



Performance of Natural Coagulants in the Treatment of Vegetable Oil Industrial Effluent

**C. F. Okey-Onyesolu^{1*}, C. C. Okoye¹, C. N. Ude², O. D. Onukwuli¹
and O. E. Achugbu¹**

¹*Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.*

²*Department of Chemical Engineering, Michael Okpara University of Agriculture, Umudike, Umuahia, Abia State, Nigeria.*

Authors' contributions

This work was carried out in collaboration among all authors. Authors CFOO and ODO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors CFOO and CCO managed the analyses of the study. Authors CNU and OEA managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJARR/2020/v12i130278

Editor(s):

(1) Dr. Ibrahim Yerima, University of Maiduguri, Nigeria.

Reviewers:

(1) V. S. Gnanambal, Bharathiar University, India.

(2) Sourav Majumder, University of Gour Banga, India.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/58220>

Original Research Article

Received 25 April 2020

Accepted 30 June 2020

Published 08 July 2020

ABSTRACT

The potentials of natural coagulants (egg shell and fish scale) in the treatment of vegetable oil industrial wastewater were investigated. The coagulants were characterized to determine their chemical compositions, functional groups and morphology using proximate analysis method, Fourier Infra-red spectroscopy (FTIR) and Scanning Electron Microscope (SEM) respectively. The industrial wastewater was equally characterized to determine its heavy metal composition and physico-chemical properties. The effects of various process parameters such as pH, coagulants dosage, time and temperature were examined during the treatment of the waste water using the natural coagulants. The proximate analysis shows that Fish Scale Coagulant (FSC) contains more carbohydrate, 42.30% while Egg Shell Coagulant (ESC) has protein content of 39.65%. It was discovered that the coagulating properties of both FSC and ESC improve after extraction due to presence of isocyanates, isothiocyanates, azides, ketenes, aldehydes and ketone. The turbidity of the wastewater was very high (365NTU) above the WHO recommended value. The process variables have significant effects on the coagulation with best removal efficiency of 88.54% for

*Corresponding author: Email: cf.okey-onyesolu@unizik.edu.ng, cf.onyesolu@gmail.com;

ESC and 74.12% for FSC at pH of 4.0 (ESC) and pH of 7.0(FSC); 0.5 g/L (ESC) and 0.04 g/L (FSC) coagulant dosage and temperature of 40°C. Therefore, both coagulants are effective in treating vegetable oil effluent but egg shell coagulant was found to be a better coagulant. Further research on optimization, kinetics and thermodynamics of the coagulation process using ESC and FSC should be carried out.

Keywords: Egg shell coagulant; fish scale coagulant; vegetable oil industrial wastewater.

1. INTRODUCTION

Nowadays, some developed and developing countries are complying with the local and international standards for discharging industrial effluents, through various wastewater treatment methods [1]. Vegetable oil industry wastewater contains colloidal and suspended matters beyond allowable limit, hence the need for treatment [2]. The pollutants in wastewater include nutrients, which can stimulate growth of algae that deplete dissolved oxygen, different salts, surfactants, heavy metals, mineral oils and others. Various conventional physical, chemical and biological treatments have been used to treat wastewater. Due to the nature of the colloidal suspension, these particles will not sediment or be separated with conventional physical methods (such as filtration or settling) unless they are agglomerated through coagulation and flocculation. Colloidal particles are removed from water via coagulation and flocculation processes [3].

Coagulation involves destabilization of colloidal particles and very fine solid suspensions so as to make them coagulate depending on the appropriate conditions. Flocculation refers to the process by which destabilized particles actually conglomerate into larger aggregates so that they can be separated from the wastewater [4]. Particles larger than the colloids can also be removed by entrapment in the flocs formed during coagulation.

A coagulant is a substance that is added to water to withdraw the forces that stabilize the colloidal particles and cause them to settle in the water. Though well-recognized chemical-based coagulants like Alum ($AlCl_3$), Ferric Chloride ($FeCl_3$) and Poly Aluminum Chloride (PAC) are effective, there are drawbacks associated with their usage. Such shortcomings include ineffectiveness in low-temperature water, relatively high purchase cost, harmful effects on human health, production of large volumes of non-biodegradable sludge and the fact that they largely affect pH of treated water. Natural

coagulants, on the other hand, are efficient, effective and cheaper with little or no harmful effects on human health [5]. Hence, this study focused on investigating the potential of Egg Shell (ES) and Fish Scale (FS) in treating vegetable oil effluent (VOE) by coagulation method.

2. MATERIALS AND METHODS

2.1 Materials

The coagulants used are Fish Scale (FS) and Egg Shell (ES). FS and ES were collected from Awka metropolis, Anambra State, Nigeria. The vegetable oil effluent was collected from a vegetable oil company Onitsha, Anambra State, Nigeria. The chemicals used were obtained from Bridge head market Onitsha and Chemical Engineering Laboratory, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria and were of analytical grade.

2.2 Methods

2.2.1 Preparation of the coagulants

The coagulants (ESC and FSC) were washed with water, sun dried for 3 days and grounded to fine powder. 25 g each of the coagulant was treated with 5M aqueous sodium hydroxide solution (NaOH), fluid to solid ratio of 20 ml/g, at 50°C for duration of 2 hours in a process known as de-proteinization. The resulting solution was then filtered using a filter cloth; the filtrate was allowed to settle and decanted. The bottom of the filtrate was collected as fish scale or egg shell chito-protein (coagulant). The coagulant extract was then transferred to clean plastic universal containers and stored in a refrigerator till when they were used.

2.2.2 Wastewater collection

A 5-litres polyethylene bottle was thoroughly cleaned and rinsed with the effluent sample before the final sample collection, after which the bottle was tightly closed and was kept in a

refrigerator until when it was used. This is to prevent increase in bacterial load and also to avoid depletion of the contamination due to oxidation and direct sunlight.

2.2.3 Characterization of the coagulants and the effluent

The coagulants were characterized with AOAC [6] to determine the proximate analysis while American Public Health Association, APHA [7] method was used to characterize the effluents to determine its physico-chemical properties. Also the heavy metal analysis of the effluent was determined using Atomic Absorption Spectrophotometer model AA240 by adopting the method of American Public Health Association, [8]. The functional groups of the coagulants were determined using Fourier Infra-red Transform Spectrometer (FTIR) and the morphologies of the coagulants were examined using Scanning Electron Microscope (SEM).

2.2.4 Coagulation method

The treatment of the effluent by coagulation was carried out using simulated jar test procedure. The effluent was diluted with distilled water in a ratio of 200 ml/300 ml effluent/water. 0.5 g of egg shell coagulant was mixed with 200 ml of the solution at a pH of 2 in a 500 ml beaker placed in a water bath and heated to a temperature of 40°C. The mixture was vigorously stirred with a speed of 400 rpm for 2 min then gradually stirred for additional 20 min. The suspension was allowed to settle for 90 min and 5 ml of the sample was withdrawn with a syringe for residual turbidity analysis. The procedure was repeated for coagulant dosages (0.02 g, 0.04 g, 0.06 g, 0.08 g and 0.1 g for fish scale) and (0.1 g, 0.2 g, 0.3 g and 0.4 g for egg shell); pH (3.0, 4.0, 5.0 and 7.0) and temperature (30°C and 50°C).

3. RESULTS AND DISCUSSION

3.1 Characterization of the Coagulants and Effluent

3.1.1 Proximate analyses of the coagulants

The proximate analyses of egg shell and fish scale coagulants are depicted in Table 1. From the table, it is observed that the coagulants have ash content, crude fibre, fats moisture, protein and carbohydrate contents. Carbohydrate is dominant in fish scale while the egg shell has

highest value in protein content. Both contain reasonable amount of ash content. These compositions contribute to their coagulation properties.

3.1.2 Fourier transform infra-red spectrometer analysis

The functional groups of the raw and extracted egg shell and fish scale coagulants are shown in Figs. 1 and 2. From the figures the characteristic peaks of protein and carbohydrate are 1513 – 2922 cm^{-1} (representing N–H bending vibration of amide II band, and N–H bending vibration of primary amides) and 2840.92 – 3176.48 cm^{-1} (representing carboxylic acids, aldehydes and ketones) respectively. Comparing Figs. 1(a & b) and 2(a & b), it was discovered that extracted coagulant from both the eggshell and fish scale has more active bonds and functional groups than the raw coagulants. The additional functional groups in the eggshell coagulant after extraction are isocyanates, isothiocyanadilimides with characteristic peak 2207.94 cm^{-1} . While the additional functional groups in the Fish scale coagulant is alkyne with associated peak 2648.79 cm^{-1} . The presence of these functional groups enhanced coagulation.

3.1.3 SEM analysis of the coagulants

The morphologies of the coagulants before and after extraction are shown in Figs. 3 and 4 for egg shell and fish scale respectively. From the figures it could be observed that the extraction helped to loosen the bonds thereby reducing internal resistance and increase coagulation power of the coagulants.

3.1.4 Physico-chemical properties of the effluent

The result of physicochemical analysis of vegetable oil effluent is presented in the Table 2. The effluent has turbidity beyond the international acceptable limit. It also has pale colour and acidic odour. Hence, there is need for treatment before discharging it to the environment.

3.1.5 Heavy metals analysis in the effluent

The atomic absorption spectrophotometer shows that the effluent contains more of cadmium, iron and zinc therefore requires treatment before discharging to environment to avoid contaminating ground water.

Table 1. Proximate analysis result of fish-scale coagulant

Parameter (%)	Fish scale coagulant	Egg shell coagulant
Ash Content (%)	25.08	31.65
Crude Fibre Content (%)	2.05	9.08
Fats Content (%)	4.98	9.80
Moisture Content (%)	7.48	1.75
Protein content (%)	18.11	39.65
Carbohydrate content (%)	42.30	8.07

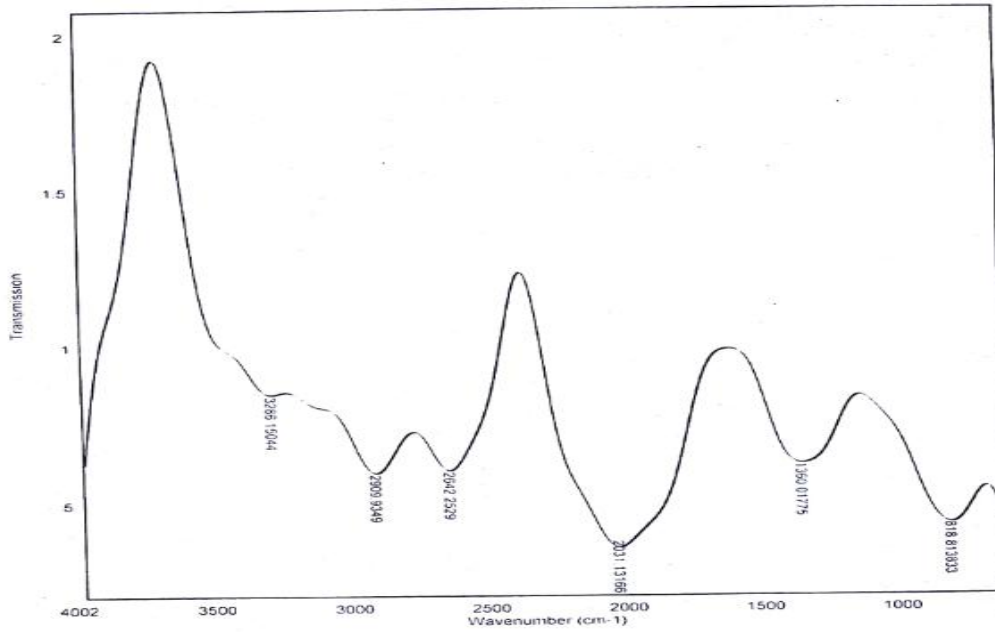


Fig. 1a. FTIR spectrum of raw eggshell

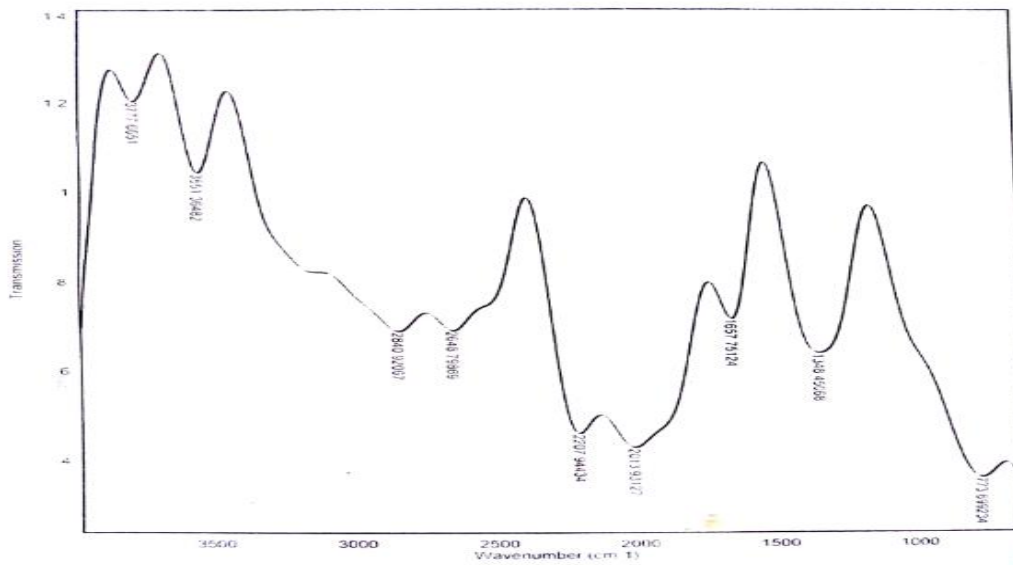


Fig. 1b. FTIR spectrum of extracted eggshell coagulant (ESC)

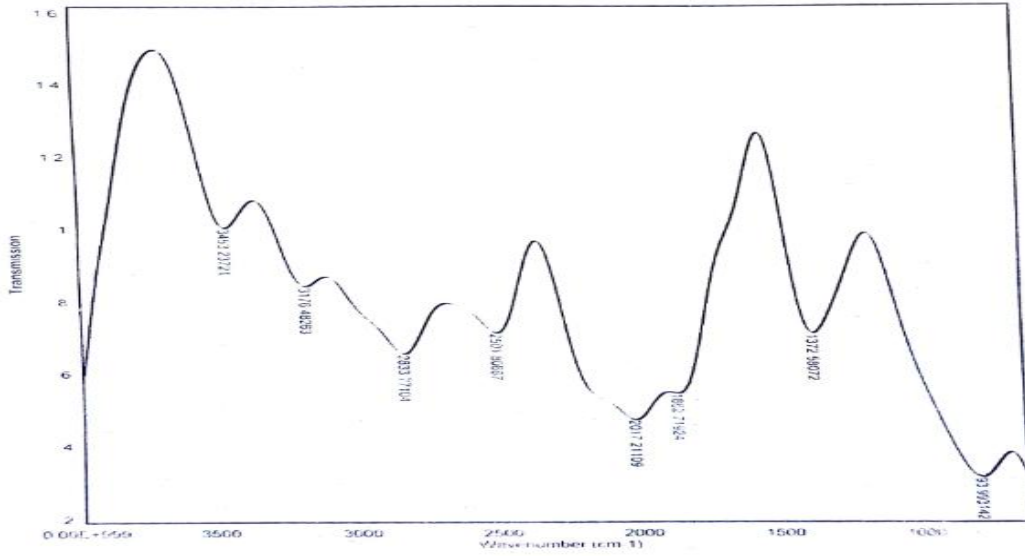


Fig. 2a. FTIR spectrum of raw fish scale

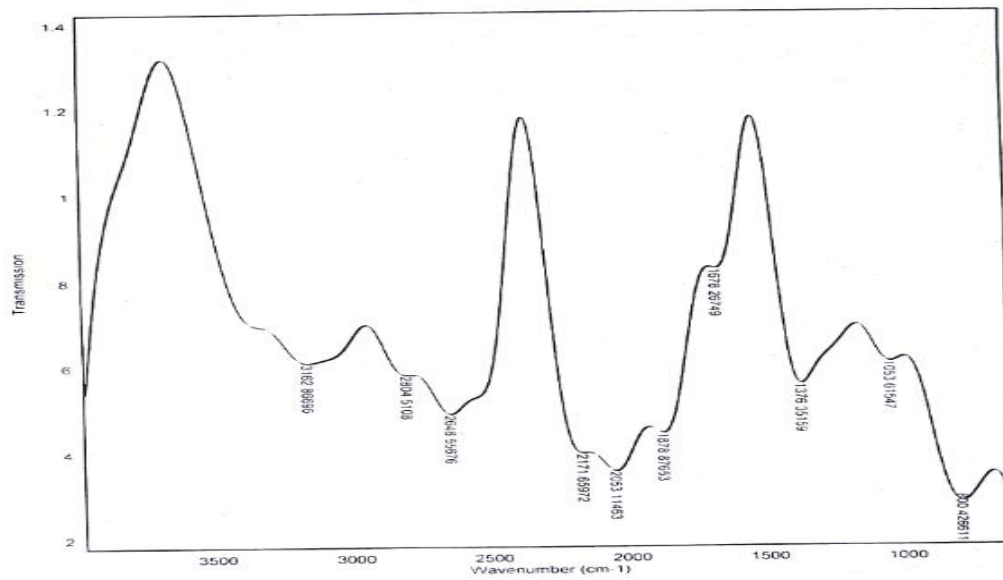


Fig. 2b. FTIR spectrum of extracted fish scale coagulant (FSC)

Table 2. Physico-chemical properties of effluent with standards

Parameter	Unit	VOE discharged	FEPA standard	WHO standard
General Appearance	-	Light	Clear	Clear
Colour	-	Pale yellow	Colourless	Colourless
Odour	-	Acidic	Unobjectionable	Unobjectionable
Turbidity	NTU	355-365		5
Temperature	°C	28	30	27
pH	-	6.5-7.0	6.0-9.0	6.5-9.0

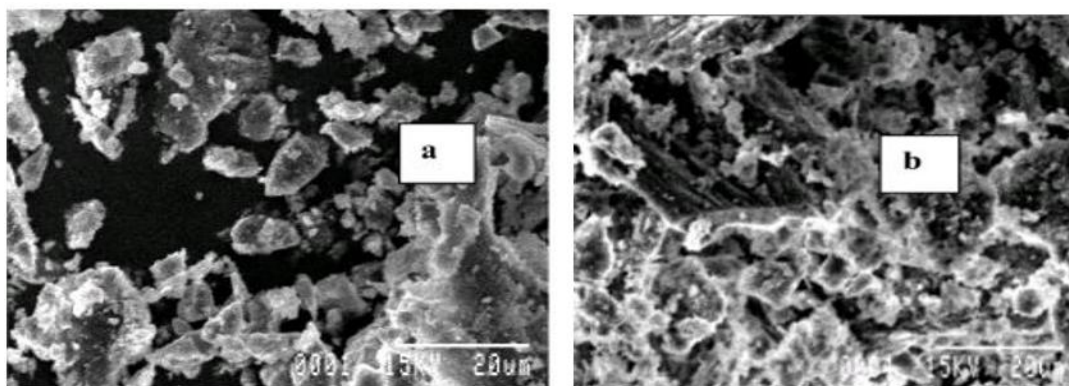


Fig. 3. Micrograph of egg shell coagulant (a) raw (b) extracted

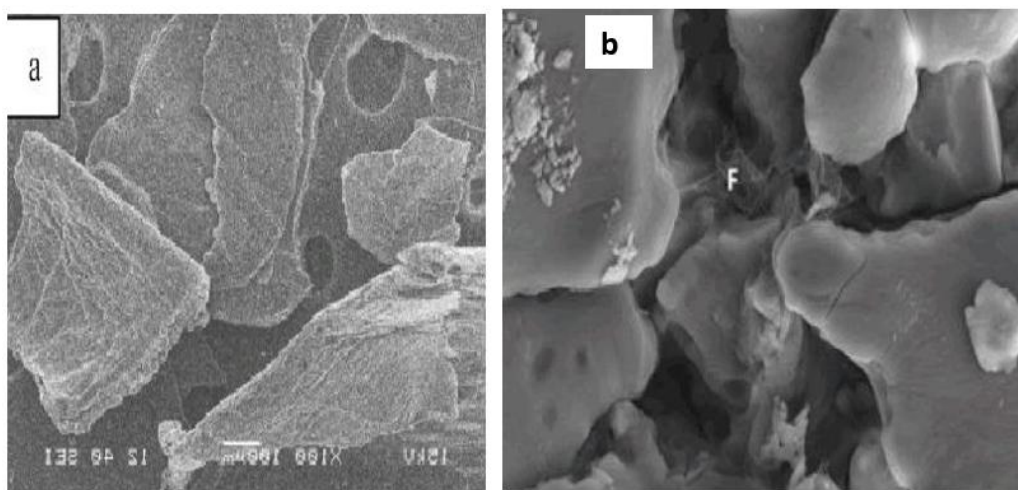


Fig. 4. Micrograph of fish scale coagulant (a) raw (b) extracted

3.2 Effect of Process Parameters on Coagulation

3.2.1 Effect of pH

In the coagulation process, the factor of pH affects the surface charge of coagulants and also the stabilization of the suspension. Figs. 5a and 5b represent the effect of pH on the treatment of vegetable oil industry effluent (VOE) using the eggshell coagulant (ESC) and the fish scale coagulant (FSC) respectively. The process was carried out under room temperature (300K) and the settling ranging from 0 second to 90 seconds.

From the figures, it is observed that the efficiency was higher at slightly acidic, to acidic condition. This may be due to strong precipitation at acidic pH, leading to higher % removal from the solution [9,10]. For the ESC, highest efficiency of 88.5% was obtained at pH 4.0 while the lowest

efficiency of 68.5% was obtained at pH 7.0 for FSC. It was found out that the optimum settling time for the realization of the highest efficiency was 40 min. This optimum settling time was found out to be the same for Eggshell coagulant and Fish scale coagulant. The optimal pH range for coagulation is 6.0 to 7.0 when using alum and 5.5 to 6.5 when using iron. For alkali water, excessive amounts of coagulant may be needed to lower the pH to the optimal pH range. In these cases, it may be beneficial to use coagulant in an acidic solution to reduce the amount of coagulant needed and effectively lower chemical cost.

3.2.2 Effect of coagulant dosage

In coagulation process, coagulant dosage is one of the most important parameter to determine not only the optimum condition for the performance of coagulant and also to a reasonable extent the

cost of coagulation. Essentially, insufficient dosage or overdosing would result in the poor performance in coagulation/flocculation. Therefore, it's significant to determine the optimum dosage to minimize the dosing cost and sludge formation and also to obtain the optimum performance in treatment. The effect of coagulant doses (0.1 g-0.5 g) on the treatment of vegetable oil industry effluent (VOE) using Egg shell coagulant maintaining pH of 4.0 and at room temperature of 30°C is represented in Fig. 6a. The best coagulate dosage was found to be 0.5 g and the optimum coagulation efficiency was 89.5% at the settling time of 40 minutes. It was also found that the efficiency of treatment of the

VOE using ESC increased while the coagulant dosage also increases. Such observation of continuous removal with increasing coagulant dosage was reported earlier by [11,12]. The effect of coagulant doses (0.02-0.1 g) on the treatment of vegetable oil industry effluent (VOE) using Fish scale coagulant maintaining pH of 7.0 and at room temperature of 30°C is represented in Fig. 6b. It was found that the optimum coagulant dosage is 0.04 g. Also the optimum settling time was 40 minutes. Furthermore, it was observed that the high concentrations (>0.04 g) of the coagulant confer positive charges on the particle surface, thus re-dispersing the particle as reported by [13].

Table 3. Heavy metal composition of the effluent

Heavy metal	Concentration (ppm)
Chromium	0.235
Cadmium	1.291
Lead	0.537
Iron	6.790
Nickel	0.008
Zinc	2.354
Copper	0.083
Cobalt	0.02
Mercury	0.051
Silver	0.465
Selenium	0.067
Aluminium	0.00
Tin	0.003
Vanadium	0.02
Molybdenum	0.010

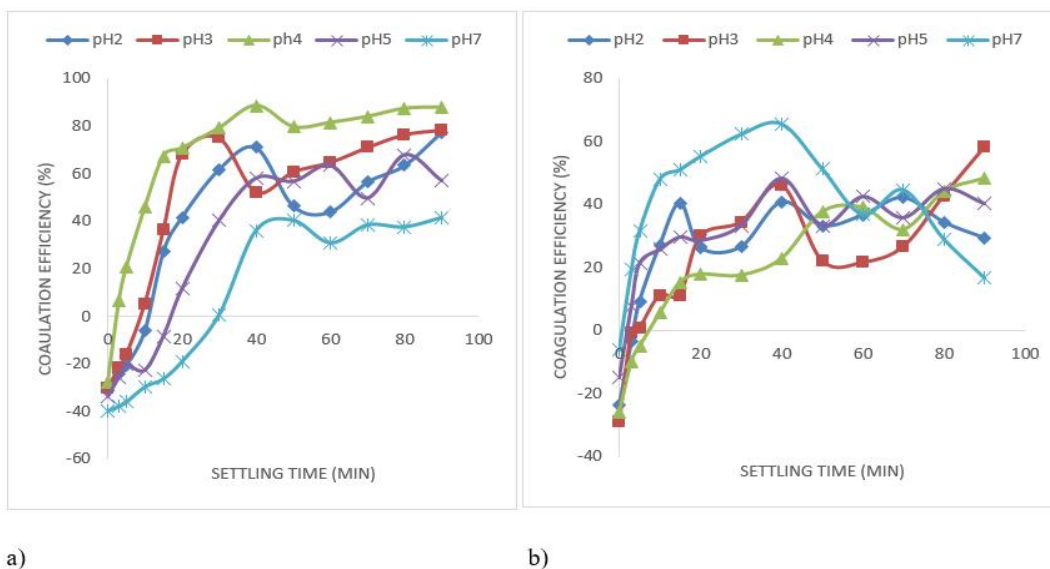


Fig. 5. Coagulation efficiency for varying pH for (a) ESC (b) FSC
 Coagulant dosage = 0.5 g (ESC) and 0.04 g (FSC); temperature = 30°C

3.2.3 Effect of temperature

Temperature also affects the efficiency of wastewater treatment. The effect of temperature (30°C-50°C) on the treatment of vegetable oil industry effluent (VOE) using Eggshell Coagulant, ESC (0.5 g) and Fish Scale

Coagulant, FSC (0.04 g) was investigated and depicted in Figs. 7(a & b). Optimum temperature was attained at 40°C for the two coagulants. At 40°C the highest efficiency of 93.68% at 90 min for the ESC and 81.84% at 40 min for the FSC were obtained. This also confirms that ESC is more effective than Fish scale coagulant.

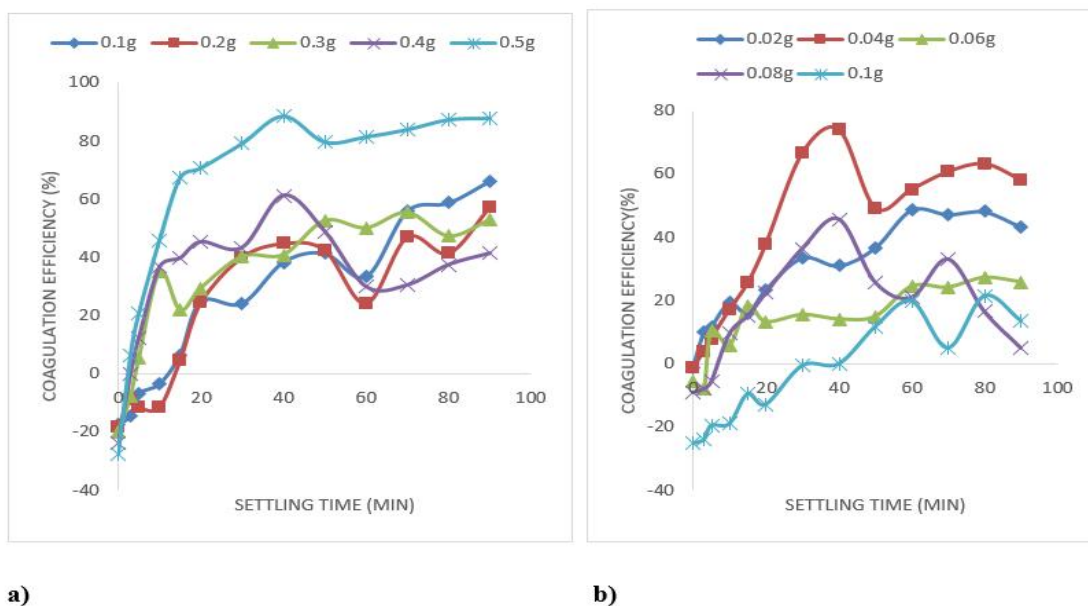


Fig. 6. Coagulation efficiency for varying dosage for (a) ESC and (b) FSC
 Conditions; pH = 4.0 (ESC) and 7.0 (FSC); temperature = 30°C

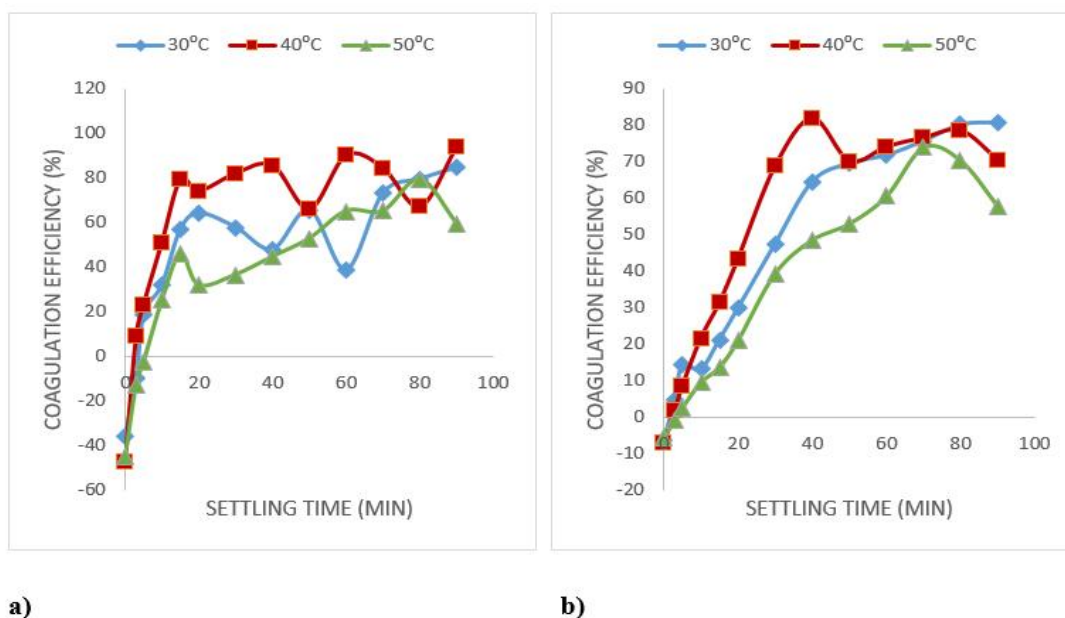


Fig. 7. Coagulation efficiency for varying temperature for (a) ESC and (b) FSC
 Conditions: Coagulant dosage = 0.5 g (ESC) and 0.04 g (FSC); pH = 4.0(ESC) and 7.0(FSC)

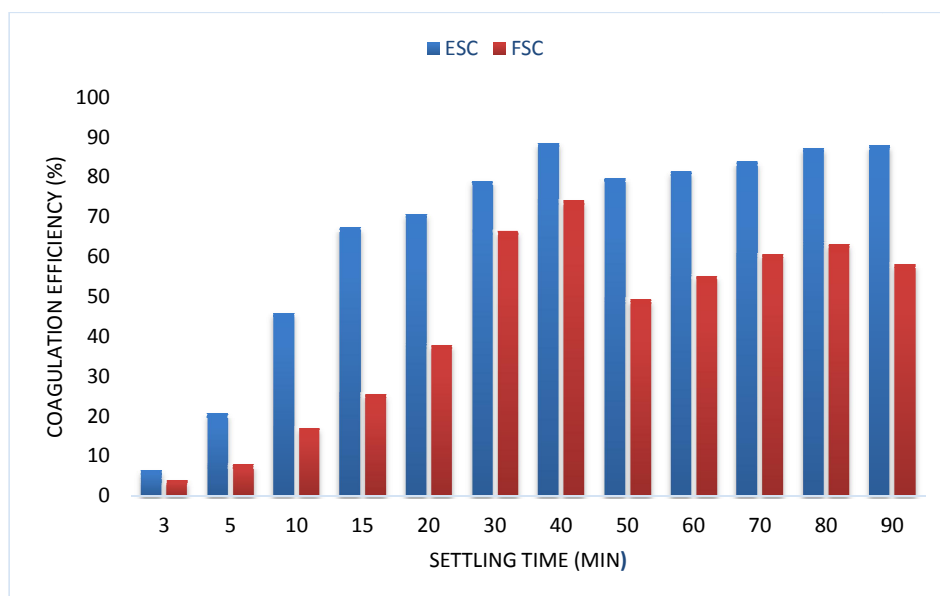


Fig. 8. Comparison of the efficiency of ESC and FSC

Conditions: Coagulant dosage = 0.5 g (ESC) and 0.04 g (FSC); pH = 4.0(ESC) and 7.0(FSC); Temperature = 40°C

Ozbelge et al. [14] concluded that flocculation settlement was reduced with a decrease in temperature from 23°C to 15°C using FeCl₃ and Carbonate as coagulants. The chemical reactions of coagulation had increased at a higher temperature of 40°C. Reduction of turbidity at higher temperatures was attributed to higher Brownian and Van Der Waals movements in water, which had enhanced the chemical reactions [15].

3.3 Comparison of the Efficiency of the ESC and FSC

The efficiencies of the coagulants, eggshell coagulant and fish scale coagulant at their optimum dosages were compared and presented in Fig. 8. From the figure, it is observed that eggshell coagulant has a better efficiency than the fish scale coagulant at any given settling time.

4. CONCLUSION

The study was carried out to investigate the ability of natural coagulants to treat and remove turbidity in an effluent from a vegetable oil industry instead of chemical coagulant like alum, etc. The two natural coagulants used in this study are ESC and FSC. The two coagulants performed well in the treatment of vegetable oil industry effluent (VOE). The use of coagulants

should be a good alternative response to the effluent treatment. It was discovered that Eggshell and Fish Scale, which are discarded as solid wastes are good coagulants and they contribute little or no hazard to the environment unlike their chemical counterpart. This makes bio-coagulation approach a good method for effluent treatment. Eggshell coagulant performed better in an acidic solution while fish scale coagulant performed optimally in a neutral solution. The optimal conditions for removal of turbidity from the effluent are coagulant dosage of 0.5 g (ESC) and 0.04 g (FSC), pH of 4.0 (ESC) and 7.0 (FSC) and temperature of 40°C with efficiency of 88.56% (ESC) and 74.2% (FSC). Hence, eggshell coagulant performed better than fish scale coagulant but both can serve as affordable and efficient bio-coagulants.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Ugonabo VI, Menkiti MC, Onukwuli DO. Effect of coag-flocculation kinetics on *Telfairia occidentalis* seed coagulant (TOC) in pharmaceutical wastewater. International Journal of Multidisciplinary

- Sciences and Engineering. 2012;3(9):22-33.
2. Okey-Onyesolu CF, Onukwuli OD, Okoye CC. Deturbidization of vegetable oil refinery wastewater with extracted fish scale biomass via coagulation process; non-linear kinetics studies. Journal of Engineering Research and Reports. 2018;2(2):1-14.
3. Ashoka HS, Inamdar SS. Adsorption removal of methyl red from aqueous solution with treated sugar bagasse and activated carbon. Global Journal of Environmental Research. 2010;4(3):175-182.
4. Prakash NB, Vimala S, Jayakaran P. Waste water treatment by coagulation and flocculation. International Journal of Engineering Science and Innovative Technology (IJESIT). 2014;3(2):479.
5. Tasneembano K, Arjun V. Treatment of tannery wastewater using natural coagulants. International Journal of Innovative Research in Science, Engineering and Technology. 2013;2(8):4061-4068.
6. AOAC. Official methods of analysis. Association of Official Analytical Chemists. 14th Edition, AOAC, Arlington; 1984.
7. APHA (American Public Health Association). Standard methods for the examination of water and wastewater, 18th Ed. Washington, DC, Fed. Reg. 1992;44:27362–27375.
8. APHA. Standard methods for the examination of water and wastewater. 19th Edition, American Public Health Association Inc., New York; 1995.
9. Irfan PK, Vanjakshi V, Prakash MNK. Calcium chloride extends the keeping quality of fig fruit (*Ficus carica L.*) during storage and shelf-life. Postharvest Biology and Technology. 2013;82:70-75.
10. Patel RA, Vashi D, Rowe R, Tchobanoglous G. Environmental engineering. International Edition. Singapore: McGraw-Hill; 2010.
11. Mohan SV, Ramanaiah SV, Sharma PN. Biosorption of direct azo dye from aqueous phase onto *Spirogyra* sp. 102: Evaluation of kinetics and mechanistic aspects. Biochemical Engineering Journal. 2008;38:61–69.
12. Liu JC, Lien CS. Pretreatment of bakery wastewater by coagulation–flocculation and dissolved air flotation. Water Science and Technology. 2001;43(8):131–137.
13. Amuda OS, Amoo IA. Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment. Journal of Hazardous Materialism. 2007;141(3):778–783.
14. Ozbelge TA, Ozbelge OH, Baskaya SZ. Removal of phenolic compounds from rubber-textile wastewaters by physico-chemical methods. Chemical Engineering and Processing. 2002;41:719–730.
15. Aziz H, Alias S, Assari F, Adlan MN. The use of alum, ferric chloride and ferrous sulphate as coagulants in removing suspended solids, colour and COD from semi-aerobic landfill leachate at controlled pH. Waste Management Research. 2007;25:556–565.

© 2020 Okey-Onyesolu et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

*The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/58220>*