Coag-Flocculation of Phosphorus Containing Waste Water Using Afzella-Africana Biomass

K.A. Babayemi Department of chemical Engineering Anambra State University Uli Nigeria

O.D Onukwuli

Department of chemical Engineering Nnamdi Azikiwe University, Awka Nigeria

A.O. Okewale Department of chemical Engineering Landmark University, Omuaran, Osun State Nigeria

Abstract

Affzella- Africana (AF), an eco-friendly biomass was used as a coagulant in this work for the waste water treatment. AF was characterized and the result of characterization shows that, the percentage content of the active agent responsible for the coagulation (protein) is 33.75%. The result of effluent analysis before and after treatment indicates that 90.57%, 37.51%, 89.94% and 84.95% of phosphorus, magnesium, sulphates and chlorides have been removed. Also that, no traces of iron, lead, copper and nitrates concentration of which were respectively 2.75mg/l, 0.90mg/l, 12.00mg/l and 0.10mg/l in the initial sample were found after treatment. Coagulation kinetics parameters such as order of reaction, α and rate constant, K were determined. Coagulation performance was measured in nephelometric jar test. Maximum parameter values are recorded at K of 5x10⁴ l/mg.min, α of 2 and optimum pH of 6.

Keywords: Coag-flocculation, biomass, Afzella-Africana Phosphorus

1. Introduction

Although industrialization is inevitable, various devastating ecological and human disasters which have continuously occurred over the last three decades or so implicate industries as major contributors to environmental degradation and pollution problems of various magnitudes. Rapid industrial developments in developed and developing countries have increased hazardous wastes generation several fold (Fridrikhsberg, 1984) Phosphorus pollution is a major problem resulting from improper disposal of the generated wastes especially from indigenous chemical industries such as fertilizers, soap and detergent manufacturing companies. The excess content of phosphorus in receiving waters leads to extensive algae growth (eutrophication), coloured, murky, odourous and unwholesome surface waters, fish kills and loss of many other aquatic animals. Failure to halt further deterioration of such environmental quality might jeopardize the health of large segment of the population with serious political and socio-economic implications.

One of the most commonly used methods for the removal of suspended solids in waste water is the addition of coagulant and flocculation aids such as alum, ferric chloride and long-chain polymers (AWWA, 1997), (James M. Ebeling and Sarah R. Ogden, 2004). Similar electric charges on small particles in water cause the particles to naturally repel each other and hold the small, colloidal particles apart and keep them in suspension. The coagulation-flocculation process neutralizes or reduces the negative charge on the particles. Then, the initial aggregation of the destabilized colloidal particles is now encouraged by the van der Waals force of attraction to form microfloc. Flocculation is the process of bringing together the microfloc particles to form large agglomerations by physically mixing them or through the binding action of flocculants.

Many coagulating agents are used in processes for treating water, such as inorganic coagulants (salts of aluminum and iron), synthetic and natural organic polymers (Cardeso, 2007). Aluminum sulphate is widely used world wide as a coagulant, but recently its use has been questioned due to evidence that Alzheimer's disease may be as a result of extensive intake of alum (Mclachlan, 1995; Divakaran and Pillai, 2001; Ani, et-al 2001) Moreover, aluminum is not biodegradable, and can cause disposal problems and require treatment of the generated sludge (Moraes, 2004; Santana et-al, 2010). The search for a more environmentally friendly and inexpensive coagulation as a viable alternative for conventional coagulants has therefore become an important challenge in the water treatment process. Some of these natural coagulants and flocculants that have been investigated by other researches include Chitosan (Ozacar and Sengli, 2002) aqueous extract of the seed of Moringa Oleifera (Oladoja and Aliu, 2008), extracts of okra seed (Roberts, 1997).

This study proposes the use of Afzella-African seed as a viable alternative for conventional coagulants in the treatment of waste water containing phosphorus. Afzella- Africana (AF) is a perennial tree which occurs in many parts of Africa where it is used as food and widely employed in traditional medicine practice. It is variously known in vernacular as Uvala (Angola) Papao (Ghana), Akparata (Nigeria), Mkora (Tanzania), Bolengu (Zaire), (Akah et-al, 2007). It grows in semi-deciduous forest and sudano-Guinea Savannah of tropical West Africa and in the dry forest Savannah borders in Ghana (Hawthrone, W.D, 1995). The seeds (fig 1) are edible and are used as thickening agents in soup in eastern Nigeria. Also, saw dust from the wood is used as a febrifuge, analgesic, laxative, emetic, anti-haemorrhagic and aphrodisiac (Akah, et-al 2007).

1.1 Coagulation kinetics

The time evolution of the clusters size distribution for colloidal particles can be described by the equation (Smoluchowski, 1917), (Ani, et-at, 2011)

$$\frac{\mathrm{dC}_{\mathrm{n}}}{\mathrm{dt}} = 1/2 \qquad \sum_{\mathrm{i}+1} K_{\mathrm{in}} \quad C_{\mathrm{i}} C_{\mathrm{j}} - C_{\mathrm{n}} \sum K_{\mathrm{in}} C_{\mathrm{i}}$$
(1)

where $C_{n(t)}$ is the time-dependent number concentration of n-fold cluster, t is the time, and K_{ij} are the elements of the rate kernel which control the rate of the coagulation between an i-fold and j-fold cluster. In the smoluchowski analysis, the coagulation process in approximated to be controlled by Brownian motion and monodispersed suspension (Ani, et al, 2011). So, the analysis attempts to interpret the kinetics of rapid coagulation on the basis of diffusion (Brownian) motion which is best studied during the early parts of the coagulation process (t \leq 30min) Menkiti et-al; 2010; Holthof et al, 1996; Fridriskhberg, 1984; Vanzanten and Elimelech, 1992; Suidan, 1998; Ma et al, 2001; WST, 2005)

The rate of depletion of particle count (Turbidity removal) can generally be expressed as:

$$\frac{dc}{dt} = -KC^{\alpha} \tag{2}$$

based on the Brownian controlled, rapid coagulation (Fridriskhberg, 1984) Applying the method of separable variable and integrating equation (2) within the following limits; At t=0, c = c_0 , at t = t, c =c and α =2, yields

$$-\frac{dc}{dc^2} = Kdt \tag{3}$$

Integrating Eq(3) above yields

$$\frac{1}{c} = \frac{1}{c_0} + Kt \tag{4}$$

Materials And Methods Collection of Effluent Sample

The turbid effluent was collected from the Federal Superphosphate Fertilizer company, Kaduna, Nigeria. A 20litre polyethylene bottle was thoroughly cleaned and rinsed with effluent sample before the final sample collection, after which the bottle was tightly closed and taken to the laboratory for experimental work. **Effluent Analysis** The analysis of the collected waste water before and after treatment was carried out using standard method (APHA, 1998) and the results of the analysis are presented in Table 2.

Afzella-Africana (AF) preparation

AF seeds were purchased at Nkwogbe market Ihiala, Anambra State. The seeds were dried in the sun for about three weeks after which their outer shells were removed. The inner seeds were further subjected to drying for another two weeks in order to reduce the moisture contents of the seeds. The dried seeds were then ground into fine power and sieved through 0.2mm sieve. The fraction with particle size less than 0.2mm was then processed into a coagulant using standard methods (Fernandez –kim, 2004; Ani, et al, 2011). The percentage of phosphorus removal was calculated using equation (5).

$$C_{o} - C_{i} \times 100$$
 (5)

Where C_o and C_i are the phosphorus concentration in raw and treated solution respectively.



Fig. 1: samples of Afzella Africana seed

2.2 Experimental procedure

The effects of various parameters were determined by jar test procedure. A period of 2 mins was allowed for the rapid mixing of the effluent containing 100mg/l AF at 200rpm followed by a 30mins period of slow mixing at 80 rpm. Then, the suspension was transferred into a 200ml measuring cylinder to allow sedimentation. After 5mins, 10ml of the aliquot of the clarified sample in the cylinder was carefully collected with the aid of 10ml pipette a few milliliters from the top of the cylinder and residual turbidity was measured using turbidmeter model WZS-185 MC. The subsequent clarified sample were collected every 10minutes and turbidity measured likewise in each case. Coagulation pH was adjusted using Hydrochloric acid and sodium hydroxide and DELTA 320 pH meter was used for pH determination. The sample procedure was repeated for 200mg/l, 300mg/l, 400mg/l and 500mg/l of the AF coagulant respectively. The results obtained for turbidity of sample in NTU were converted to concentrations (mg/l) my multiplying with a factor of 2.20 (Ozacar and Sengli, 2002).

3. Results and Discussion

The characterization results of the coagulant are presented in table (1). The active agent responsible the coagulation in the coagulant is protein. The percentage protein content of AF is 33.75%.

ble 1: Characterization res	unts of coagui
Parameter	AF
Moisture content (%)	8.5000
Ash content (%)	3.3800
Lipid content (%)	27.1800
Crude protein (%)	33.7500
Carbohydrate (%)	37.2000
Crude fibre (%)	8.0000

Table 1: Characterization results of coagulant

Parameter	S.I. Unit	Before Adsorption	After Adsorption
Colour	Hazen	250	18.50
рН		8.0	10
Conductivity	$\mu/ \text{ cm}^3$	$1.88 imes 10^4$	$2.1 imes 10^4$
Turbidity		Not clear	Mil clear
Total solid	Mg/l	6530	471.8
Acidity	Mg/l	30	20
Alkalinity	Mg/l	485	505
Manganese	Mg/l	410.7	3.35
Potassium	Mg/l	420	1.28
Chloride	Mg/l	996.43	150
Nitrogen	%	27.65	1.93
Chemical oxygen demand	Mg/l	289.77	71.77
Dissolved Oxygen	Mg/l	28.52	76.50
Biochemical oxygen demand	Mg/l	318.29	48.27
Sulphate	Mg/l	185	18.6
Nitrate	Mg/l	0.1	-
Copper	Mg/l	12	-
Phosphorus	Mg/l	378.34	35.67
Total Hardness	Mg/l	80	50
Lead	Mg/l	0.9	-
Magnesium	Mg/l	19.46	12.16
Iron	Mg/l	2.75	-

Table 2: Characterization of waste water effluent before and after coagulation

3.1 Effect of coagulant Dosage

From the obtained results, it was observed that coagulant dosage played an important role in turbidity removal. Increase in coagulant dosage brought about an increase in turbidity removal. By increasing the coagulant AF dosage from 100mg/l to 500mg/l at the same pH of 6 and 10 mins of sedimentation, turbidity of between 69.97% and 73.72% was removed respectively. Similar results were obtained for AF coagulant at pH of 2,4,8,10 respectively and are graphically presented in figures (2 to 6)

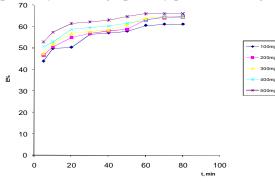


Fig. 2: Coagulation efficiency profile for varying AF dosage at pH =2

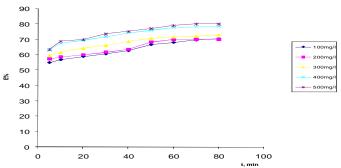


Fig. 3: Coagulation efficiency profile for varying AF dosage at pH =4

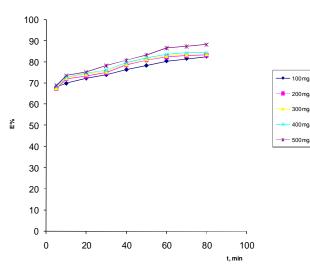


Fig. 4: Coagulation efficiency profile for varying AF dosage at pH =6

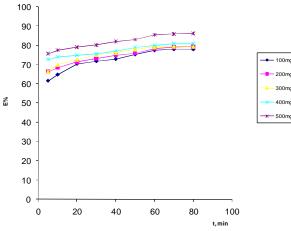


Fig. 6: Coagulation efficiency profile for varying AF dosage at pH =10

3.2 Effect of pH

pH as a parameter plays important roles in determining the ability of coagulants to remove colloidal particles. Removal efficiency of the coagulant AF increased with increasing pH. The results which are graphically presented in figure 7 show that, with an increase in pH from 2 to 6, there was a progressive increase in removal efficiency of the coagulant from 65.95% to 86.59% respectively. However, a light decrease in the coagulant performance was observed as pH was further increased from 6 to10.

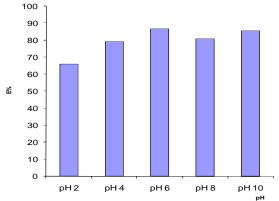


Fig. 7: Effect of pH on coagulation performance of AF at 60 mins and dosage of 500 mg/l

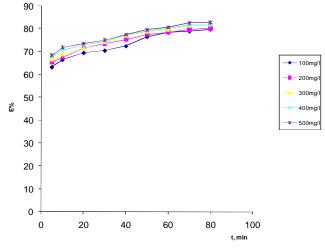


Fig. 5: Coagulation efficiency profile for varying AF dosage at pH =8

3.3 Coagulation kinetic results and parameters

The kinetic results of phosphorus containing effluent for varying pH and dosage are presented in table 3-7. The linear equations, R^2 , C_o and K contained in the various tables were determined from plots I/C_t versus time as shown in figures (8 to 12). The values of R^2 being greater than 0.9000 are satisfactory and this confirms the theory of perikinetic as the controlling mechanism of coag-flocculation under study (Menkiti, 2010). The values of K obtained from the linearized equations from the figures (8 to 12) were used to formulate the rate equations for the removal of turbidity from waste water as contained in tables (3 to 7). The highest value of K was obtained at the optimum value of pH 6.

Coagulant dosage (mg/l	K-value (1mg.min)	Rate equation (mg/l. min)	\mathbf{R}^2	α	C _o (mg/l)
100	3x10 ⁻⁵	$-r = 3x10^{-5}C^2$	0.9260	2	250
200	$3x10^{-5}$	$-r = 3x10^{-5}C^2$	0.9360	2	200
300	$4x10^{-5}$	$-r = 4x10^{-5}C^2$	0.9380	2	200
400	$3x10^{-5}$	$-r = 3x10^{-5}C^2$	0.8950	2	200
500	$3x10^{-5}$	$-r = 3x10^{-5}C^2$	0.9060	2	200

Table 4; Coagulation	Kinetics of AF f	for a second	order system	at nH =4
Table 7, Coaguiation	Minutes of AF	ior a second	oruci system	ai pii -7

Coagulant dosage (mg/l	K-value (1/mg.min)	Rate equation (mg/l. min)	\mathbf{R}^2	α	C _o (mg/l)
100	$4x10^{-5}$	$-r = 4x10^{-5}C^2$	0.9700	2	250
200	5×10^{-5}	$-r = 5x10^{-5}C^2$	0.9300	2	200
300	5×10^{-5}	$-r = 5x10^{-5}C^2$	0.9930	2	166.67
400	8×10^{-5}	$-r = 8x10^{-5}C^2$	0.9890	2	142.85
500	$9x10^{-5}$	$-r = 9x10^{-5}C^2$	0.9810	2	142.85

Table 5; Coagulation Kinetics of AF for a second order system at pH=6

Coagulant dosage (mg/l	K-value (1/mg.min)	Rate equation (mg/l. min)	\mathbf{R}^2	α	C _o (mg/l)
100	9x10 ⁻⁵	$-r = 3x10^{-4}C^2$	0.9880	2	142.85
200	5x10 ⁻⁵	$-r = 3x10^{-4}C^2$	0.9740	2	142.85
300	5×10^{-5}	$-r = 4x10^{-4}C^2$	0.9730	2	142.85
400	5x10 ⁻⁵	$-r = 3x10^{-4}C^2$	0.9730	2	142.85
500	5x10 ⁻⁵	$-r = 3x10^{-4}C^2$	0.9750	2	142.85

Table 6; Coagulation Kinetics of AF for a second order system at pH = 8

Coagulant dosage (mg/l	K-value (1/mg.min)	Rate equation (mg/l. min)	\mathbf{R}^2	a	C _o (mg/l)
100	9x10 ⁻⁵	$-r = 9x10^{-5}C^2$	0.9620	2	166.67
200	9x10 ⁻⁵	$-r = 9x10^{-5}C^2$	0.9930	2	142.85
300	1×10^{-4}	$-r = 1x10^{-4}C^2$	0.9930	2	142.85
400	$9x10^{-5}$	$-r = 9x10^{-5}C^2$	0.9910	2	125
500	1×10^{-4}	$-r = 1x10^{-4}C^2$	0.9860	2	125

Table 7; Coagulation Kinetics of AF for a second order system at pH =10

Coagulant dosage (mg/l	K-value (1/mg.min)	Rate equation (mg/l. min)	\mathbf{R}^2	α	C _o (mg/l)
100	8x10 ⁻⁵	$-r = 8x10^{-5}C^2$	0.9690	2	166.67
200	7×10^{-5}	$-r = 7x10^{-5}C^2$	0.9870	2	142.85
300	8×10^{-5}	$-r = 8x10^{-5}C^2$	0.9830	2	142.85
400	8×10^{-5}	$-r = 8x10^{-5}C^2$	0.9830	2	125
500	8x10 ⁻⁵	$-r = 8x10^{-5}C^2$	0.9690	2	125

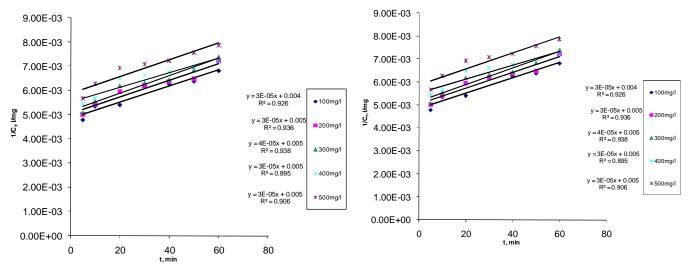


Fig.8: Kinetic plot of 1/C_t **versus time for varying** varying



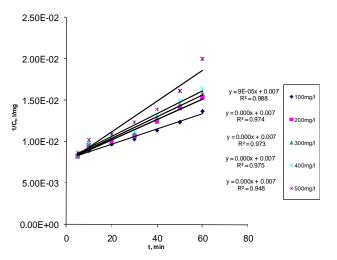


Fig.10: Kinetic plot of 1/C_t versus time for varying AF dosage at pH=6

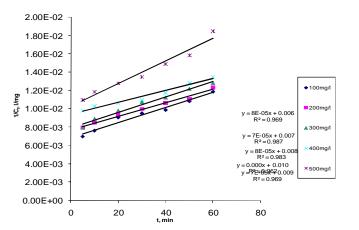


Fig.12: Kinetic plot of 1/C_t versus time for varying AF dosage at pH=10



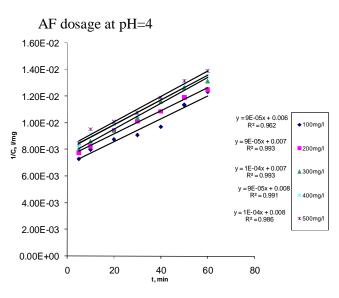


Fig.11: Kinetic plot of $1/C_t$ versus time for

AF dosage at pH=8

Conclusion

Afzella-Africana was effectively used for the coagulation of phosphorus contaminated suspension. Maximum coagulation of the suspension was achieved at 500mg/l AF concentration and the removal percentage was 73.72% after 10mins at the optimum pH of 6. The kinetics of the coagulation reaction results agree with previous similar works and conform with theory of perikinetic coagulation (Menkiti et al, 2001; Ani et al, 2010)

Acknowledgement

The authors appreciate the managing Director and the Technical staff Federal Superphosphate Fertilizer Company, Kaduna for making the waste water effluent available for the work. Our appreciations also go toDr. Menkiti, M.C and Dr.Nwabanne J.T of the Department of Chemical Engineering Nnamdi Azikiwe University, Awka for their useful contributions to this work.

References

- Akah, P.A; Okpi, O; Okoli, C.O(2007) Evaluation of the anti-inflammatory, analgesic and antimicrobial activities of Afzella Africana. Nig. J. Nat. Prod. Med. , 11, 48-52
- Ani J.U, Menkiti, M.C and Onukwuli, O.D (2009), Coagulation and Flocculation Behaviour of Snail Shell. Coagulant in fibre-cement plant Effluent, J. Eng. Appl. Sci Vol. 67,2
- APHA and AWWA (1998); Standard Method for the Examination of water Effluent, New York, U.S.A
- AWWA (American Water Works Association) 1997, Water treatment plant design. American Water Works Association and American Society of Civil, Engineers, 3rd edition. MC Graw Hill, New York.
- Divakaran, V.N.S. Pillai, (2001) Flocculation Kaolinite suspension water by chitosan, Water Res. 35 (3904 3908).
- Fernandez-Kim(2004); physiochemical and functional properties of crawfish as affected by different processing protocols, M.Sc Thesis, Louisiana State University and Agricultural and Mechanical College, U.S.A.
- Fridriskhberg, D.A (1994), A course in colloid chemistry, Mir publishers, Moscow, Russia.
- Hawthorne, W.D (1995) Ecological profiles of Ghanaian forest trees. Oxford Forestry Institute, Oxford p.345.
- Holthof, H. et al (1996); Coagulation Rate measurement of colloidal particles by simultaneous static and dynamic light scattering, Langmuir 12, 5541-5549, Switzerland.
- Ma J. Li G et al (2001), Enhanced coagulation of surface wat4ers with high organic content by permanganate preoxiation; water science and Technology, Water supply vol. 1, No 1., pp 51-61. China.
- Mclachlan D.R.C (1995); Aluminum and the risk for Alzheimers disease, Environmetrics 6233-6275.
- Menkiti M.C (2010); Sequential treatment of coal washery effluents by biocoag-flocculation and activated carbon adsorption. Ph.D thesis. Nnamdi Azikiwe University, Nigeria.
- Moraes, L.C.K. Estudo da Coagulacao-ultrafiltra cao com o Biopholimero Quitosana para a producao de agua Potavel, Dissertacao de
- Mestrado programa de Pos-Graduacao em Engenharia Quimica, Universidade Estadual de Maringa, 2004 (in Portuguese).
- Oladoja M.A and Aliu Y.D (2008) Evaluation of plantain peelings ash extract as coagulant of colloidal particles in low p^H aqua system, Water Quality Research Journal, Canada.
- Ozacar, M. and Sengil, I.A (2000); Effectiveness of tannis obtained from velonia as a coagulant aid for dewatering of sludge. Water Res. 34(4); 1407 1412.
- Roberbts G.A.F, Adv. Chitin Sci. 11 (1997), 22, proceedings of the 7th International conference on Chitin R Chitosoa Lysons.
- Smoluchowski M. (1917), Verscuheiner Mathematischen Theories der koagulations kinetic kolloides lousungen. Phs. Chem. 92. 129-168
- Swidan, MT. (1998); Coagulation and Flocculation, Environmental engineering unit operations and Unit process Lab. Manical, 4th Ed. Association of Environmetal Engineering professors, Canada.
- Van Zanten, J.H Elimelechi, M (1992) Determination of Absolute coagulation Rate constant by Multiangle light scattering, Journal of colloids and interface science, vol. 154, No 1, U.S.A
- W.S.T (2005), About coagulation and Flocculation; Information Bulletin, U.S.A.