



Research Article

COMPARATIVE STUDIES ON REMOVAL OF TURBID-METRIC PARTICLES (TDSP) USING ANIMAL BASED CHITO-PROTEIN AND ALUMINIUM SULFATE ON PAINT WASTEWATER (PWW)

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ABSTRACT

The comparison of parametric statistics for effective removal of turbid-metric particles (TDSP) with extracted natural coagulant “chito-protein” (CP) and aluminum sulphate has been successfully studied using PWW through coagulation process. PWW contains 2669mg/l relative to the national environmental regulation standard of 100mg/l for dischargeable effluents. CP was extracted from snail shell flour (SSF) using the modified Fernandez-kin method. The extracted CP contains mainly protein (86%). From the FTIR analysis traces of lysine, valine, serine and Phenylalanine were observed from the major functional groups (NH_3^+ bending, NH_3^+ rocking, CH_3 asymmetric, OH bending and benzene ring vibration observed at 1456 cm^{-1} , 1154 cm^{-1} , 1336 cm^{-1} , 781 cm^{-1} , 713 cm^{-1} respectively) present in CP. The unit cell dimension a_0 for CP were estimated as 21.3 through the sample's XRD spectra. The maximum TSDP (Total suspended and dissolved particles) removal efficiency of 91.3% was obtained at 4g/l, pH of 4, and 45°C at 25mins for CP-PWW while 90.2% was obtained at 2g/l, pH of 6, 35°C and at 20mins for Alum-PWW system. Floc strength of 1.03 was obtained using alum while a floc strength of 1.322 was obtained using CP. Collision efficiency (ϵ_p) of $5.03\text{E}+13$ and menkonu constant (k_m) of $6.00\text{E}-5$ were obtained for CP-PWW coagulation. CP can be an effective alternative to alum in treatment of PWW.

Keywords: Paint wastewater, coagulation, Chito-protein.

1. INTRODUCTION

The impact of discharging paint wastewater on Nigerian water bodies has become significant issue of national concern (Aniyikaiye et al., 2019; Izah et al., 20116; Alam et al., 2007). Paint wastewater results from production of water-based paints. Generally, paint wastewater contains a mixture of dissolved and suspended solids, among other contaminants in such that exceed the maximum discharge limit according to environmental effluent discharge regulation 1999 (Standards for discharge of effluent, 1999) (Menkiti and Ejimofor, 2016; Menkiti et al., 2016). For effective disposal, paint wastewater should be treated.

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Various methods have been applied in wastewater treatment such as: adsorption, filtration, sedimentation, centrifugation and coagulation among other separation methods (Pan et al., 2020; Ghernaout & Ibn-Elkhatab, 2020; Shankar et al., 2020; Menkiti et al, 2018; Vepsäläinen & Sillanpää, 2020).

Coagulation and flocculation processes have been identified as an excellent method of handling wastewaters especially such as contain colloidal particles (Khouini et al., 2020; Hube et al., 2020; Teh & Wu, 2014).. It is effective neutralization of the stabilization charges by introduction of counter charges thereby causing particle aggregation; these counter charges are introduced using coagulants (Ratnaweera, 2020; Jabin & Kapoor, 2020; Menkiti et al.,2016).

Coagulants are substances capable of supplying positive charges into the effluent sample which can neutralize the existing negative charges of the particles. For long, global utilization of these substances (chemical coagulants) are on the high side. Coagulants can be chemical or natural (Vijayaraghavan et al., 2011).

Chemical coagulants are either metallic salts or polymers that are employed in coagulation process. The main chemicals used as chemical coagulants include aluminum sulphate (alum), poly-aluminum chloride (PAC), alum potash, ferric sulphate or ferric chloride among others (Anthony,1997). These chemicals have been extensively used for wastewater management however, various limitations, such as ineffectiveness in low temperature samples, relative high procurement cost, detrimental effects on human health, production of large sludge volume and their effect on treated samples pH (Menkiti et al., 2015)], lead to global search for a replacement that will be natural, either from microorganisms, plants or animal source which will be biodegradable, safe to human health, of relatively low cost and may generate less sludge than chemical coagulants (Emodi, 2015).

Natural coagulants are coagulants obtained from natural materials. Some are sourced from waste materials or natural materials that are of less economical values, like shells, leaves, bark and wood of trees, some parts of fruits that are not edible among other sources. Many researchers have reported the use of moringa olifera extract (Francis, 2009), mucuna (Menkiti et al., 2010), tannin (Sanchez-Martin et al., 2010) etc. natural coagulants are sourced from nature(not chemicals) hence can be freely returned to nature without adverse effect. They are renewable and of less cost. If properly utilized generates less sludge volume.

The availability of snail shells as waste and the already known components (protein, calcium etc) arose the interest of using it as an active source (precursor) of coagulant for wastewater treatment. The shells are made of mostly calcium carbonate crystals organized in a matrix of proteins. The shells have been a source of chitosan production. (Ugonabo et al., 2012).

During chitosan production, the precursor passes through deproteinization (removal of loosely attached protein), demineralization, and deacetylation stages. During the deproteinization stage, the loosely attached proteins that bind the calcium matrix are removed and discarded as waste. This crude extract is called chito-protein.

This work characterized chito-protein (CP), established the best operating conditions for using it as a coagulant for paint wastewater treatment and compares the efficiency of using it to that of aluminum sulphate.

2. MATERIALS AND METHOD

2.1. Material collection

2.1.1. Paint wastewater

Paint wastewater was collected from a paint industry at Onitsha in Anambra state. The influence of sunlight was prevented by preserving the effluent in a black plastic air tight

container, the samples were characterized according to the standard methods adopted from American water works association (AWWA, 2005).

2.1.2. Snail shell

Snail shells were collected from Onitsha in Anambra State, Nigeria. The shells were washed, dried and processed to snail shell floor (SSF). The SSF were stored in air tight sack prior to coagulant extraction.

2.2. Experimental Method

2.2.1. Effluent Characterization

The physiochemical characteristics of paint wastewater were determined using AWWA standard procedure

2.2.2. Characterization of Bio-coagulant precursor

The bio-coagulant precursor was characterized based on standard methods as shown in Table 2.1.

Table 2.1. Standard method for characterization of the precursor

Properties	Test method
Protein content	ASTM D5712/15 (2016)
Tapped Bulk Density	ASTM C357/07 (2015)
Ash Content	ASTM D5040/90 (2016)
Moisture content	ASTM D5348/95 (2012)
Oil content	ASTM D5555/95 (2017)

2.2.3. Extraction of Bio-coagulant from precursor

CP was extracted using the modified Fernandez-Kim method (Menkiti et al., 2016). In this method, sample deprotonization, was carried out using a 1M NaOH solution. 100 g of SSF was continuously stirred at 70 °C for 2h in 500ml NaOH. The resultant mixture was filtered using filter sack. The resulting solid sample from the deproteinization process has the potential of being processed further to obtain chitosan. However, the extract (liquid filtrate) from de-protenization contains some percentage of radical protein (chito-protein or conchiolin) that will become a waste if not harnessed. Hence, the liquid filtrate containing the crude extract (chito-protein) was allowed to settle for about 40mins, the concentrated slurry at the bottom of the containing beaker was collected after decantation and dried. The potential of the dried sample obtained (chito-protein) as coagulant was harnessed in this present study.

2.2.4. Instrumental characteristic of CP

The CP was subjected to elemental characterization, FTIR and SEM instrumental characterization. Prior to the instrumental characterization, the sample was dehydrated using 100% methanol. Before subjecting the sample to the imaging system, CP was dried 120°C for 40min to ensure complete drying. Thereafter, the sample was glued to a stub and place on the vacuum chamber of Zeiss Evo EDX/WDS unit for SEM imaging. The prepared dried sample of CP was also subjected to FTIR characterization using Nexus Model 870 FTIR Spectrophotometer.

2.2.5. Coag-Flocculation Experiment

2.2.5.1. Influence of coagulant dosage

(i) 800mL of PWW was poured into six different 1000mL beakers after the initial sample parameters (pH and turbidity) were measured and recorded, 0.5g – 5g of the coagulants (CP and Alum) sample were dosed into the PWW samples. The resultant mixtures were subjected to 2 min rapid mixing at 250rpm ($G = 550 \text{ sec}^{-1}$), and 20 min slow mixing at 30 rpm using magnetic stirrer. 35min settling time was allowed at the end of the 20 mins flocculation time. The treated samples were allowed to settle for 35 min. At desired intervals, 20 mL was pipetted from the treated PWW for impact assessment. The data obtained were used in estimation of the best operation condition as regards the coagulant dosage. The residual turbidity was converted to TDSP (mg/L) using a conversion factor of 2.35 (Menkiti et al., 2016).

2.2.5.2. Influence of pH

The pH of PWW samples was adjusted using 0.1M H_2SO_4 and 0.1 M NaOH. PWW of pH 2-10 were obtained. 800mL of the samples were dosed with the best dosage obtained from 2.2.4.1 for both coagulants (alum and chito-protein). The jar test experiment was carried out as in 2.2.4.1 and the residual turbidity recorded.

2.2.5.3. Effect of temperature

The result obtained from 2.2.4.1 and 2.2.4.2 was used for jar test experiment at 25°C, 35°C and 45°C. The treated PWW was allowed to settle for 35min, the residual turbidity was recorded for analysis.

2.2.5.4. Influence of settling time

The result obtained from 2.2.4.1, 2.2.4.2 and 2.2.4.3 were used to perform Jar test experiment. The resultant data were analyzed to verify the influence of settling time.

2.2.5.5. Coagulation -flocculation kinetics

A modified description of the coag-flocculation kinetic theory reported by Menkiti 2012, was adopted for the coag-flocculation kinetics studies. The theory was modified to account for the rate of floc formation K_f and also the collision koppa, " \aleph " which described the effect of sample efficiency on the rate of particle aggregation.

A system operating at equilibrium phase, if there are negligible impact from the surrounding can be described using Equations 1 and 2.

$$\mu_i = \bar{G}_i = \left[\frac{\partial G}{\partial n_i} \right]_{P,T,n} = \text{a constant} \quad (1)$$

Equation 1 relates the chemical potential to the thermodynamics free energy (δG) of the "i" sized particles. While the particle diffusion coefficient is a function of temperature and friction factor.

$$D' = K_B \frac{T}{B} \quad (2)$$

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

The rate of floc formation resulting from an effective collision of two sized particles x and y , assuming bi-particle collision and insignificant separation force between the collision of the particles.

For a floc of size “ Z ” to be formed from particles of sizes x and y , the rate is drawn from the relation between the individual component sizes, the product of the particle aggregation concentrations and the collision factor (Ugonabo et al., 2012). Equation 3 described the rate relationship.

$$\frac{dn_z}{dt} = \frac{1}{2} \sum_{x+y=z} \beta_{BR}(x, y)n_x n_y - \sum_{x=1}^{\infty} \beta_{BR}(x, k)n_x n_z \quad (3)$$

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

n_x, n_y is particle aggregation concentrations for particles of size x and y , respectively.

According to Jin , Hunter and Fridkhsberg in [13]:

$$\beta_{BR} = \frac{8}{3} \aleph K_B T \quad (4)$$

Where \aleph is collision koppa, a collision constant defined as the product of collision efficiency and the inverse of sample viscosity.

$$\aleph = \epsilon_p \frac{1}{\eta} \quad (5)$$

Assuming the particles transfer to be attributed to particle diffusion, for a fast coagulation Von smoluchowski rate constant for diffusion-controlled particles interaction (Gedan et al., 1982) assumed to be independent of x and y is given by

$$K_v = 4\pi d D' \quad (6)$$

Where $d = 2a$,

K_v 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):

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

And in relation to collision efficiency, and Brownian collision koppa

$$K_v = 1.4\epsilon_p \frac{K_B T}{\delta} \tag{8}$$

Equations 3-8 could also be transformed to Eq. (9):

$$K_m = \frac{1}{2} \beta_{BR} \tag{9}$$

Where K_m is defined as Menkonu coagulation-flocculation rate constant accounting for Brownian coagulation-flocculation transport of destabilized particles at α^{th} order.(Menkiti et al., 2016)

The difference between K_m and K_v (K_f) accounts for rate of floc formation.

For Brownian coag-flocculation

$$dN_t = -K_m N_t^\alpha dt \tag{10}$$

where N_t is the particle load at time, t

For a fast coagulation process, it follows that: $1 \leq \alpha \leq 2$. Graphical representation of linear version of Equation. 10 at $\alpha = 1$ or 2 should produce a linear graph from which K_m could be determined from the slope of either Eqs 11 or 12:

$$\alpha=1: \ln\left(\frac{1}{N}\right) = K_m t - \ln N_0 \tag{11}$$

$$\alpha=2 \frac{1}{N} = K_m t + \frac{1}{N_0} \tag{12}$$

Where N_0 is the initial N_t at time = 0

N is N_t at upper time limit > 0

Equation. (12) could be solved to obtain Eq.(13) which is the coagulation-flocculation half-life $\tau_{1/2}$

$$\tau_{1/2} = 2N_0 K_m \tag{13}$$

For Brownian controlled aggregation at $t \leq 30$ min, Equation. (11) could be solved exactly to generate Eq.14

$$\frac{N_{m(t)}}{N_0} = \frac{\left[\frac{t}{\tau_{1/2}} \right]^{m-1}}{\left[1 + \frac{t}{\tau_{1/2}} \right]^{m+1}} \tag{14}$$

For particle floc diameter, within the experimental conditions.

3. RESULTS AND DISCUSSION

3.1. Wastewater Characterization

The effluent properties obtained from the effluent characterization compared with the national environmental regulatory standard are presented in Table 3.1. Table 3.1 shows that the TSS is above dischargeable standard. High TSS of this magnitude (2669mg/l) suggests that the effluent contains large quantity of colloidal particles. Hence, the need for treatment before discharge.

Table 3.1. Effluent Characterization and national regulatory standard

Value	2669	1330	3999	7.1
NERS	100	1200	1300	6-8

NERS: National environmental regulatory standard

3.2. Physiochemical characterization

Proximate analysis of SSF

The bio-coagulant precursor was analyzed before coagulant extraction. Table 2 shows that SSF has high content of protein (45%). This protein content majorly informs the choice of SSF as a precursor for bio-coagulant extraction. The weight loss of 14% can be attributed to the volatile component of SSF. The sample oil content was < 10%. According to Menkiti and Ejimofor, 2016, oil content \leq 10% will not have any inhibitory effect on extraction of the active coagulative components of the sample. Hence, there will be no need for oil extraction as sample pretreatment before coagulant extraction.

Table 2. Proximate analysis of SSF

Components	.
Weight loss (%)	14
Protein (%)	45
Oil content (%)	6.0
Ash content (%)	10
Bulk density (g/ml)	0.35
Moisture Content	7.6

Elemental analysis of SSF

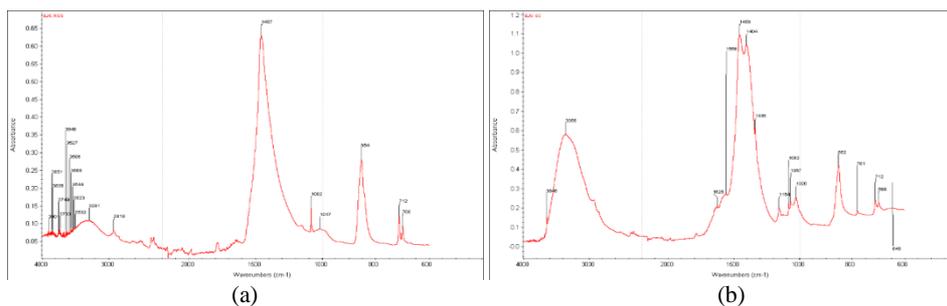
Elemental analysis carried out on both SSF and CP presented in Table 3 shows that SSF has a high content of calcium. The calcium content of 70 % was recorded. The findings were like the report of Houndonougbo et al.,2012. The high calcium content aids body replenishment in snails. The high content of oxygen (26.36%) in SSF can be traced to the presence of protein in the shells (Bella, 2014). The presence of carbon (7.47%) in a trace value is attributed to the carbonaceous nature of SSF.

Table 3. Elemental Characterization of SSF and CP

Elements	SSF	CP
C	7.47	6.53
Na		21.7
Mg	-	0.23
Al		0.24
P	-	
Si	-	0.14
Cl	-	0.21
K	-	0.19
Ca	65.8	45.1
O	26.36	25.94

From the elemental characterization of CP (Table 3), it could be observed that more elements were present (Na, Mg, Al, P, Si, Cl, K) which were not in SSF. The additional elements and the observed 20.7% reduction in calcium content can be attributed to the reaction between the extraction solution and some elements present in SSF. The oxygen content of both SSF and CP were observed to be approximately the same (26.36 and 25.94%), indicating an effective deproteinization process.

3.3. FTIR spectra of SSF and CP

**Figure 1.** FTIR spectrum (a) SSF (b) CP

The spectrum presented in Fig 1a was obtained from the FTIR characterization of SSF. Some major functional groups present in SSF were detected. Fig. 1a shows that the FTIR spectra fall within the mid infrared region (4000–600 cm^{-1}). 19 major peaks were observed with principal peaks at 3648, 3627, 3580, 3291 cm^{-1} , 1457 cm^{-1} , 1082 cm^{-1} , 1017 cm^{-1} , 844 cm^{-1} , 712 cm^{-1} , and 700 cm^{-1} . The highest peak was observed at the frequency of 1457 cm^{-1} which characterize methyl group of C-H bending. The presence of aromatic group and aliphatic C-H stretching group was observed through the broad band above 3000 cm^{-1} , 1082 cm^{-1} and 844 cm^{-1} . Fig 1b shows the spectra pattern of chito-protein. The CP FTIR spectra also fall within the mid-infrared region, the principal peak was observed within the fingerprint region at 1456 cm^{-1} and threshold frequency of 1.07. From Fig 1b traces of lysine, valine, serine and Phenylalanine can be observed from the major functional groups such as NH_3^+ bending, NH_3^+ rocking, CH_3 asymmetric, OH bending and benzene ring vibration observed at 1456 cm^{-1} , 1154 cm^{-1} , 1336 cm^{-1} , 781 cm^{-1} and 713 cm^{-1} respectively. The presence of other functional groups such as Si–OH stretching, C–O stretching band (Ethers) due to the C–O–C linkage was also observed from bands at 3645 cm^{-1} , and 1082 cm^{-1} . The appearance of the weak peak at 1625 cm^{-1} shows the secondary structure of the protein

content of CP as intermolecular β -structure (Singh, A. (2013). The presence of this protein is desirable in bio-coagulants (Menkiti et al., 2018; Menkiti et al., 2016; Ugonabo et al., 2012) Furthermore; reduction in peaks can be observed by comparing Fig 1a and 1b. This peaks reduction shows the difference in structural makeup of the precursor(SSF) and the extracted bio-coagulant(CP).

4.5. SEM characterization of CP

SEM micrographs of the dried sample of chito-protein were obtained for the study of the coagulants morphology. Fig 2(i and ii) shows the surface morphology of CP at 100 μ m and 20 μ m respectively.

Tiny pores could be observed across the large spacious and dark background in Fig 2. These tiny pores are much desirable as it creates enabling surface area for particle adsorption. **At a higher resolution**, elongated stick like particles could be observed; this shows the nature of the coagulants surface.

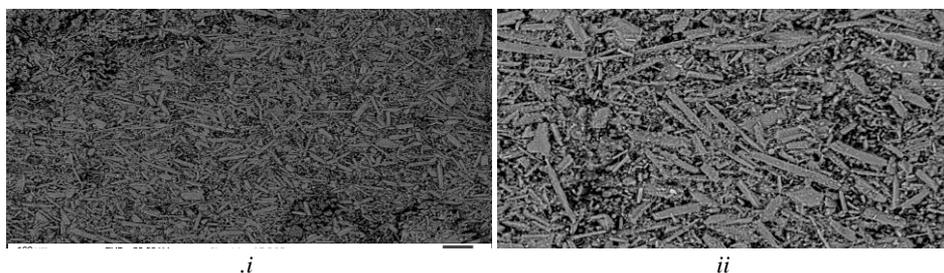


Figure 2. CP micrograph (i) 100 μ m (ii) 20 μ m

4.6. Power X-Ray Diffraction (XRD) of CP

Power X-ray diffraction techniques were used to study the crystalline nature of CP sample. Fig 3 shows the XRD spectral pattern.

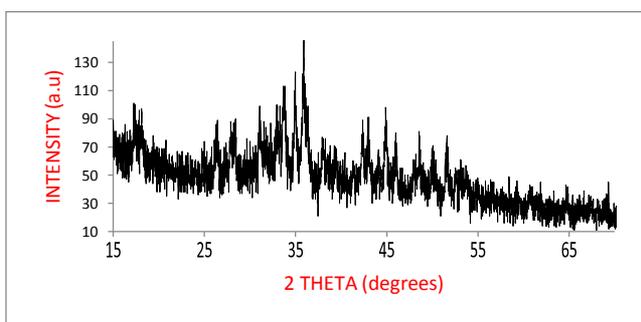


Figure 3. XRD spectrum of CP

The peaks in Fig 3 were observed to be unsymmetrical, unorganized and of relatively low intensities. This trend of spectral pattern reveals that CP lacks the long-range order and therefore cannot be regarded as having crystalline nature. It then infers that CP is amorphous in nature. At scattering angles of 18 $^{\circ}$ and 24 $^{\circ}$, the inter-planner spacing, and their corresponding millers' plane

were obtained to be 4.76 at 101 and 3.7 at 100 respectively using Braggs method. The unit cell dimension a_0 for CP were estimated based on the two prominent peaks as 21.3 and 16.6.

4.7. Effect of process variables

4.7.1. Comparison of effect dosage for CP and Alum on TDSP removal efficiency

The effect of different dosages of CP and Alum on TDSP removal efficiency in paint wastewater were analyzed at the effluent's initial pH and settling time of 35mins. Fig 4 shows the plot of removal efficiency against dosages.

Fig 4a shows the effect of coagulant dosage on the particle removal efficiency of paint wastewater coagulation using chito-protein while Fig 4b shows the effect of alum on the particles removal efficiency. At the effluents initial pH of 7.1, coagulant dosage of 0.5g – 5g were considered. From Fig 4a, it was observed that the removal efficiency at the samples initial conditions were very low. The highest efficiency of 13.4% was obtained at 4g of CP while from Fig 4b; 2g of alum gave the highest removal efficiency of 78.2%. Fig 4a was observed to be sinusoidal; this trend indicates the effect of specific CP dosage on the coagulation system. The peaks observed at 0.5 g and 4g show effective discharge of positive charges by the coagulant for the destabilization of the negatively charged suspended particles in the wastewater, while the minimum peaks observed at 0.5g, 2g, 3g and 5g show that at these dosages of CP, the positive charges produced were insufficient to effect particles destabilization. The minimum TDSP removal at 5g could be attributed to charge reversal due to excess coagulant concentration which resulted in re-turbidization of the effluent. CP zero-point was observed at 1g where the coagulant produced least net positive charge for particles destabilization. Similar sinusoidal trend was observed in Fig 4b, the minimum efficiency was also observed at 0.5g of alum.

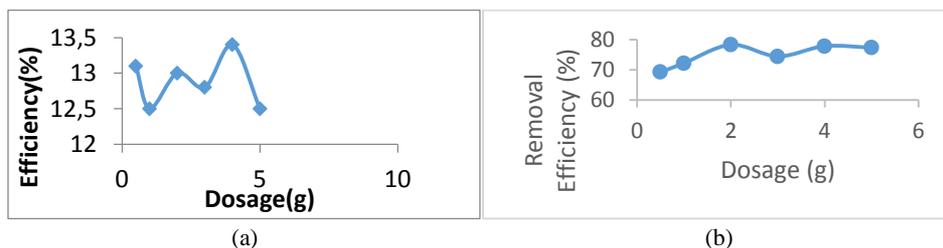


Figure 4. Effect of coagulant dosage on TDSP removal efficiency at initial pH of 7.1, 35min and 25°C (a) CP-PWW (b) Alum -PWW

4.7.2. Effect of pH on effective TDSP removal on PWW using CP and Alum

Effluent pH is an important factor that affects the efficiency of TDSP removal (Jarvis et al., 2005).. The influence of pH investigated under the optimum dosage obtained in section 4.7.1 is presented in this section. Fig 5(a and b) shows the influence of pH on the coagulation process of paint wastewater using CP and alum respectively. The removal efficiency was observed in Figure 5a to increase with pH till the best removal efficiency was attained at pH of 4. At this pH (4) 84% particle removal was achieved. A clear sinusoidal trend was observed in Fig 5b and the point of highest particle removal was observed at the pH 6. The least effect was observed at pH of 8 both in CP-PWW and Alum-PWW. This can be attributed to poor effect on the electrophoretic mobility of particles in suspension resulting to poor surface charge neutralization.

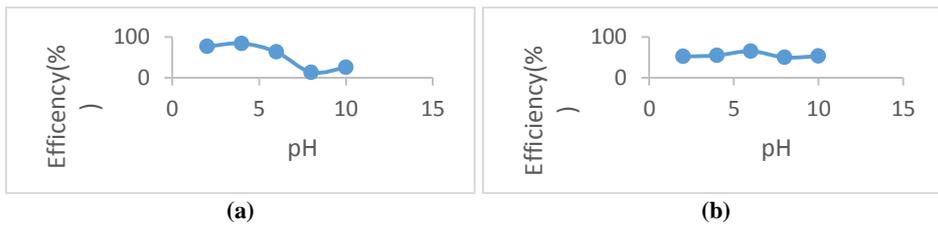


Figure 5. Influence of pH on efficiency (a) CP –PWW at 4g of CP and 35min (b) Alum – PWW at 2g of alum and 35min

4.7.3. Effect of Temperature on removal efficiency

The effect of temperature on the coagulation systems (CP-PWW and Alum-PWW) was studied and compared. Temperature affects the rate of coagulant dispersal; coagulants solubility is also dependent on temperature. Fig 6 shows the comparative representation of the effect of temperature on CP - PWW and Alum - PWW. At 25°C alum performed better than CP in PWW, this indicates that alum is more soluble than CP at room temperature, however as the temperature increased, the performance of CP was observed to be higher than the performance of alum. Alum perform best at the temperature of 35°C while CP’s performance is proportional to temperature (increases with temperature within the temperatures studied). Remarkable decrease was observed in the efficiency at 45°C for alum-PWW coagulation which can be attributed to charge reversal due to excess temperature. The trend of variation in efficiency with temperature for CP-PWW system indicates that CP is more stable with temperature than alum.

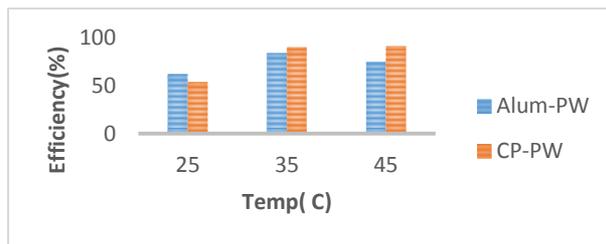


Figure 6. Plot of efficiency vs. temperature at 25, 35 and 45⁰C, 35min

4.7.4. Variation of percentage removal efficiency with settling time

The effect of time on the settling of the flocs formed during flocculation period for CP- PWW and Alum - PWW were studied. At the best obtained dosage and pH, the settling time is known to be an inverse function of the floc size (Tao et al., 2006). Hence, the larger the floc size, the less time it will take to settle.

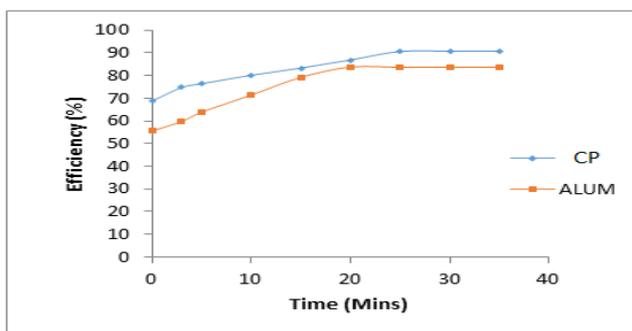


Figure 7. Variation of efficiency with settling time at the best-established conditions (35 min, pH of 4 for CP and 6 for alum)

Fig 7 shows the variation of removal efficiency with settling time for the two systems under study. It could be observed that the efficiency of particle removal increases with the settling time until equilibrium was established after which further increase in time yielded a negligible increase in removal efficiency. The plot revealed that a higher percentage of the flocs settled within 20 mins in Alum - PWW system while in CP - PWW, most of the flocs settled within 25mins. Hence it took more time for the flocs formed in CP-PWW system to settle. This can be attributed to the size of the flocs with respect to the flocs formed using alum in PWW. The best process efficiency considering the combination of the best process parameters were established using Fig 7. Alum at 20mins, 2g/l, pH of 6 and the best process temperature of 35°C gave the maximum process efficiency of 90%, while CP at 25 min, 4g/l, pH of 4 and 45°C gave the maximum process efficiency of 91.6%.

4.7.5. Temporal variation of aggregate diameter with dosage

The radius of aggregate particles formed within the coagulation time at varying coagulant dosages were estimated using equation 15, and is presented in Table 4.

$$r = \beta_{B,r} / 6\mu\pi \tag{15}$$

and

$$d = 2r \tag{16}$$

Where:

$\beta_{B,r}$ is the Brownian peri - kinetic aggregation collision factor

μ is the dynamic viscosity of the sample

Fig 8 shows the temporal variation of aggregate diameter with dosage for CP - PWW and Alum - PWW. The aggregate diameter (floc diameter) is a direct indication of the floc size.

From Fig 8, it was observed that the aggregate diameter increases with the increase in coagulant dosage to the optimum. Three stages could be observed from Fig 8, an initial stage characterized by stable floc size variation with dosage, the period of the significant increase in aggregate diameter with an increase in coagulant dosage and a stage of decline in aggregate diameter which may be attributed to floc breakage. At the best coagulant dosage of 4g in CP - PWW and 2g in Alum -PWW, Fig 8 show that the aggregate diameter was smaller in CP-PWW with respect to Alum-PWW. This trend is an indication that at the best coagulant dosage, the floc size produced using CP was smaller and hence stronger and more resistant to floc breakage.

Table 4. Variation of Floc radius with dosage

Dosage(g)	floc radius(um)	
	CP-PWW	ALUM-PWW
0.5	1.31E-08	5.68E-07
1	2.84E-08	3.84E-07
2	1.70E-07	4.60E-07
3	70E-07	3.84E-07
4	2.84E-07	4.60E-07
5	2.84E-07	2.30E-07

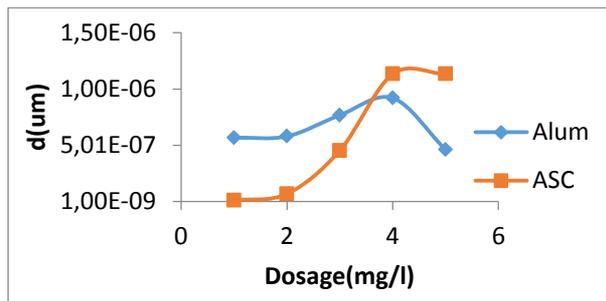


Figure 8. Variation of aggregate diameter with Dosage

4.8. Effect of coagulant on the final characteristics of the treated wastewater

The characteristics of the treated sample for CP-PWW and Alum-PWW coagulation system were analyzed after the experiment conducted at the best operating conditions. The characteristics of the recovered water in terms of sample suspended particles (TSS) and pH were compared with initial effluent parameters and NERS dischargeable standard in table 5. Table 5 shows that for both CP-PWW and Alum-PWW, the final characteristics fall below NERS acceptable standard in terms of particle load, however a decrease was observed in pH for Alum-PWW from the best pH of 6 to a more acidic pH of 3, while for CP-PWW the pH increased from the best pH of 4 to a neutral pH (7) within NERS acceptable standard. Thus, for sample treated with alum, a further pH adjustment will be recommended before discharge.

Table 5. Treated wastewater final parameters

	PWW (mg/l)	CP-PWW(mg/)	Alum-PWW (mg/l)	NERS(mg/l)
TSS	2669	53.7	40.07	100
Best pH	7.9(Initial pH)	4	6	6-8
Final pH		7	3	

4.9. Kinetics of coagulation process

The kinetic studies of coagulation give insight into the particles movement from the bulk of the wastewater sample to the surface of the coagulant after charge neutralization and destabilization, the rate of this transport (process rate), and the particles collision effect. The parameters for CP and Alum in PWW were evaluated and compared in Table 6. The values of Menkonu-coagulation rate constant K_m , and the order of coagulation reaction α , were evaluated from the plot of $\frac{1}{C_t}$ vs t (Fig 10).

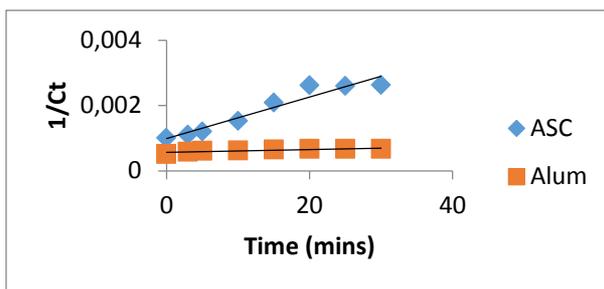


Figure 10. Plot of 1/Ct against settling time for CP-PWW and Alum-PWW

The slope of the plot (Fig 10) gives the value of K_m , while $\alpha = 2$. While Von smoluchowski's coagulation constant (K_R) accounts only for the rate of particles coagulation considering the rate of flocculation as being negligible, (K_m) defined as Menkonu coagulation-flocculation rate constant accounts for Brownian coagulation-flocculation transport rate of destabilized particles at α^{th} order. Hence, the difference between K_m and K_R accounts for the rate of particle flocculation ($K_f - E_{jimenk}$ constant) at α of 2. Higher K_m ($6.00E-05$) was obtained for CP - PWW relative to Alum - PWW ($4.00E-6$), this indicates that particles motion and floc formation after destabilization was faster in CP-PWW system. The particles collision efficiency (ϵ_p) accounts for the number of effective collisions for floc formation. From Table 6, higher value of (ϵ_p) obtained in CP-PWW system suggests that more collision lead to floc formation than in Alum- PWW system. Also, at low K_R , ϵ_p relates directly to β_{BR} . Therefore, high ϵ_p leads to high kinetic energy which depresses the zeta potential leading to double-layer collapse and promotes high rate of effective collision. The constant value of Von smoluchowski's constant results from the constant values of the effluents viscosity and temperature. The difference between K_m and K_R (K_f) in Table 6 shows that K_R is quite negligible relative to K_m , this is an indication that the entire process is greatly influenced by the rate of floc formation than the actual rate of coagulation. The Coag-flocculation period $t_{1/2}$ is inversely dependent on the initial particle concentration (N_o) and the menkonu Coag-flocculation constant (K_m). It had overwhelming impact on the rate of both aggregation and settling in the system (Tasneembano et al.,2013). The efficiency of coagulation-flocculation system was influenced by low settling period, also from the inverse relation between $\tau_{1/2}$ and K_m , high values of K_m corresponded to low period ($\tau_{1/2}$). From table 4 the lower period of $1.40E+01$ was observed in CP-PWW system relative to Alum-PWW system, confirming the faster Coag-flocculation process observed in CP-PWW system.

Table 6. Kinetic parameters for CP and Alum in PWW

	K_m	B_{br}	R	K_R	K_f	ϵ_p	$\tau_{1/2}$	D	$T_{1/2}$	R2
CP	6.E-05	1.20E-04	4.7 E-4	1.1E-18	6.E-05	5.03E+13	9.11E+14	5.14E-16	1.40E+01	0.93
Alum	4.E-06	4.E-05	2.40E-3	1.19E-2	4.E-06	1.68E+13	3.04E+14	5.2E-17	2.19E+02	0.76

5. CONCLUSION

Paint wastewater has been treated using two different coagulants. The conventional available chemical coagulant (Alum) and CP extracted from natural available shells (snail shell) which is of a little economic importance. The potential of CP as a coagulant was established and its efficiency and process parameters compared with that of Alum based on the outcome of bench scale jar test. From this study, the following major conclusions were drawn

- At very low concentration of both CP and Alum, (0.5g/l) Alum performed better than CP, however with increase in concentration CP was found to be relatively more effective than Alum.
- The best coagulant concentration at the effluent's initial pH condition was established (4g/l for CP and 2g/l for Alum)
- The zero point for CP was observed at 2.5g/l while for Alum was found to be 0.5g/l
- Paint wastewater can be effectively treated using either of the coagulants at pH of 4 and 6 for CP and Alum respectively.
- CP can be effective in effluent with higher temperature than Alum
- The equilibrium time for settling flocs was lower in Alum-PWW system than in CP-PWW system
- At the best combination of process condition the removal efficiency of the CP and Alum was almost the same, and below the desired target (NERS), however Alum increased the pH of the treated sample, while the pH of the treated water recovered from CP-PWW was found to be neutral.
- The floc diameter and size were larger in Alum-PWW system than in CP-PWW system
- The floc strength of flocs formed using CP are stronger and more resistant to floc breakage than those formed in Alum-PWW system.
- The kinetic study indicates that coagulation process was faster and more efficient in CP-PWW system

Hence, CP can be used as an alternative to alum; it is within reach in our environment as a waste of less economic value.

Recommendation for further studies:

This work has provided little information on the potentials of chito-protein, it is important to further establish other area in which chito-protein can be utilized. One of such areas include cream production.

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Nomenclature

D'	Diffusion coefficient,
B	Friction factor,
K_B	Boltzmann's constant
T	Temperature
G	Total Gibbs free energy
n_i	Number of moles of component i
μ_i	Chemical potential
" \aleph "	koppa,
K_f	Floc formation rate constant
K_m	Menkonu coag-flocculation rate constant
K_v	Von smoluchowski rate constant for fast coagulation.
a	Particle radius.
ϵ_p	Collision efficiency.
η	Viscosity of the fluid medium

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