Original Research Article

Deturbidization of vegetable oil refinery wastewater with extracted fish scale biomass via coagulation process; Non-linear kinetics studies

Abstract

Chito-protein was successfully synthesized from fish scale. The ability of a coagulant (chito-protein) prepared from fish scale (FSC) to carry out an effective removal of pollutants from food processing industry (vegetable oil industry wastewater, VOW) was evaluated at bench scale using a simulated jar test analysis. The coagulant was characterized via proximate analysis and instrumental analysis: Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The maximum kinetic parameters determined were recorded at K of $2x10^{-5}$L/mg.min, 1g, $t_{1/2}$= 50 min, R^2= 0.9245 and pH of 2.Regression coefficient analysis (R^2) was used to ascertain the accuracy of the fit to the postulated kinetic model. However, it was concluded that the second order kinetic model described the reaction most adequately. Removal efficiency of turbidity (87.21%) was obtained at optimum contact time of 30 min, pH 2, coagulant dosage of 1.5g and temperature of 323K. Kinetic study showed that Pseudo first order and pseudo second order models were the best two models in describing the coag-adsorptive kinetics of the coagulant. Similarly, the predicted kinetic data were adjured statistically significant using F- test and T-test.

Keywords: Wastewater, coagulation, fish scale, turbidity, kinetic model, non-linear

1.0 INTRODUCTION

Rapid industrialization has led to generation and unwholesome disposal of contaminated wastewater. Food processing (abattoir, vegetable oil etc.), paint, textile, pharmaceutical, cosmetics and plastic industries are among the industries that generates large volume of wastewater. Most of these wastewaters contain toxic substances (Okey-Onyesolu et al. (2016), high organic and inorganic dissolved solids, COD, BOD, and oil end which can be harmful if discharged untreated. The treatment of vegetable oil refinery wastewater (VOW) has been a major issue of environmental concern. Refining of crude vegetable oils generates large amounts of wastewater, which come from the degumming, de-acidification, deodorization and neutralization steps (Dkhissi et al., 2018). Its characteristics depend largely

on the type of oil processed, resulting in both high inorganic as well as organic pollutants Moka (2015). Many processing techniques have been employed in the fight against pollution in VOW, a wide variety of physicochemical processes has been proposed (coagulation/flocculation, adsorption, photocatalysis, electrocoagulation, membrane filtration) [Dkhissi et al., 2018]. Oil refinery wastewater treatment have gained increasing importance, it can be treated either separately or in conjunction by chemical or biological means. Biological treatment methods offer an easy and cost effective alternative to chemical methods. Coagulation and flocculation as a unit process, in water and wastewater treatment entails the use of metal salts (Al and Fe salts) (Xu et al, 2009). Also, the coagulation process is one of the most effective methods of reducing/removing pollutants from wastewater. But there are problems associated with chemical treatment which includes; the increased handling costs and the production of chemical sludge that is difficult to treat (Dkhissi et al., 2018).

However, studies have discovered a number of drawbacks concerning the use of these conventional coagulants. For example, Alzheimer's disease and other related problems are associated with residual alum in treated water (Divakaran et al, 2001). To solve this problem many types of natural reagents have been developed for removing pollutants from wastewater chitosan (Roussy et al, 2005), tannins (Ozacar et al, 2002), aqueous extract of the seed of moringa oleifera; extract of plantain peelings ash (Oladoja, 2008); and extracts of okra and nirmali seed (Ani et al, 2010), they have advantages of being biodegradable and without risk to public health, so a number of plant, animal or micro- organism sources are used in wastewater treatment.

The present paper aims to valorise the fish scale chito-protein as a techno – economically and eco-friendly coagulant for the treatment process of wastewater taken from vegetable oil refining industry located at the south-east of Nigeria. The effects of the main experimental conditions (initial solution pH, coagulant dosage, settling time and operating temperature) on the coagulation treatment performance were studied. The coagulation process performance in all cases was evaluated by means of the turbidity (TDSP).

2.0 MATERIALS AND METHODS

2.1 Effluent collection and analysis

A sample of vegetable oil refinery wastewater (VOW) was collected from an oil refinery industry located in Onitsha, Anambra State, Nigeria and stored at room temperature. The vegetable oil refinery effluent was preserved in dark plastic container to avoid photo-

reactions. The vegetable oil refinery wastewater sample was characterized before and after treatment using standard methods (APHA, 1998).

2.2 Processing of the coagulant from fish scale (FS)

The fish scale (FS) was obtained from Otuocha market in Anambra East, Anambra state of Nigeria. The FS (Fig. 1) was washed thoroughly with water to remove unwanted materials and sun dried for 14 days. It was crushed using a pestle and mortar to reduce the size. The crushed sample was further air dried for five days to remove possible remaining moisture. The FS sample was then transformed into powder using a grinding machine and sieved with a laboratory sieve of known mesh size.

The powdered FS (Figure 2) was then processed into a coagulant (FSC), by adopting modified Fernandez-Kim method described by (Ani et al., 2011). The product of deproteinization of fish scale flour (FSF) was utilized instead of chitosan. For the deprotenization, 1 L of 1M NaOH solution containing 100 g of FSF was stirred continuously at 70 °C for 2h. The mixture was allowed to settle and cool. The mixture was separated (using filter paper), the resulting solid sample has the potential of being processed further to obtain chitosan however the extract from deprotenization process contains some percentage of radical protein that will become a waste if not harnessed. The liquid extract was allowed to settle for 30mins. The concentrated slurry settled at the bottom of the beaker was collected (chito-protein), dried and stored for use.

Fig. 1 : Fish scale

Fig. 2: Fish scale flour

2.3 Coagulation-Flocculation Experiment (Jar Test)

The coagulation-flocculation experiments were performed using jar test apparatus. The operating variables investigated were; initial effluent pH, chito-protein dosage, settling time and operating temperature. The pH was controlled by adding either IM HCl (acid) or 1M

NaOH (base). The VOW sample was mixed homogeneously before being fractionated into beakers containing 250ml of suspension each. The desired amount of chito-protein was added to each beaker containing the wastewater. Thereafter, the beakers were agitated at 250 rpm (fast mixing) for 2 minutes and 30 rpm (slow mixing) for 20 minutes. The effect of pH was studied at pH range (2 - 10) at varying chito-protein dosages in the range (0.5g – 2.5g) at different settling time and constant temperature. Thereafter, the effect of settling time was studied in the range (5 - 60 minutes) at varying coagulant dosages, optimum pH and constant temperature. The effect of temperature was then studied in the range (30 – 60^{o}C) at varying settling time, optimum pH and coagulant dosage. The coagulation efficiency of the coagulants was investigated in terms of turbidity removal. Prior to the test, the sample was measured for turbidity, representing an initial turbidity. After settling at a specified time, samples were collected at 2 cm depth beneath the surface of the water for further turbidity measurement, representing the final turbidity. The residual turbidity (final turbidity) was converted to TDSP (mg/L), using a calibration curve at intervals of 5mins. The efficiency of turbidity removal was then evaluated using equation 1.

$$\%\text{Removal} = \frac{T_0 - T}{T_0} \times 100 \quad (1)$$

Where; T_o is the turbidity of raw effluent and T, the turbidity of effluent after treatment.

2.4 Coagulation kinetic model description and theoretical principles

The non-adsorptive kinetics of the process was modelled according to the description reported by (Menkiti et al., 2015; Ugonabo et al., 2012).

For a system operating at equilibrium phase with negligible impact of external Equations 2 and 3 hold (Ugonabo et al., 2012):

$$\mu_i = \overline{G_i} = \left[\frac{\partial G}{\partial n_i}\right]_{P,T,n} = \text{a constant} \quad (2)$$

$$D' = K_B \, T/B \quad (3)$$

Where: D' is diffusion coefficient; B is friction factor; K_B is Boltzmann's constant; T is temperature; G is the total Gibbs free energy; n_i is the number of moles of component i; μ_i is the chemical potential

for a case of mono dispersed, no break up and bi particle collision, floc formation depends on the rate of successful particles collision. For a particular floc size (Z) to be formed from particles of sizes i and j, this rate can be expressed as (Ani et al., 2011; Ugonabo et al., 2012):

$$\frac{dn_z}{dt} = \frac{1}{2}\sum_{i+j=z}\beta_{BR}(i,j)n_i n_j - \sum_{i=1}^{\infty}\beta_{BR}(i,k)n_i n_z \quad (4)$$

Where $\beta_{BR}(i,j)$ is Brownian collision factor for flocculation transport mechanism.

$n_i n_j$ is particle aggregation concentrations for particles of size i and j, respectively.

According to Ugonabo et al (2012):

$$\beta_{BR} = \frac{8}{3}\varepsilon_p \frac{K_B T}{\eta} \quad (5)$$

And $K_R = 8\pi a D'$ (6)

Where: K_R is the Von smoluchowski rate constant for fast coagulation; a is particle radius; ε_p is the collision efficiency; η is the viscosity of the fluid medium.

Simplifying equations (6):

$$K_R = \frac{4}{3}\frac{K_B T}{\eta} \quad (7)$$

Equations 4-5 could also be transformed to Eq. (7):

$$K_m = \frac{1}{2}\beta_{BR} \quad (8)$$

147 Where: K_m is defined as Menkonu coagulation-flocculation rate constant accounting for
148 Brownian coagulation-flocculation transport of destabilized particles at α^{th} order.

149 For Brownian coag-flocculation (Ugonabo et al, 2012):

150 $$-\frac{dN_t}{dt} = K_m N_t^{\alpha}$$

151 (9)

152 N_t is the concentration of TDSP at time, t

153 Practically, it has been observed that: $1 \leq \alpha \leq 2$ (Ugonabo et al., 2012). Graphical
154 representation of linear version of Eq. 9 at $\alpha = 1$ or 2 should produce a linear graph from
155 which K_m could be determined from the slope of either Equation 10 or 11:

156 $\alpha = 1$: $$\ln\left(\frac{1}{N}\right) = K_m t - \ln N_0$$

157 (10)

158 For $\alpha = 2$: $$\frac{1}{N} = K_m t + \frac{1}{N_0}$$

159 (11)

160 Where N_0 is the initial N_t at time = 0

161 N is N_t at upper time limit > 0

162 Eq. (11) could be solved to obtain coagulation-flocculation period $\tau_{1/2}$

163 $$\tau_{1/2} = {}^{1}\!\!\diagup\!\!_{\left(0.5 N_0 K_m\right)}$$

164 (12)

165 For Brownian controlled aggregation at t≤30 min, Eq. (12) could be solved exactly to
166 generate Eq.13

$$\frac{N_{m(t)}}{N_0} = \frac{\left[t/\tau_{1/2} \right]^{m-1}}{\left[1 + t/\tau_{1/2} \right]^{m+1}} \quad (13)$$

2.5 Particle Variations Behaviour as a Function of Time.

The particle variations behavior plots of turbidity removal from vegetable oil refinery wastewater (VOW) was investigated.

2.6 Adsorption kinetic model description

The influence of adsorption on the coagulation process was investigated. The jar test data were subjected to series of adsorptive analysis. Three kinetic models were studied which includes: Pseudo first order, Pseudo second order and Elovich kinetic model. Table 1 presents the linear and corresponding non-linear model equations.

Table 1: Linear and non-linear kinetic models

Kinetic equations	linear form	Non-linear	plot made	Eqn. No	Reference
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - (\frac{K_s t}{2.303})$	$q_t = q_e[1 - \exp(-k_1 t)]$	$\log(q_e - q_t)$ vs. t	(14)	(Okoye et al., 2013)
Pseudo-second-order	$t/q_t = \frac{1}{K^2 q_e^2} + \frac{t}{q_e}$	$q_t = \frac{k_{2q_e^2 t}}{1 + k_2 q_e t}$	$\frac{t}{q_t}$ vs. t	(15)	(Okoye et al., 2013)
Elovich	$qt = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$	$q_t = (\frac{1}{\beta})\ln(1 + \alpha_1 \beta t)$	q_t vs. t	(16)	(Okoye et al., 2013)

Where qt and qe = quantity adsorbed at a time and equilibrium respectively, K_1 = pseudo first order constant, t = time, K_2 =pseudo second order constant, αβ = Elovich constant

3.0 RESULTS AND DISCUSSION

3.1 Characterization of vegetable oil refinery wastewater (VOW) before and after coagulation

The characterization result of the vegetable oil refinery wastewater before and after coagulation process is presented in Table 2. The vegetable oil refinery wastewater possessed high values of total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and colour before treatment compared with the national regulatory standard for effluent discharge. Table 2 shows that the values of TSS, COD BOD among others recorded for the raw sample were well above national discharge standard, hence there is need for treatment before discharge. These values were reduced drastically after the coagulation treatment (see table 2), affirming the effectiveness of the coagulation in achieving organic load reduction (Obiora-Okafo and Onukwuli, 2013).

Table 2: Characterization result of VOW before and after coagulation using FSC

Parameter	Before Coagulation	After Coagulation	WHO standard
Turbidity(NTU)	280	14	< 11.75
TSS (mg/l)	389.2	24	30.00
COD (mg/l)	933	65	NS
BOD (mg/l)	634	37	30
pH(-)	6.9	7.3	6.6-8.56
Colour (mg/l)	630.6	88	-
TS (mg/l)	688	58	500
TDS (mg/l)	298.8	34	50.00
Total hardness(mg/l)	43.8	19	500.00
Sulphate (mg/l)	18	2.4	-
Iron (mg/l)	0.632	0.13	0.3
Potassium (mg/l)	2.87	0.6	-
Magnesium (mg/l)	19.49	4.71	75
Lead (mg/l)	0.10	-	0.1

Note: NTU-nephelometric turbidity unit, TDS-total dissolved solids, TSS-total suspended solids, COD-chemical oxygen demand and BOD -biochemical oxygen demand

3.2 Characterization result

3.2.1 Physiochemical characterization

The bio-coagulant extracted from the fish scale flour was subjected to proximate analysis. The properties measured are percentage moisture, crude protein, ash content, crude fibre, carbohydrates and lipid content. The characteristics of FSC presented in Table 3 show that it has a reasonably high content of protein (19.11%). This is an indication of its likely good performance as a coagulant for wastewater treatment.

Table 3: Proximate analysis of FSC

Moisture (%)	7.48
Crude protein (%)	19.11
Ash content (%)	25.08
Crude fibre (%)	3.05
Lipid content (%)	2.98
Carbohydrates (%)	42.3

3.2.2 FTIR analysis

The FTIR spectra of the raw and extracted polymer (chito-protein) derived from fish scale are shown in figures 3 and 4 respectively. The results were analyzed based on the standard peaks as presented by Silverstein et al. (1981) for various functional groups. The comparison of the spectra results of the coagulant precursors and the synthesized coagulants indicates an obvious shift, disappearance and detection of new wave numbers. This observation could have existed as a direct consequence of the chemical reaction process involved in the coagulant synthesis and further elucidates the existence of improved/modified chemical species on the coagulants. This chemical modification could ultimately result in an improved coagulation performance by the respective coagulants. Table 4 provides detailed information on raw and extracted coagulant with respect to the various peaks that shifted, vanished or appeared. The wave number shifts in the spectra image of the coagulant are observed to range between $\pm 2 cm^{-1}$ to as high as $\pm 147\ cm^{-1}$ (see Table 4). Another important observation made with respect to Table 4 is that there were negligible wave number differences between FSF and FSC when compared to the other materials. This finding suggests a limited reactivity of the respective functional groups in FSF during the synthesis of FSC.

Vibrational peaks observed from the analysis are presented in table 4 and figures 3 and 4. Usually the absorption peaks observed below 500 cm^{-1} are not applicable for the

characterization of fish scale (Fernandez-Kim, 2004). At the higher wave number end of the spectra, the C – H stretching region provides important information about the coagulants' chemical composition. The distinct stretching band at wave numbers greater than 3000 cm^{-1} suggests the existence of aromatic ring groups in the coagulant structure (Günter and David, 2014). The peak at 793.9931cm^{-1} can be attributed C-H bending vibration while that at 1348.451cm^{-1} can be assigned to SO_2 asymmetric band. Additionally, the absorption peak at 3453.237cm^{-1}which is within the range of 3200 and 3500 cm^{-1} which were characteristic of N-H stretching of amides (Stuart, 2004).

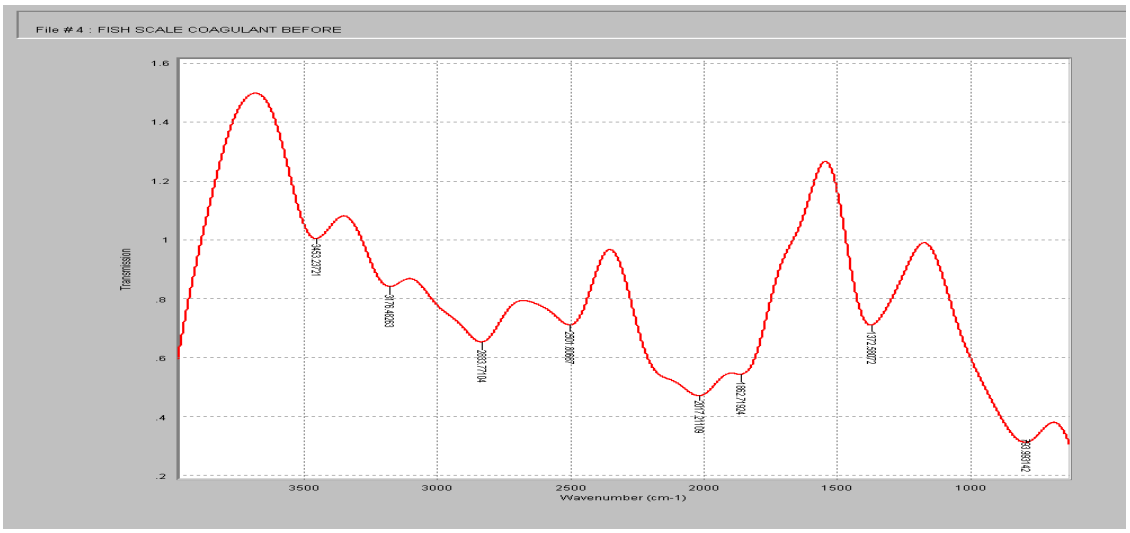

Figure 3: FTIR spectrum analysis of FSF sample

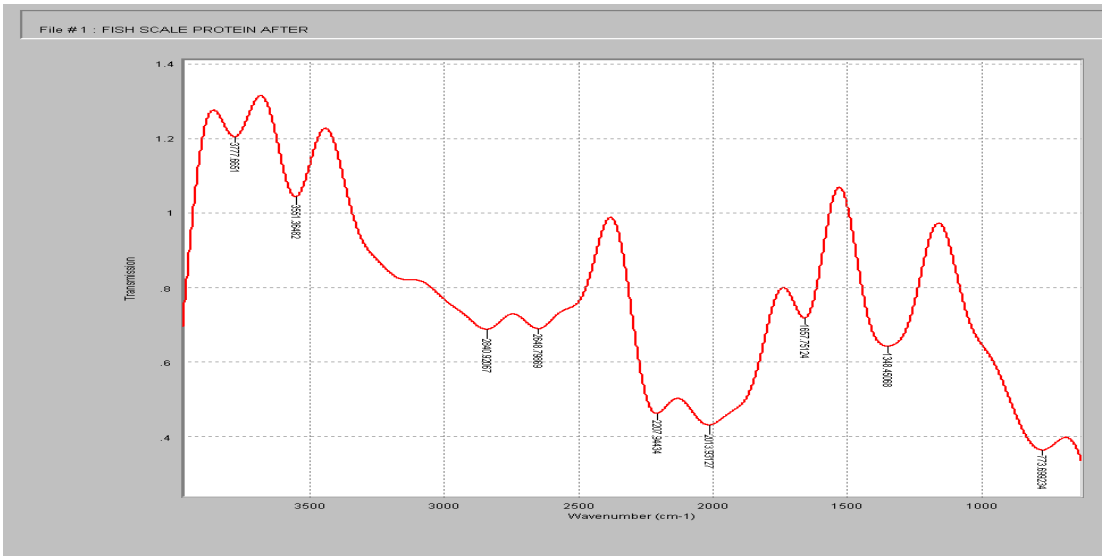

Figure 4: FTIR spectrum analysis of FSC sample

Table 4: FTIR table for vibrational peaks of fish scale (FSF and FSC)

Peak (cm^{-1})			
FSF	FSC	Differences	Assignment
793.9931	773.6992	20.29	Out – of – plane C – H bending
1372.581	1348.451	24.13	SO_2 asymmetric band
x	1657.751	x	NO_2 asymmetric stretching
1862.719	x		C = O stretching
2017.211	2013.944	3.28	Metal carbonyl C = O
x	2207.94	x	
2501.807	2648.799	146.99	Phosphoric acid and Ester O – H
2833.771	2840.921	7.15	C – H stretching of aldehyde
3176.483	x	x	O – H stretching of carboxylic acid
3453.237	x	x	N – H stretching
x	3551.365	x	Si – OH stretching

3.2.3 Scanning electron microscopy (SEM) characterization of FSC and FSC

The SEM technique, a powerful tool for analysing the surface morphological make-up of the polymeric coagulants was employed. SEM image was used to elucidate the surface texture and morphology of the synthesized coagulant. The result of the SEM studies for the raw (fish scale flour) extracted (FBC) samples were presented in plates 1 and 2.

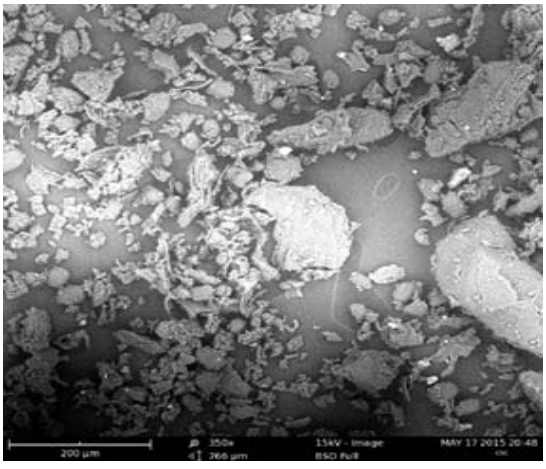

Plate 1: SEM micrograph of FSF

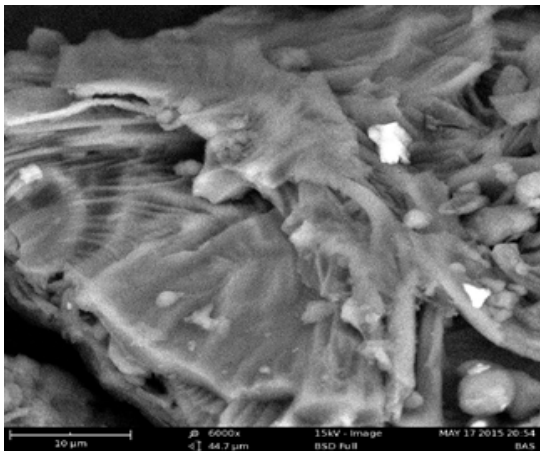

Plate 2: SEM Micrograph of FSC

Plates 1 and 2, show the SEM micrographs of fish scale flour and fish scale chito-protein respectively. Plate1 was mainly characterized by smooth surface with seemingly compact structures. It also exhibits the appearance of tiny homogenous pores. While, Plate 2 shows the existence of irregular granular structure on the coagulant morphology. The appearance of irregular platelets on plate 2 shows that fish scale coagulant (FSC) has rough edges which may be attributed to high brittle property of the coagulant, (Obiora-Okafo et al., 2014). Also, according to Obiora-Okafo (2011), irregular granular structures are desirable characteristics of any coagulant with regards to adsorbing and bridging of colloidal particles and further enhancing the sedimentation of flocs. Multiple pores can also be visualized on plate 2; these pores are available sites for particles adsorption.

3.5 Factor Sensitivity studies

Various factors influence the coagulation performance of any given coagulant. The influences of the variation of some of these factors are highlighted in section 3.5.1 to 3.5.3;

3.5.1 Effect of FSC dosages and setting time on TDSP removal efficiency

The effect of coagulant dosage (FSC) at different settling time on TDSP removal efficiency from vegetable oil refinery wastewater was analysed at initial pH of the wastewater. Fig. 5 shows the plots of removal efficiency of TDSP against settling time at varying dosages. The result of the turbidity removal with respect to FSC dose is presented in Fig. 5. The dosage studied varied from 0.5-2.5g of FSC in 500ml of VOW. The graph (Fig.5) indicates that the removal TDSP increased with increase in the coagulant dosage. The percentage turbidity removal recorded for coagulant dose of 1g was 74.7% at 30min. Similarly, at a coagulant dose of 1.5g over the same time, the percentage TDSP removal was 84.0%. The increase in the TDSP removal with an increase in FSC dose could be attributed to the availability of large content of protein created by more quantity of coagulant deposited to the wastewater which aid to fast coagulation process.

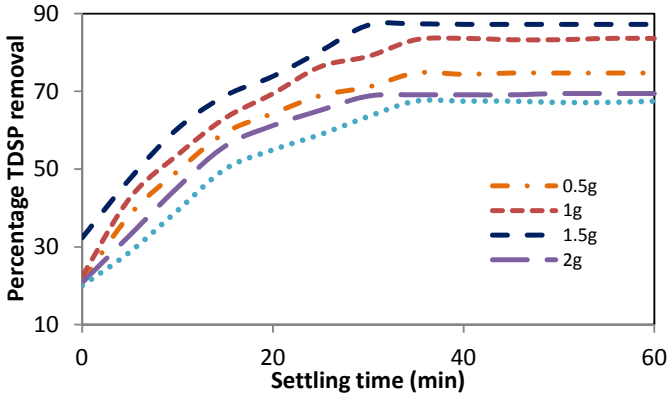

Fig 5: Effect of coagulant dosage

3.5.2 Effect of pH on turbidity removal efficiency

The effect of pH was studied at the varying coagulant dosage, temperature of 30^{o}C, and time of 60min as shown in Fig.6. The pH of the wastewater was varied from 2-10 using H_2SO_4 and NaOH. The result is shown in Fig. 6 for TDSP. An optimum TDSP removal efficiency of 84% was obtained at pH of 2 with 1.5g optimum coagulant dose. This shows that the treatment process performs better when the solution is in acidic medium. In addition, after the pH of 2, the removal efficiency of the particles decreased continuously till the minimum value was attained, this trend can be attributed to decrease in solubility of coagulant with increase in pH. Hence, it was evident that FSC may not be very effective in alkaline solution. Similar works were reported by Devi et al (2012).

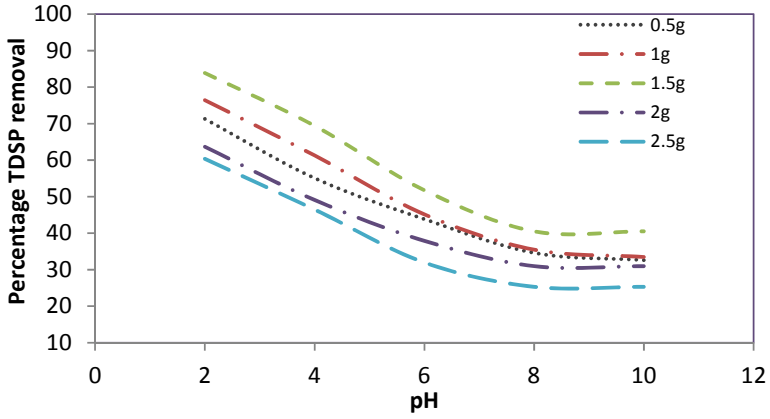

Fig 6: Effect of pH

3.5.3 Effect of temperature on TDSP removal efficiency

The effect of temperature on the coagulation efficiency was investigated at the best pH and best coagulant dose while varying the temperature between 30 – 60°C. From the efficiency analysis, it was observed that the coagulation efficiency varies directly with temperature to the maximum (Fig. 7) and decreased thereafter. The ascending part can be attributed to particle excitement; hence at this stage more flocs are formed. After the maximum stage (50^0C), decrease in particle removal with temperature was observed at temperature of 60^0C. This could be as a result of denaturation of the coagulant particles which may cause slight inhibition of the process. Similar result was obtained by Babayemi et al. (2013)

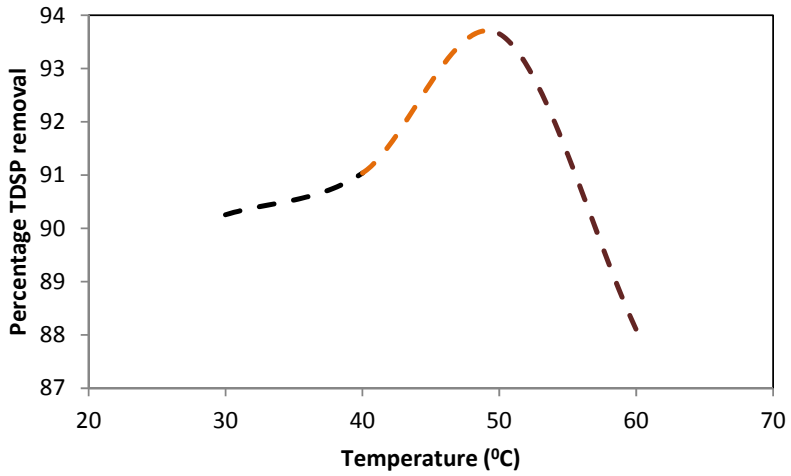

Fig. 7: Effect of temperature on turbidity (%) removal

3.6 Coagulation Kinetics

The kinetics of TDSP removal was evaluated to study the effect of time on the particle movement from the bulk of the effluent sample to the surface of the coagulant after charge neutralization and destabilization, the kinetic plot ($\frac{1}{C_t}$ vs t) that described the rate of particle transport is presented in Fig. 8, while the calculated parameters are presented in table 5.

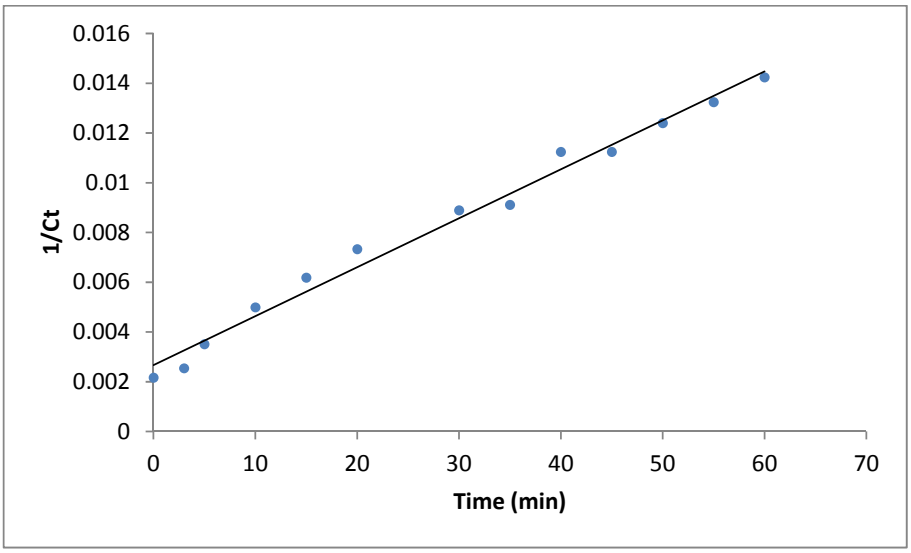

Fig. 8: Plot of 1/Ct against settling time for

Brownian transport of destabilized particles (K_m) for the rate constant was evaluated from the slope of the kinetic plot of 1/Ct against t (Fig 8), while the Von smolushoski's coagulation constant (K_R) accounts for the rate of rapid coagulation was determined based on equation 11. For perikinetic coagulation with a constant order of 2, the difference between K_m and K_R accounts for the rate of particle flocculation (K_f). The Km was obtained as 2E-05g/min while K_m was obtained as 4.86E-21. The rate of particle flocculation was 0.00002g/min. The number of effective collision was estimated as a function of particle collision efficiency (ε_p). Higher value of (ε_p) obtained in the system suggests that more collision leads to floc formation. Table 5 shows the parameters obtained. From table 5, it can be observed that $K_m \gg K_R$ which shows that K_R is quite negligible relative to K_m. The result suggests that the entire process is greatly influenced by the rate of floc formation than the actual rate of coagulation.

Table 5: coagulation kinetic parameters

Parameters	
K_m(g.min)	2.00E-05
R^2	0.9245
ßBr(g.min)	0.00004
$\tau_{1/2}$(min)	50.00
R	1.11E-05

ε_p	4.12E+15
K_R	4.86E-21
D'	1.74E-17
B	0.000239917
A	2.0000

3.7 Particle distribution

The total number of turbidity concentration, N_t and the concentration of the species N_i both decrease monotonically with increasing time. From the plot (Fig. 9), the concentrations of N_2 (t), N_3 (t) and N_4 (t) pass through a maximum (Santhanam et al., 2014). This is because they are not present at t = 0 and $N_0 = 0$. The number of singlet (N_1) can be seen to decrease more rapidly than the total number of particles Ni. This happens as a result of increasing number of particles concentration on aggregate formation with time (Menkiti and Ejimofor, 2016). Here, the total number of particles decreases according to a bimolecular reaction. From the plot, it can be observe that the lower the value of K, the higher the coagulation time T_{ag} with respect to its N_o and the more the effect of high period of particle distribution (Obiora et al., 2014). At low K the rate process is very slow which gives rise to more time for the coagulation-flocculation process. Fig. 9 shows the effect of high period of particle distribution. Here, the decrease of singlets from initial particle concentration and increase in doublets, triplets and quadruplets from zero concentration occur. The sum of all the distribution particles from singlets (N_1), doublets (N_2), triplets (N_3) and quadruplets (N_4) display the overall effects of high period on the reactor. This suggests low rate of particle aggregation and poor particle removal efficiency (Menkiti and Ejimofor, 2016).

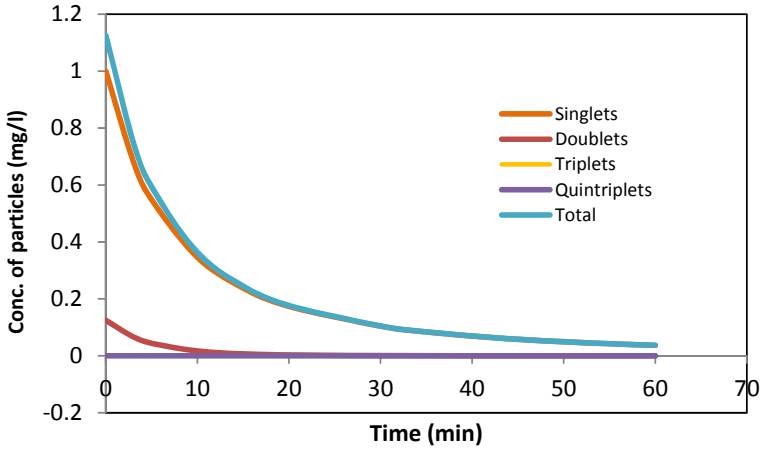

Fig.9: Particle distribution plot for TDSP removal

3.6 Coag-adsorptive kinetic studies

Coagulation is known to be a multi-component process where four mechanisms can be identified. The mechanisms include; double layer compression, adsorption and charge neutralization, sweep flocculation and adsorption and inter-particle bridging. These mechanisms are grouped into adsorptive and non-adsorptive components. To describe the adsorptive component of the process, adsorption kinetic models were used to model the coagulation kinetic data obtained during the experimental studies. For this present studies, three (3) kinetic models were considered which includes: PFO, PSO and Elovich kinetic models. Figs. 10, 11 and 12 show the linear plots of PFO, PSO and Elovich kinetic models. While Fig. 13 shows the comparative relationship between the nonlinear model data and the experimental data. Also, table 6 shows the calculated model parameters, their statistical T-Test, F-test, STD and Chi test estimated can also be identified in the same table 6.

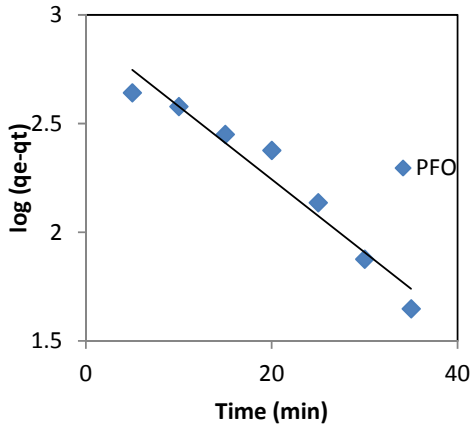

Fig. 10: Linear plot of PFO kinetic model

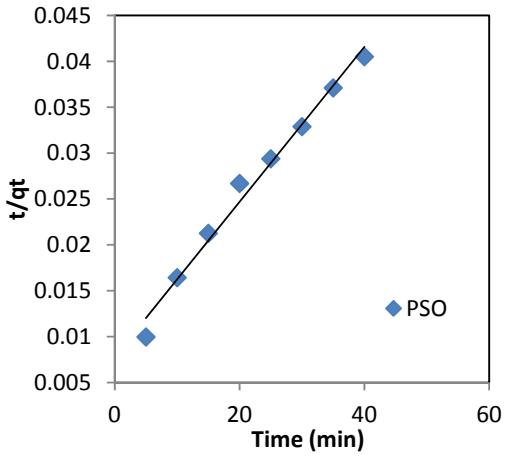

Fig. 11: Linear plot of PSO kinetic model

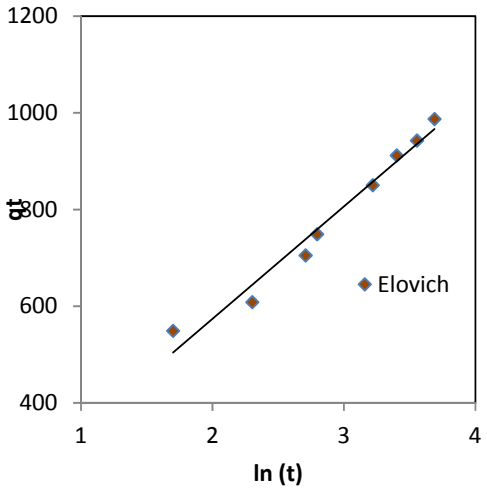

Fig. 12: Linear plot of Elovich kinetic model kinetics

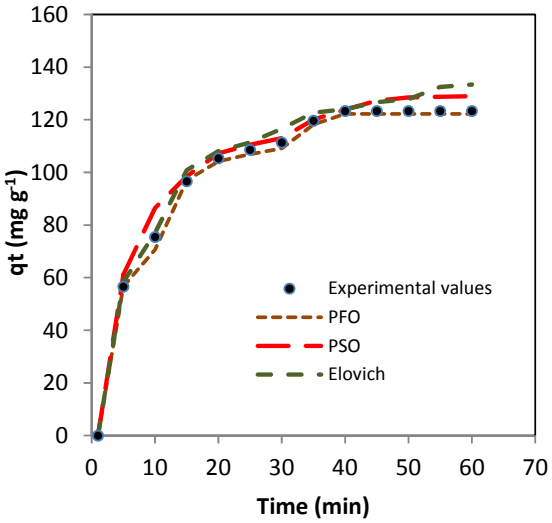

Fig. 13 Non-linear kinetic modeling of the coag-adsorptive

Table 6: kinetic parameters for linear and non-linear kinetic models

PSO		PFO		Elovich	
K (linear)	0.000846	K (linear)	0.01624	ß (linear)	0.046268
R^2 (linear)	0.9974	R^2 (linear)	0.9873	α(linear)	24.89146
K(non-linear)	0.00283	K (non-linear)	0.01624	R^2 (linear)	0.9607
qe(linear)	129.9479	qe (linear)	107.9941	ß (non-linear)	0.163284
qe(non-linear)	129.7413	qe (non-linear)	109.0498	α (non-linear)	44.72479
R^2 non-linear	0.9945	R^2 non-linear	0.9909	R^2 (non-linear)	0.9738
T-test	0.036036	T-test	0.000715	T-test	0.000232
F-test	0.712126	F-test	0.886854	F-test	0.835209
Chi test	0.99906	Chi test	0.994527	Chi test	0.996882
STD	20.08663	STD	20.8065	STD	21.98474
Δqe	0.206587	Δqe	1.0557	Δqe	10.05778

The Pseudo first order and pseudo second order models assume that the adsorptive component of coagulation is a pseudo chemicals reaction, while the kinetic data follow Elovich model if the adsorption is chemical in nature. In this present study, it was observed that the coefficient of correlation for models considered were above 0.9 for both linear and non-linear studies. Hence the difference between $q_{(e\ exp)}$ and $q_{(e\ cal)}$ (Δqe) was used as the basis of model comparison. Where $q_{(e\ exp)}$ is the quantity adsorbed at equilibrium time, while $q_{(e\ cal)}$ is model generated data. From table 6, the models with (Δqe) ≥ 2 were considered as having poor description of the experimental kinetic data. Hence, pseudo second order and pseudo first order kinetic models with (Δqe) < 2 were considered.

4.0 CONCLUSION

Fish scale has been identified as a potential source of coagulation agent for the removal of turbidity from vegetable oil industry effluent. Some of the parameters that control bio-coagulation were found to include coagulation pH, coagulant dosage, and coagulation temperature. It was observed that the percentage turbidity removal increased with increase of the settling time. The optimum contact time, pH and temperature were 30 min, 2 and 323K respectively. By applying 3 different linear and nonlinear kinetic models to evaluate the optimum parameter sets; Pseudo first order and Pseudo second order models were found to be the best two most suited models (judging by the maximum correlation coefficient, R^2 and least Δqe value. Using statistical tools (F-test and student's t-test) the predicted kinetic data were adjured statistically significant. The FT-IR spectrum confirmed the chemical structures of both the fish scale flour and their corresponding coagulant (FSC) with the functional ester groups present. The kinetics of the coagulation/flocculation reaction presented showed that the reaction followed second order kinetic model. Since, fish scale performed very well in the coagulation studies performed, there is therefore great possibility of replacing chemical coagulants with less hazardous and efficient bio-coagulants.

ABBREVIATIONS

VOW: Vegetable oil refinery wastewater

FSF: Fish scale flour

FSC: Fish scale coagulant

TDSP: Total suspended and dissolved particles

FTIR: Fourier transforms infrared

T_o: Turbidity of raw effluent

T: Turbidity of effluent after treatment

TSS: Total suspended solid

TS: Total solid

COD: Chemical oxygen demand

BOD: Biochemical oxygen demand

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