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TREATMENT OF PHARMACEUTICAL EFFLUENT USING SEED OF *PHOENIX DACTYLIFERA* AS A NATURAL COAGULANT

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Abstract
Phoenix dactylifera is used to treat pharmaceutical effluent by coagulation-flocculation process. Physicochemical analysis was carried out on the effluent while the coagulant was subjected to proximate analysis and characterization. Coagulation-flocculation process was analyzed as a function of pH, settling time and dosage of the coagulant. The efficiency of coagulation-flocculation process was quantified on the colour removal. The result of physicochemical analysis obtained indicated that the effluent was highly polluted hence the, need for treatment. The proximate composition of this coagulant was found to be in this order carbohydrate (72.1%)>fat(14.9%)>protein(8.051%)>ash content(1.54%)>moisture content(1.15%). The maximum colour removal efficiency is 99.86% at the dosage of 100 mg/L, settling time of 50 minutes at constant pH of 2. The scanning electron microscopy of Phoenix dactylifera before and after treatment showed that there were changes in the surface morphology of this coagulant before and after treatment. FTIR result of the coagulant after treatment showed remarkable shift in the spectra bands, some new bands were added while some were removed; hence seed of Phoenix dactylifera can serve as an alternative coagulant.
Keywords: pharmaceutical, effluent, *Phoenix dactylifera,* coagulation-flocculation

Introduction
Effluent, according to WHO, is any wastewater treated or untreated that flows out of the treatment plant or sewer. Pharmaceutical effluent is wastewater generated by pharmaceutical industry during the process of drugs manufacturing [20, 2]. Due to challenges of diseases and man's quest to solve his problems hence demands for drugs have been promoted, which led to an increase in the number of pharmaceutical industries whose methods of drugs production involve chemical synthetic routes. Sometimes, the operation demands series of complex chemical reactions which discharged pharmaceutical effluent to the environment. This pharmaceutical effluent is characterized by high organic and inorganic chemical contents [14], colours and heavy metals [24] that if left untreated before being discharged pose health risk to the environment, receiving water bodies and farmlands. For example, if effluent has high concentration of biological oxygen demand (BOD) and chemical oxygen demand (COD), when discharged into inland rivers, streams or lakes, their biological stabilization can deplete natural oxygen resources and cause septic conditions that are detrimental to aquatic species [11]. The leaching of heavy metals and some of the pollutants can mar our crops adversely that their root will pick up these heavy metals and come back to us (the consumers). Some of them destroy vital organs like liver, kidney cause cancer, neurological disorder, Alzheimer diseases etc when accumulated in body system [13].

Coagulation-flocculation is a physicochemical method of treating wastewater which is widely used because of its simplicity and cost effectiveness. With the emergence of green chemistry natural coagulant came to the forefront since they are environmentally friendly, non-toxic and biodegradable. Some of the natural coagulant that have been studied are *Moringa oleifera*, *Cicer arietinum*, and *Dolichos lablab* [8], Dragon fruit foliage [22], Okra pod [19], *Cactus opuntia* (*ficus-indica*)[25], *Descurainia sophia L.* [16], *Corchorus Olitorius* L. [3], Aloe Vera, Moringa Oleifera seeds and Cactus [6].

Phoenix dactylifera is called date or date palm in English. Date palm tree belongs to *Arecaceae* family (Angiosperms, monocotyledon) [5]. It is a one-seeded fruit, usually oblong as shown in Figure 1. It has been the staple food and chief source of wealth in the irrigable desert from ancient times [1]. *Phoenix dactylifera* has been found to originate from North Africa and grows in

country such as Arabia , Persian Gulf, Canary Islands, in the northern Mediterranean and in the south of the United States. It has palm with a very slender trunk, up to 30 m tall, conspicuously covered with the remains of sheaths from fallen leaves. Its leaflets are clustered together in a maximum number of 20-30 and forming a loose crownshaft. The leaves also are pinnated up to 6 m long, upper leaves are ascending, basal leaves are recurved, the segments are coriaceous, linear, rigid, sharp pointed and blue-green in colour [21].
The study is aimed at treating pharmaceutical effluent with the seed of *Phoenix dactylifera* in order to remove colour from the effluent.

Figure 1: Phoenix dactylifera fruit

Figure 2: The seed of *Phoenix dactylifera*

Materials and methods

Collection of pharmaceutical effluent samples

The pharmaceutical effluent was collected from the waste channel of a pharmaceutical industry at Awka, Anambra, state, Nigeria. The colour of this effluent is purple. The effluent was collected in a 10 litres polyethylene bottle tightly closed and stored in a cool dry place.

Preparation of Coagulant

Phoenix dactylifera was purchased at Eke Awka market, Awka, Anambra State, the edible body was eaten leaving the seed which was sun-dried for two weeks to remove moisture after which it was ground using a grinder until its particles were reduced to powder of particle size 1.18 μm using sieve, after which it was kept in a cool, dry container.

Physicochemical analysis

Determination of chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solid (TDS), total suspended solid (TSS), total hardness, chloride, phosphate, nitrate and sulphate were carried out according to the standard method for the examination of water and wastewater [9, 7]. Electrical conductivity, turbidity and pH were determined using electrical conductivity meter Model DDS-307, Turbid meter Lab. Tech. model 038, pH meter Hanna model HI991300.

Characterization of the *Phoenix dactylifera* seed

The seed of *Phoenix dactylifera* was characterized using standard methods and instruments [23].

Coagulation-Flocculation Experiment

The initial absorbance of the pharmaceutical effluent was taken at 510 nm. Exactly 100 mg of the coagulant (*Phoenix dactylifera*) was weighed into 250 mL beaker and 100 mL of the effluent which was made to be at pH 2 was added into it. Desired pH was obtained by adding (1M HCl for acidic pH or 1M NaOH for basic pH) to the effluent. The content of the beaker was stirred for 2 mins of rapid mixing (100 rpm) and 20 mins for slow mixing (40 rpm) with a magnetic stirrer and then left undisturbed for 50 mins. It was filtered and the filtrate was subjected to colour removal analysis using UV/VIS spectrophotometer at 510 nm as λ_{max}. The experiment was repeated for the dosages of 200-500 mg/L, pH 4, 6,8,10, then time of 10-50 mins and dosage of 100-500 mg/L at constant pH 2. The colour removal efficiency is calculated thus:

$$\% \text{ colour removal efficiency} = \frac{\text{Initial absorbance} - \text{finial absorbance}}{\text{Initial absorbance}} \times 100\%$$

Results and discussions

Physicochemical analysis of the pharmaceutical effluent

The result of the physicochemical analysis of the pharmaceutical effluent is shown in Table 1. It can be inferred from the result that all the physicochemical characteristics were within WHO limit of effluent discharge, except total hardness, and turbidity. This pharmaceutical effluent is observed to be purple with absorbance of 5.073 hence the need for treatment for the removal of colour before being discharged into the environment. The presence of colour in effluent is caused by various manufacturing processes and the synthetic chemical dyes. Colour affects the aesthetic value of water, if coloured effluent is discharged to nature, photosynthesis activity is limited which will have prejudicial effects on aquatic ecosystems [3].

Table 1: Physicochemical characteristic of the pharmaceutical Effluent

Parameters	Concentration	WHO (STD)	NESREA(STD)
Colour of the effluent	Purple (Absorbance of 5.073)	-	-
pH	7.55	6-9.5	6-9
Total hardness mg/L	444	70	-
Conductivity μS/cm	359	-	
Nitrate mg/L	19.7	20	10
Phosphate mg/L	5.38	-	5
Chloride mg/L	172	250	600
Sulphate mg/L	431	500	500
Alkalinity mg/L	35	-	-
BOD	46.6	-	-
COD	229	50	
TSS	2.34	30	
TDS	4.18	<1200	2000
Turbidity (NTU)	870	5	-

WHO standard from Olaitan *et al*., 2014 and National Environmental Standard and Regulation Enforcement Agency of Nigeria (NESREA), 1991)

Table 2: Proximate composition of theseed of *Phoenix dactylifera*

Parameters	Concentration (%)
Ash	1.55
Moisture	1.15
Fibre	2.25
Fat	14.9
Protein	8.05
Carbohydrate	72.1

Proximate analysis of the seed of *Phoenix dactylifera*

Result obtained from proximate analysis is recorded in Table 2. From the Table, the ash content of the seed of *Phoenix dactylifera* is recorded as 1.547%. The ash content shows the presence of carbon compounds and inorganic components in the form of salts and oxides [23]. Carbon plays a critical role in the adsorption and removal of metals, colour and particles from wastewater because of its porous nature [14]. This is an indication that the seed of *Phoenix dactylifera* in its granular or ash form can act as a coagulant. Moisture content is 1.15%, this shows that *Phoenix dactylifera* seed could be stored for a very long time since high percentage of moisture on seeds could lead to high microbial activities during storage hence facilitating spoilage [4]. Fibre content, fat content and protein were found to be (2.25, 14.935 and 8.05 %) respectively. Carbohydrate content of *Phoenix dactylifera* seed is 72.069%. Carbohydrate has oxygen and hydrogen elements as some of its chemical composition, therefore, the propensity of the formation of charges such as hydrogen and oxygen ions [17]. Carbohydrate has oxygen atom, in solution it becomes oxygen ion which is negatively charge and can attract metallic ions and possibly remove them from solution.

Impact of coagulant dosage, pH and time on the colour removal efficiency

Figures 3 and 4 are Plots of colour removal efficiency against dosage at varying pH and dosages at constant time of 50 minutes. The Figures depict that the coagulant dosages and pH have significant effect in the colour removal efficiency, thus as the coagulant dosage decreases from 500-100 mg/L, there is an increase in the colour removal efficiency of the pharmaceutical effluent. This is because above 100 mg/L of coagulant dosage, excess coagulant has been introduced, therefore, restabilization of charges take place consequently a decrease in the colour removal efficiency is detected [12,6,18]. Lowest pH favour the highest colour removal efficiency. The maximum colour removal efficiency lies at 93.81% at coagulant dosage of 100 mg/L and pH of 2 in both Figures.

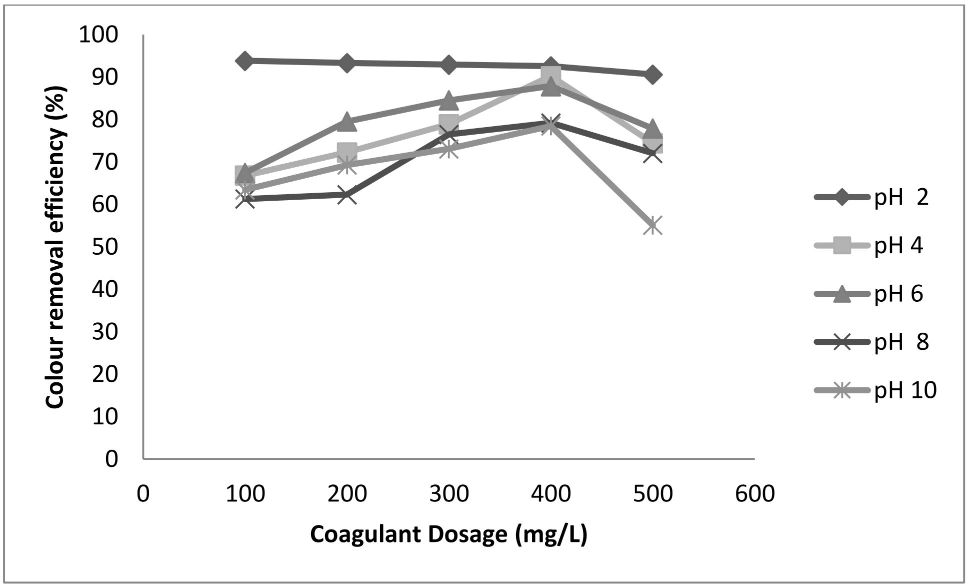

Figure 3: Plot of colour removal efficiency against coagulant dosages with varying pH at time of 50 mins

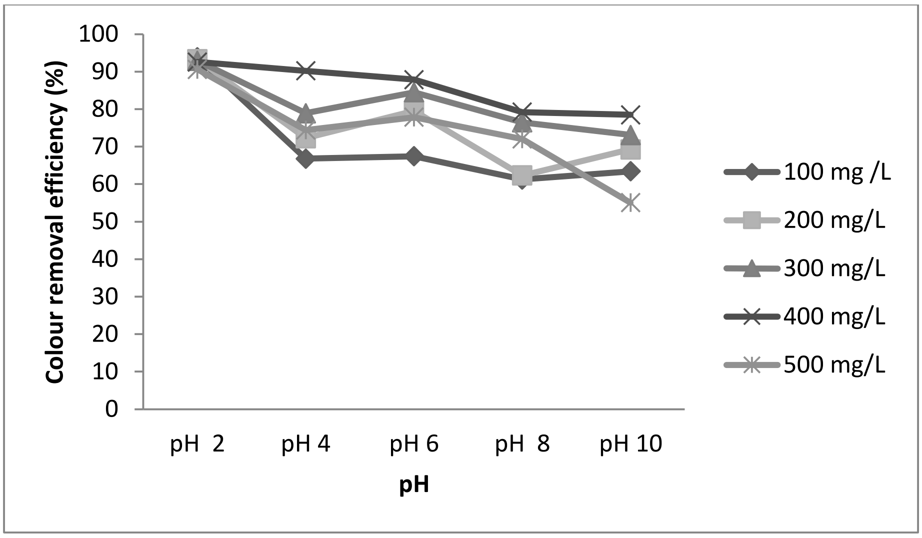

Figure 4: Plot of % colour removal efficiency against pH with varying coagulant dosages at time of 50 mins

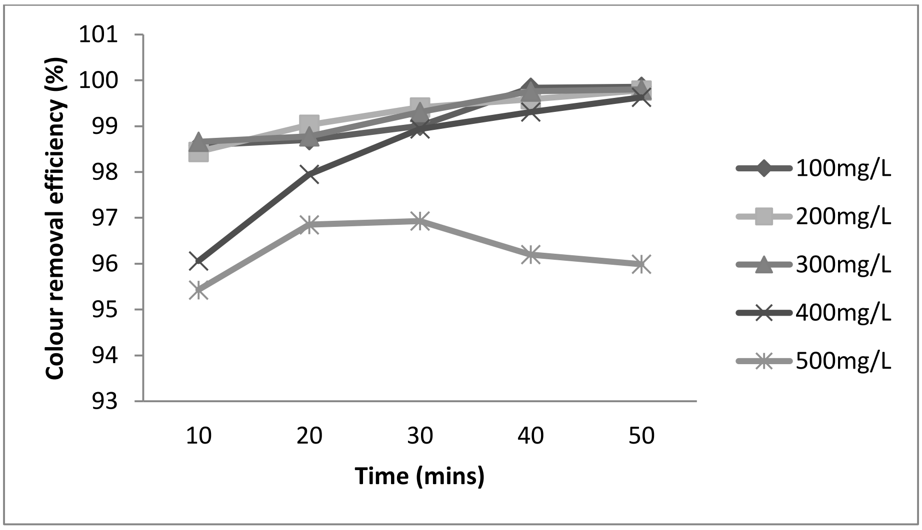

Figure 5: Plot of % colour removal efficiency against time with varying coagulant dosages at pH 2

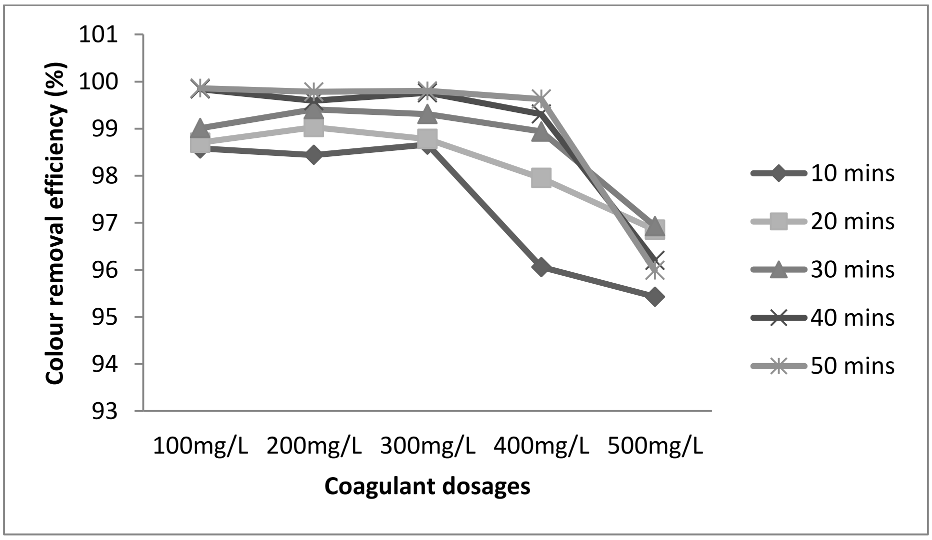

Figure 6: Plot of % colour removal efficiency against coagulant dosages with varying time at pH 2

Time is another significant variable that determines colour removal efficiency as can be observed in Figures 5 and 6. The observable pattern of coag-flocculation behavior in Figures 5 and 6 shows that colour removal efficiency increases as the time ascends to 50 mins with the coagulant dosage decreasing from 500 mg/l to 100 mg/L. The optimal colour removal efficiency is 99.8% obtained at the settling time of 50 mins and dosage of 100 mg/L.

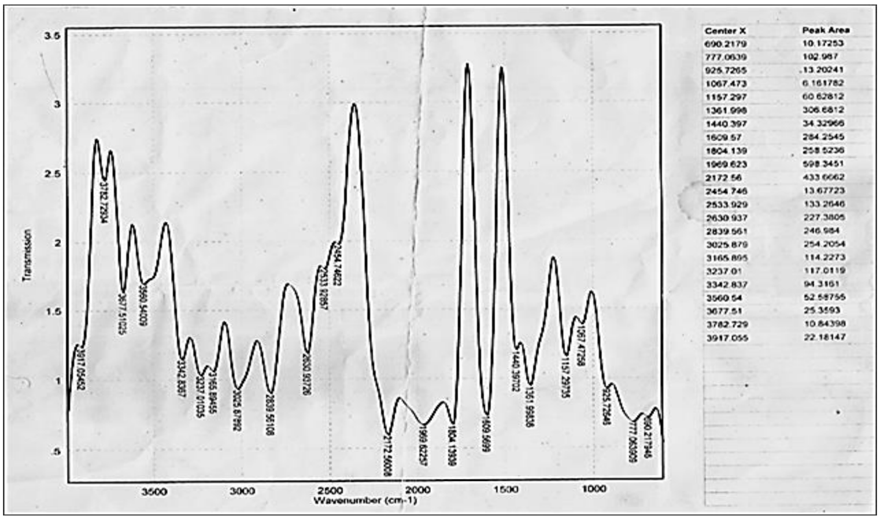

Figure 7: FTIR spectra of Phoenix dactylifera before coagulation- flocculation process

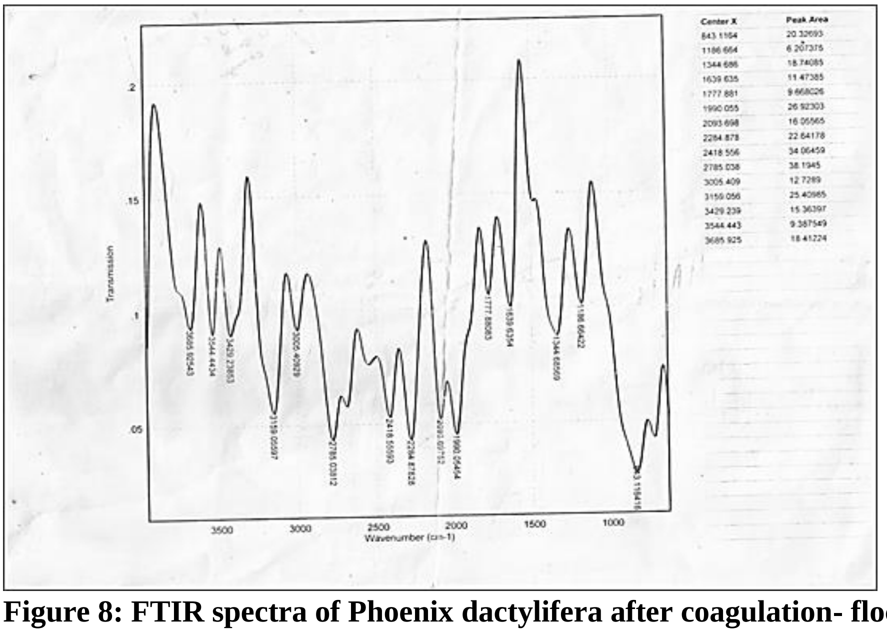

Figure 8: FTIR spectra of Phoenix dactylifera after coagulation- flocculation process

IR analysis

IR analysis of the seed of *Phoenix dactylifera* before and after coagulation-flocculation process was done using Fourier transformed infrared spectroscopy (FTIR) and the result in Figures 7 and 8. Figure 7 shows FTIR spectra of *Phoenix dactylifera* before coagulation-flocculation process. Spectra bands at 3917.055 cm^{-1}, 3782.729 cm^{-1}, 3560.540 cm^{-1}, 3342.837 cm^{-1}, 3237.010 cm^{-1} and 3165.895 cm^{-1} are assigned to O-H stretch which depicts the presence of alcohol. 3025.879 and 2839.561 cm^{-1} denote C-H stretch from alkane group, this shows the presence of carbon and hydrogen in the date seeds. This report is in agreement with the work of Praveen, (2012) [25]. Absorption band at 2533.929 cm^{-1} is O-H stretch from carboxylic acid, 2172.560 cm^{-1} shows S-C≡N stretch from thiocyanate. Spectral bands at 1969.623 cm^{-1}, 1804.139 cm^{-1} and 1609.570 cm^{-}

^{1} are assigned C-H bend which suggests the presence of an aromatic ring. 1440.397 cm^{-1} and 1361.998 cm^{-1} signified O-H bend from carboxylic acid. 1157.297 cm^{-1} and 1067.473 cm^{-1} is C-O stretch. Absorption bands at 777.0639 cm^{-1} and 690.2179 cm^{-1} are C-H bend from aromatic compound.

Figure 8 is FTIR spectra of *Phoenix dactylifera* after Coagulation- flocculation process. It was observed from the Figure that the spectral bands at 3005.409 cm^{-1}, 3685.925 cm^{-1}, 3544.443 cm^{-1}, 3429.239cm^{-1}, 3159.056 cm^{-}1, 3005.409 cm^{-1}, and 2785.038 cm^{-1} denote O-H stretch. 2093.698 cm^{-1} indicates N=C=S stretch, 1990.055 cm^{-1} and 1639.635 cm^{-1} is C-H bend from aromatic ring, 1777.881cm^{-1} is C=O stretch , 1344.686 cm^{-1} is O-H bend, 1186.664 cm^{-1} is C-O stretch. Comparing the FTIR spectra of the coagulant before and after coagulation-flocculation process (Figures 7 and 8), it can be seen that there is a remarkable shift in the spectra bands, some new bands were formed and some bands were removed in Figure 8, this is as result of interaction between the colloid particles of pharmaceutical effluent and that of the coagulant.

SEM analysis of Phoenix *dactylifera*

Figures 9 and 10 are the SEM analyses result of the Phoenix *dactylifera* before and after coagulation-flocculation process. Critical examination of Figure 9 discloses that the surface of this coagulant look sticky and rough with tiny pores in it. The rough sticky surface and pores are the point of attachment of the colloidal particles of the pharmaceutical effluent. This property makes *Phoenix dactylifera* to be qualified as suitable coagulant.

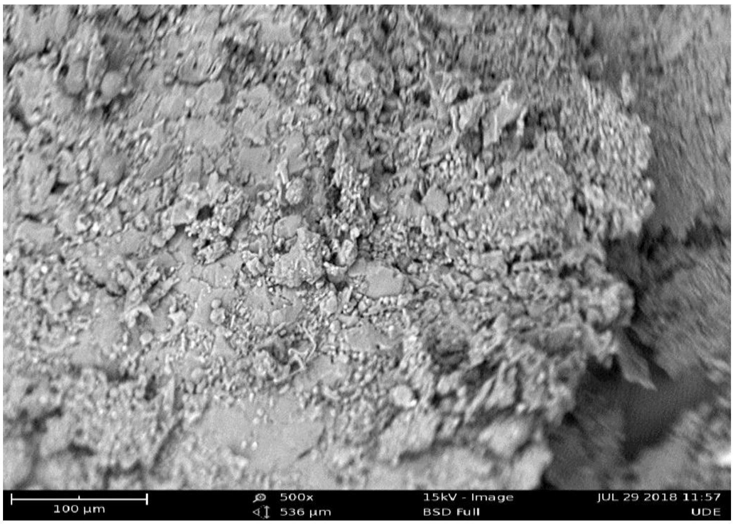

Figure 9: SEM of Phoenix dactylifera before Coagulation- flocculation process

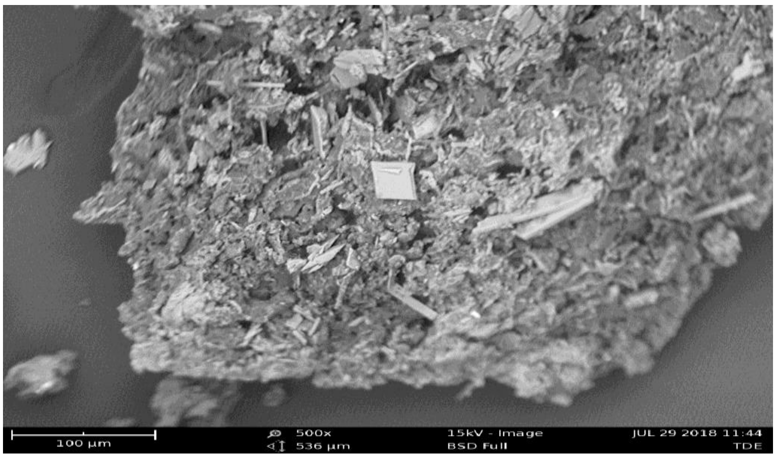

Figure 10: SEM of Phoenix dactylifera after Coagulation- flocculation process

Inspection of Figure 10 shows that coagulant surface is compressed as a result of the rough sticky nature of the coagulant which attracted the colloidal particles of the pharmaceutical effluent thus clumped together. These changes in the surface condition of the coagulant after coagulation-flocculation process demonstrated that the seed of *Phoenix dactylifera* removed pollutants from the pharmaceutical effluent.

Conclusion

At optimum condition, *Phoenix dactylifera* is found to be an effective natural coagulant in the treatment of Pharmaceutical effluent. Coagulant dosage of 100 mg/L, pH 2 and time of 50 mims were found to give the highest colour removal efficiency. FTIR spectra of the coagulant after coagulation-flocculation process indicated some shift in wave number indicating bond breakage and displacement of functional group hence color removal and other pollutants was suggested. SEM image before coagulation- flocculation process established that *Phoenix dactylifera* has rough surface and tiny pores. SEM image of the *Phoenix dactylifera* after using it to treat pharmaceutical effluent clearly showed that some particles of Pharmaceutical effluent had adsorbed on the surface of the coagulant, this further proved that the *Phoenix dactylifera* is a good coagulant for colour removal.

References

1. Abdessalem M., Ali Ferchichi, Nizar Chaira, Mohamed B. S., Mohammed B. and Threadgill M. P,, (2008). Physico-Chemical Characteristics and Total Quality of Date Palm Varieties Grown in the Southern of Tunisia. Pakistan Journal of Biological Sciences, 2008; 11: 1003-1008.
2. Abioye O.P., Afolayan, E.O. and Aransiola, S.A., (2015). Treatment of Pharmaceutical Effluent by *Saccharomyces cerevisiae* and *Torulaspora delbrueckii* ; Isolated from Spoilt Water Melon. Research Journal of Environmental Toxicology, 9: 188-195.
3. Ahmadi, N. Chaibakhsh and Zanjanchi, M.A (2016). Use of *D*escurainia Sophia *L*. As a natural coagulant for the treatment of dye-containing wastewater. Environ. Prog. Sustainable Energy, 35: 996–1001.
4. Ajayi O. B., Akomolafe S. F., Adefioye A. (2014). Proximate Analysis, Mineral Contents, Amino Acid Composition, Anti-Nutrients and Phytochemical Screening of *Brachystegia Eurycoma* Harms and *Pipper Guineense Schum and Thonn*. American Journal of Food and Nutrition, (2); 11- 17.
5. Al-Alawi, R.A., Al-Mashiqri, J.H., Al-Nadabi, J.S.M., Al-Shihi BI, Baqi Y. (2017). Date Palm Tree (*Phoenix dactylifera* L.): Natural Products and Therapeutic Options. *Frontiers in Plant Science*. ;8:845
6. Altaher, H. E. Tarek, Khalil and R. Abubeah, (2016). An Agricultural waste as a novel coagulant aid to treat high turbid water containing humic acids. *Global NEST Journal*, 18(2), 279-290.'
7. APHA , AWWA, and WEF (2012) Standard Methods for the Examination of Water and Wastewater. 22nd Edition, New York
8. Asrafuzzaman, Md., Fakhruddin, A. N. M., and Alamgir Hossain Md. (2011). Reduction of Turbidity of Water Using Locally Available Natural Coagulants. International Scholarly Research,2(3):1-6.
9. Association of Official Analytical Chemists (AOAC). Official Methods of Analysis of AOAC International, 17th ed.; AOAC International: Gaithersburg, MD, USA, 2000.
10. Bhagawan Saritha, D.P, Shankaraiah, G. and Yamuna rani M. (2017). Pharmaceutical wastewater treatment using chemical and natural coagulants. 3rd National Conference on Innovative Research in Civil Engineering 1-5
11. Economic and Social Commission for Western Asia,(ESCWA) (2003). Waste-Water Treatment Technologies: a General Review, United Nations, New York p. 4

12. Harold, V. 1963. Practical Chemical Biochemistry. 3rd Edition. William Heinemann Medical Books Ltd.: New York, NY. 122, 184.
13. Järup, (2003). Lars. Hazards of heavy metal contamination. British Medical Bulletin, 68: 167–182
14. Jatto, O.E., Asia, I.O. and Medjor, W.E. (2010). "Proximate and Mineral Composition of Different Species of Snail Shell". Pacific Journal of Science and Technology. 11(1):416-419.
15. Kolpin, D.W., Furlong, E.T., Meyer, M., Thurman E.M., Zaugg, S.D., Barber, L.B. and H.T. Buxton. Pharmaceutical, hormones and other organic waste water contaminants in U.S. streams, 1999 – 2000.
16. Muruganandam Saravana L., Kumar, M.P. Amarjit Jena, Sudiv Gulla and Bhagesh Godhwani (2017). Treatment of waste water by coagulation and flocculation using biomaterials. IOP Conf. Series: Materials Science and Engineering 263:1-12
17. Njuguna, A., Mayabi, A. and Ndirangu W. (2014). Removal of organic pollutants from pharmaceutical industry wastewater by chemical coagulation and bentonite clay pretreatment. Proceedings of 2014 International Conference on Sustainable Research and Innovation, 5: 205-208
18. Nurul' Ain Binti Jamion, Nor Haziqah Binti Abd Hafiff, Nurul Huda Abd Halim, Sheikh Ahmad Izzaddin Sheikh Mohd Ghazali, Jamil Mohamed Sapari (2017). Preparation of Date Seed Activation for Surfactant Recovery. Malaysian Journal of Analytical Sciences, 21(5): 1045 – 1053
19. Okolo, B.I., Nnaji P.C., Menkiti, M. C. Onukwuli, O. D. (2015). A Kinetic Investigation of the Pulverized Okra Pod Induced Coag-Flocculation in Treatment of Paint Wastewater. American Journal of Analytical Chemistry, 6: 610-622.
20. Olaitan O. J., Sulola E. O., Kasim L. S., Daodu J. O. (2014). Physico-Chemical Characteristics of Pharmaceutical Effluents from Sango Industrial Area, Nigeria, Bull. Env. Pharmacol. Life Sci., 3 (10) :78-81
21. Praveen K. V. (2012). Date Fruits (*Phoenix dactylifera* Linn): An Emerging Medicinal Food,Critical Reviews in Food Science and Nutrition. 52:3,249-271
22. Shafad, M.R., Ahamad, I,S., Idris A. and Zainal Abidin Z. (2013). A preliminary Study on Dragon Fruit Foliage as Natural Coagulant for Water Treatment. International Journal of Engineering Research & Technology (IJERT), 2(12):1057-1063
23. Usman Ameh. (2006). "Standard Operating Procedure National Agency for Food and Drug Administration and Control (NAFDAC) Boriki Port Hacourt, Nigeria". PP 07/14.Heinemann Medical Books Ltd.: New York, NY. 122, 184.
24. Vineeta Kumari, A. K. Tripathi, and Kannan, A. (2017). Evaluation of Heavy Metals Toxicity of Pharmaceuticals Industrial Wastewater by Pollution Indexing and Chemometric Approaches**.** International Journal of ChemTech Research**,** ,10(5): 718-730
25. Vishali S. and Karthikeyan, R. (2014).*Cactus opuntia* (*ficus-indica*): An eco-friendly alternative coagulant in the treatment of paint effluent. Journal of Desalination and Water treatment, 56(6):1489-1497.