample. The pH was adjusted from 2 to 10, the dosage w from 1 g to 5 g, and the settling time was set to 60 min. The effect of temperature was investigated in the range of 303 K, 313 K, 323 K, and 333 K. The study applied several equilibrium models such as Langmuir, Freundlich, Frumkin, and Tempkin, and kinetic models of Pseudo first order, Pseudo second order, and Elovich model. The result of the study shows that optimum pollutant removal efficiency was achieved at low or acidic pH, while 3 g dosage value resulted in optimum removal. For the settling time, 30 to 35 min was observed, while a temperature of 323k was effective for all the parameters, except turbidity which had an optimum temperature of 313 K. For the material characterization study, the results of the SEM studies for the morphology of the bio-coagulant precursors indicate that it is mainly characterized by smooth surfaces with seemingly compact structures and the appearance of tiny homogenous pores. From the XRF analysis, the elemental composition of the bio-coagulant indicates that it is predominantly composed of Al_2O_3, CaO, and SiO_2. This study demonstrates that fish scale, which was previously considered waste by many members of the local community, can now be used as a coagulant. The broader research community can develop a low-cost abattoir wastewater treatment technology, which is critical for the development of wastewater management in Africa and other developing countries.

Author contributions

C.F.O (Researcher) and C.C.O (Researcher) conceived and designed the experiments; C.F.O performed the experiments; C.F.O, E.C.C, and A.E.T (Researchers) analyzed and interpreted the data; and wrote the manuscript. All authors read and approved the final manuscript.

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Declaration of competing interest

The authors declare no conflict of interest.

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Supplementary materials

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