

Kinetics Studies on the Coagulation of Abattoir Wastewater using Groundnut shell extract as a natural coagulant.

ABSTRACT

This paper investigated the use of extract from groundnut shells as a natural coagulant for the reduction of turbidity in abattoir wastewater using the coagulation process. The ideal concentration of NaCl for coagulant extraction was established through a series of jar tests. The effects of process variables of coagulant dosage (1-5 g/L), settling time (0-60 min), pH (2-10) and temperature (298-318 K) on the turbidity reduction efficiency were examined using a bench-scale jar test. At an optimal condition of 4g/L, pH 8, temperature of 318K, and settling period of 20 minutes, a reduction efficiency of 94.33% was achieved. The Second-order per-kinetic theory of Von-Smoluchowski's was used for kinetic evaluation at temperatures of 298 K, 308 K and 318 K. At a temperature of 298 K, the experimental data fit perfectly into the Von-Smoluchowski second-order per-kinetics theory, with a correlation coefficient of 0.952, coagulation rate constant of 0.00002 L/(mg.min), collision efficiency of 8.703×10^{-12} and coagulation time of 48.27 min, establishing that the rapid coagulation theory holds true for the coagulation of abattoir wastewater using groundnut shell extract and under the experimental conditions. As a result of the findings, it is proposed that groundnut shell extract, which is readily available and environmentally safe, is effective for turbidity reduction of sewage water and can be used as an alternative to chemical coagulants for the pre-treatment of abattoir wastewater.

Keywords: Coagulation, Abattoir, Wastewater, Groundnut shell, Turbidity.

1. INTRODUCTION

The abattoir industry is one of the industrial processes that utilize a large quantity of water in its operation and, in that process, also generates a large amount of wastewater. These wastewaters traditionally are not treated, they are simply dumped on the environment and surrounding water bodies [1]. Abattoir wastewater composed mainly of animal blood, proteins, fat, animal excreta etc., when disposed of into the environment, becomes a breeding ground for insects and pathogens as a result of having a high rate of decomposition, thereby causing odour, contamination of soil, surface and groundwater [2].

According to Connor et al. [3], " Degradation of water quality through severe pathogen pollution affects around one-third of all rivers that stretch in Latin America, Africa and Asia, thereby putting the health of millions of people at risk." It is a result of these that sustainable

development goal target 6.3 aims that by 2030, water quality should be improved by reducing pollution, the proportion of untreated wastewater should be halved, and recycling and safe reuse of water should be encouraged [3].

One method of treatment of abattoir wastewater is by coagulation and flocculation through the use of coagulants to reduce the concentration of pollutants in the wastewater. Inorganic coagulants of aluminium and iron salts together with synthetic organic polymers are most commonly used in the treatment of water [4]. There are a lot of concerns and drawbacks with the use of these aluminium salts, such as concern about residuals in the treated water, link to Alzheimer's disease and strong carcinogenic properties. The cost of the imported chemicals can be an issue for developing countries [4]. This has led to increased interest in the development of natural coagulants such as peanut [4], Moringa Oleifera [1,5], Okra pod [6], cottonseed [2], *Brachystegia Eurycoma* extract [7], Beans extract [8], *Garcinia kola* Seeds [9]. These natural coagulants have the advantage of being cost-effective, readily available, highly biodegradable and producing minimal residue.

Three steps are involved in the processing of plant-based coagulants before their use in the treatment of wastewater, namely; primary, secondary and tertiary [10]. The primary processing step involves washing, drying, and grinding, and direct use of the material in the treatment of wastewater. This method of processing has high efficiency for low turbid water and at a higher dose of the coagulants, a negative impact on the turbidity was observed [11]. The secondary step involves extracting the active components from the grounded plant material using either water, salt or organic solutions [10]. Okuda et al. [12] discovered that the coagulating capacity of Moringa Oleifera seed extracted with 1 M NaCl solution was 7.4 times higher than that extracted with distilled water for the treatment of low-turbid kaolin solution. Similarly, Birima et al. [4] discovered that the coagulating ability of peanut coagulants extracted with different types of salts was 8.2 times better than that of distilled water. The extraction process aids in the removal of lignin and other plant materials that might contribute to increasing the turbidity of the wastewater [9]. An improvement to the second step is the tertiary step, which involves purification of the extracted active coagulating agent through dialysis, lyophilization, ion exchange, and precipitation [10].

Although much study has been conducted on the use of natural coagulants for wastewater treatment, the majority of these natural coagulants compete with food stocks such as peanut, okra pod, and bean extract, as described previously. The objectives of this study were to investigate the potential use of groundnut shell coagulant (GSC), a readily available material, does not compete with food stock, and environmentally friendly coagulant, in the treatment of abattoir wastewater via turbidity reduction by examining the effect of dosage variation, settling time variation, pH variation, and temperature variation on the turbidity reduction efficiency of GSC, as well as kinetics studies.

2. Materials and Methods

2.1 Wastewater collection

The wastewater was collected from Kwata Abattoir Awka, Anambra State, Nigeria. The wastewater was generated from the washing and cleaning of the cows after slaughter. The wastewater is usually disposed of in a nearby river without treatment. A 10-litre amber-coloured plastic container was used to collect the wastewater before its disposal and preserved at a temperature of 277 K.

The wastewater was characterized for turbidity, pH, conductivity, total hardness and Biochemical Oxygen Demand (BOD) following the standard methods for the examination of water and wastewater [13] and presented in Table 1.

2.2 Preparation and Extraction of Groundnut shell coagulants (GSC)

The groundnut shells (Fig. 1A) was collected from groundnut sellers before their disposal, washed several times to remove specks of dirt and mud, dried under the sunlight for one week, after which it was ground (Fig. 1B) and stored in an airtight plastic container. The GSC (Fig. 1C) was extracted using the method of Menkiti et al.[7], which involved defatting the powdered sample with n-hexane and extracting it with 0.2, 0.6, 1, 2, and 4 molar concentrations of NaCl in a 1:10 (w/v) ratio (solid-solution ratio). A magnetic stirrer was used to swirl this mixture for 30 minutes, and the obtained solution was filtered with Whatman filter paper # 3 to remove the spent solid. To precipitate specific organic molecules that may be present in the solution, the extract was heated to 70°C while stirring for 1 minute. The bio-coagulant was concentrated after the mixture was filtered and allowed to settle for 30 minutes. To obtain powdered GSC, the concentrated bio-coagulant was dried and pulverized. The GSC was subjected to FTIR (Fourier Transformed Infrared) analysis using a Buck scientific infrared Spectrophotometer (Model 530, England) to determine the functional groups prevalent in the sample utilizing Mid-Spectrum (400-4000cm⁻¹) wavelengths.



Fig 1. A: Groundnut shells B: pulverized Groundnut shells C: Groundnut Shell Coagulant (GSC)

2.3 Evaluation of the effect of varying process variables on the Coagulation Process

2.3.1 Effect of variation of Coagulant dosage

The coagulation experiment was carried out using a standard Jar test setup. Following the method of Okolo et al. [6], varying doses (1, 2,3, 4, and 5g/l) were dosed into five beakers of 1000ml of Abattoir wastewater at its initial pH and ambient temperature. The wastewater and coagulants were stirred for 2 minutes at 250rpm for rapid mixing and 20 minutes at 30rpm for slow mixing, using a magnetic stirrer. The stirrer was switched off at the end of the gradual mixing and the suspension was allowed to settle for 5, 10, 15, 20, and 60 minutes. During the settling process, 20 ml of the supernatant was pipetted into 50ml plastic bottles from a depth of 2cm, and the residual turbidity was measured.

2.3.2 Effect of varying pH of wastewater

The effect of varying the pH of the wastewater on the efficiency of the coagulants' coagulating property was assessed by varying the pH of the wastewater using 0.1 M H₂SO₄ and/or 0.1 M NaOH between pH (2-10) at ambient temperature before the optimum dosage determined above was dosed into 1000ml of wastewater and the same experimental procedure was repeated.

2.3.3 Effect of Temperature Variation

To investigate the effect of variation of temperature on the effectiveness of the GSC as a coagulant for the reduction of turbidity of abattoir wastewater. The optimum dosage and pH determined above were employed at temperatures of 298 K, 308K and 318K, taking into account the temperature at which the wastewater was discharged into the environment. Also, there is a possibility of commencement of floc clogging and splintering at temperatures below 298 K and above 318 K [7]. Equation 1 was used to calculate the percentage of turbidity reduction [2]

$$\%R = \frac{C_o - C_e}{C_e} * \frac{100}{1} \quad (1)$$

Where the initial turbidity (untreated wastewater) and final turbidity (treated) of the wastewater (NTU) are C_o and C_e respectively.

2.4 Coagulation Kinetics Theoretical Principles

The general form of Brownian coagulation kinetics of monodispersed particles at an early stage is given as [14];

$$\frac{dc}{dt} = -KC^\alpha \quad (2)$$

Where; C is the Particles concentrations (TSS)

α is the order of coagulation reaction.

K is the rate constant of coagulation

According to Van-Zanten and Elimelech [15] and Sonntag and Strenge [16], the coagulation reaction is of second-order ($\alpha=2$).

Integrating equation 1 with $\alpha=2$ yields;

$$\frac{1}{C_t} = Kt + \frac{1}{C_o} \quad (3)$$

The coagulation rate constant (K) can be determined the slope of the Plot of $\frac{1}{C_t}$ against t .

The coagulation rate constant is also the product of the Smoluchowski rate constant (K_s) for rapid coagulation and collision efficiency (ϵ_p)[15].

$$\text{ie, } K = \epsilon_p k_s \quad (4)$$

According to the kinetic theory of Maxwell and Boltzmann in Sonntag and Strenge [16]

$$\frac{1}{2}m\bar{v}^2 = \frac{2}{3}k_B T \quad (5)$$

Where T the absolute temperature, \bar{v} is the average velocity, K_B is the Boltzmann constant ($1.38064852 \times 10^{-23}$ J/K), and m is the mass of the molecules.

For a particle moving with velocity $\frac{dx}{dt}$, the frictional force is given by [16];

$$F_R = f_s \frac{dx}{dt} \quad (6)$$

Where f_s is the frictional coefficient,

The relationship between f_s and the diffusional coefficient is given as;

$$D = \frac{K_B T}{f_s} \quad (7)$$

The frictional coefficient is determined by;

$$f_s = 6\pi\eta a \quad (8)$$

Where a is the particle radius and η is the viscosity.

Substituting 7 in 6 gives;

$$D = \frac{K_B T}{6\pi\eta a} \quad (9)$$

The Van der Waals force of attraction affects two uncharged particles in a suspension that are in continuous motion as they approach one other. Fick's first law states that the number of particles crossing the surface of one sphere per second (i.e. the particle flux I) is as follows [16]:

$$I = 4\pi R^2 D \left(\frac{dz}{dr} \right)_{r=R} \quad (10)$$

Where; $4\pi R^2$ is the area within the sphere of action, r is the centre to centre distance of the particle, R is the radius of the sphere of action and Z is the particle concentration

Therefore,

$$\left(\frac{dz}{dr} \right)_{r=R} = \frac{Z_0}{R} \quad (11)$$

Where; Z_0 is the initial particle concentration

Substituting 10 into 9 gives

$$I = 4\pi R D Z_0 \quad (12)$$

Assuming a monodispersed system;

$$D_{11} = 2D_1 \quad (13)$$

Combining equations 11 and 12,

$$I_{11} = 8\pi R D_1 Z_0 \quad (14)$$

For all particles in the system,

$$\frac{dz_0}{dt} = I_{11} = -8\pi R D_1 Z_0^2 = -2k_s Z_0^2 \quad (15)$$

Comparing equation 2 and 15, the coagulation rate is of second order

Also coagulation rate constant $K = 2k_s$

(16)

Substituting $R=2a$, equation 9 into 15 and solving for k_s ,

$$K_s = \frac{4K_B T}{3\eta} \quad (17)$$

Time for coagulation can be evaluated using [16];

$$T_{ag} = \frac{1}{4\pi D_1 R_1 Z_0} = \frac{1}{k_s Z_0} \quad (18)$$

The time required for the number of aggregates (duplets, triplets, and quadruplets) to reach its maximum value is given by;

$$t_{max} = \frac{i-1}{2} T_{ag} \quad (19)$$

Hence for doublet;

$$t_{max} = \frac{1}{2} T_{ag} \quad (20)$$

Triplet;

$$t_{max} = T_{ag} \quad (21)$$

Quadruplets;

$$t_{max} = \frac{3}{2} T_{ag} \quad (22)$$

Menkiti et al. [8] cited Metcalf and Eddy (2003), who asserted that the relationship between Turbidity (NTU) and Total Suspended Solid (mg/L) is as follows;

$$TSS(mg/L) = (TSS.f) \cdot T \quad (23)$$

Where; TSS = Total Suspended solid

T = Turbidity (NTU)

3. Result and Discussion

3.1 Characterisation of Wastewater

From the analysis carried out on the Abattoir wastewater and presented in Table 1. The wastewater's turbidity, conductivity, total hardness, and BOD levels were significantly higher than those recommended by the Nation Environment Regulations Standard [17] for effluent discharge into water or on land. Therefore there is a need for the Abattoir wastewater to be treated before discharge.

Table 1: Characteristic of Abattoir Wastewater

Parameter	Values
Turbidity (NTU)	882
Conductivity (ms/cm)	202.2
Total Hardness(mg/l)	2700
pH	6.40
BOD(mg/l)	226

3.2 FTIR Characterization of the GSC

The FTIR spectrum of the GSC presented in Fig. 2 detected the presences of O-H stretching of the broadband centred at 3664.91, 3541.24, 3397.97, 3264.35 and 3165.35 cm^{-1} , N-H stretching of amide group was identified at 2976.378 and 1613.53 cm^{-1} peaks, which reflects the cationic tendency of the GSC extract, this is comparable to the result obtained by Afolabi et al. [5] in the FTIR characterization of cellulose from *Moringa Oleifera* seed for use in water purification.

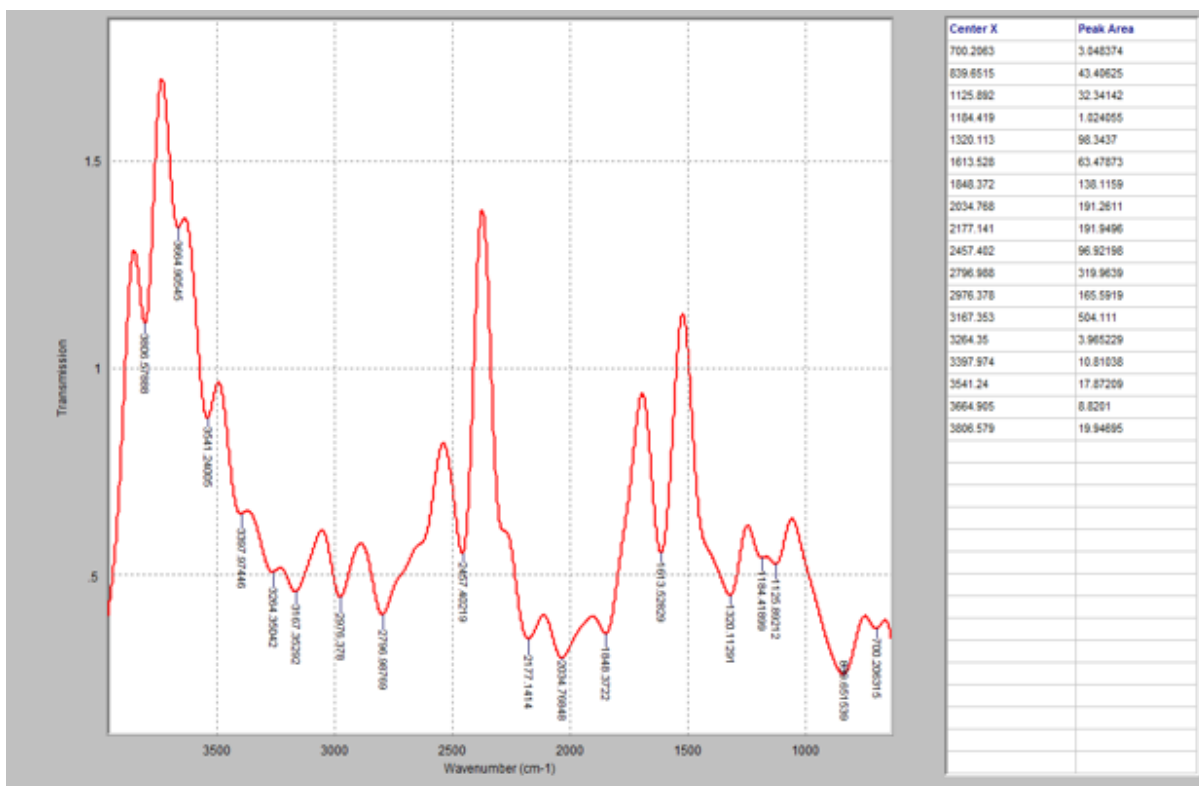


Fig. 2. FTIR Spectrum on the GSC

The presence of -CN groups stretching at 1184.419 cm^{-1} and 1125.892 cm^{-1} in the fingerprint area of $600\text{-}1500\text{ cm}^{-1}$ indicate the existence of aromatic secondary amine. At 2796.988 cm^{-1} and 839.65 cm^{-1} , the presence of -CH bending was identified. The coagulating capacity of the GSC can be attributed to the presence of hydroxyl and amine groups [5,9,18].

3.3 Effect of varying the concentration of salt used in the extraction of the coagulant.

An increase in the concentration of NaCl used in the extraction of the active component from the groundnut shell led to the reduction of turbidity in the wastewater from an initial 882 NTU to 192 NTU. When the salt concentration was increased from 0.2M to 2M, the turbidity decreased rapidly, but the rate of reduction was negligible from 2M to 4M, as shown in Fig. 3. As a result, 2M was identified as the optimal salt concentration for the extraction of coagulant utilized in subsequent coagulation experiments.

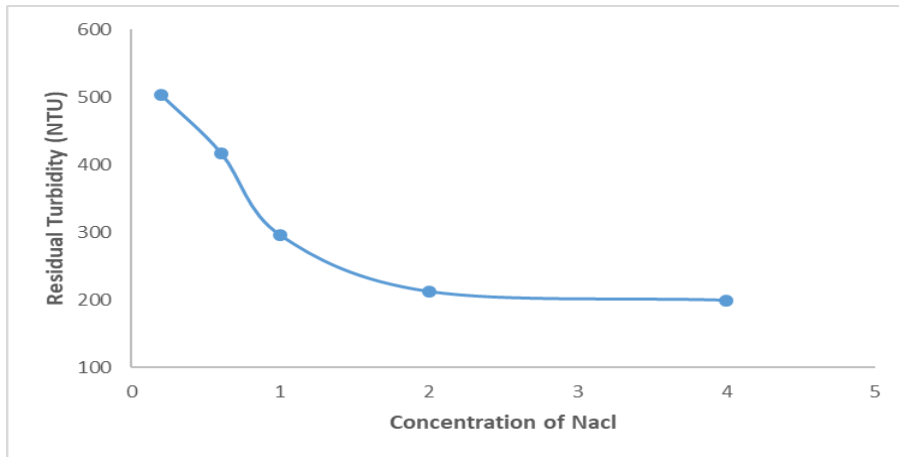


Fig. 3. Effect of varying concentration of NaCl used in the extraction of the coagulant on the residual turbidity

3.4 Effect of varying Coagulant dosage and settling time on Turbidity Removal efficiency

The residual turbidity decreases when the coagulant dosage was increased from 1 to 4g, after which the amount of residual turbidity slightly increased. From Fig. 4, It was observed that 4g of GSC could effectively reduce 76.19 % turbidity of the Abattoir wastewater. Therefore the optimal dose of GSC to treat 1litre of Abattoir wastewater is 4g, a similar trend was observed by Menkiti and Ejimofor, [19] and Igwegbe et al. [9] which was attributed to excess positive charges supplied by the GSC on the particles' surface, resulting to surface saturation and then decrease in the turbidity reduction efficiency, it also suggested that the principal mechanism in the coagulation process is neutralisation and adsorption.

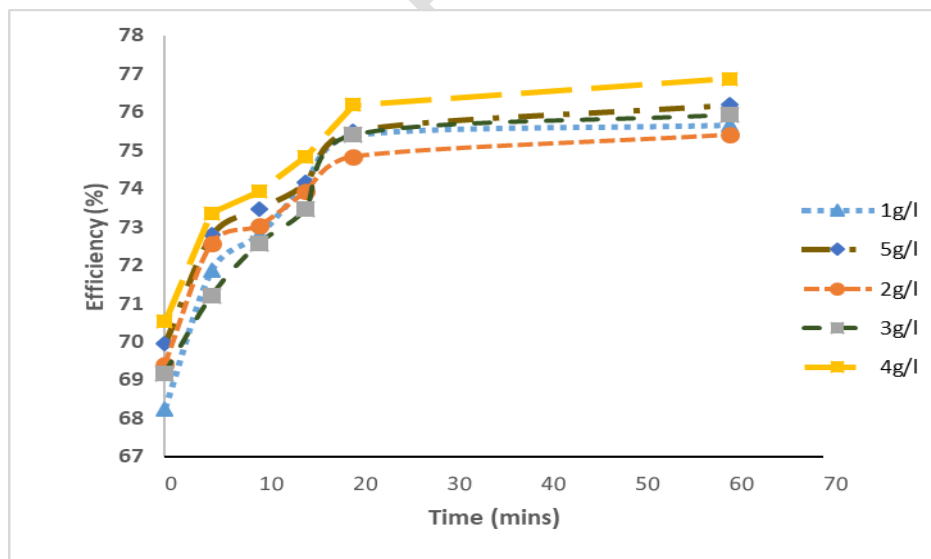


Fig.4. Effect of varying coagulant dose on percentage turbidity reduction efficiency.

Fig. 4 also illustrated the effect of settling time on turbidity reduction efficiency at varying coagulant dosages, it can be observed that the turbidity reduction efficiency increased as the settling time increases, from 0 – 20 min, after which equilibrium was attained, this could be attributed to the formation of the double fold of aggregates, which occur rapidly within this time, while for the higher fold of aggregates require more time at ambient temperature. A similar result was obtained by Menkiti and Ejimofor [19] in the coagulation of paint effluent using *Achatinoide* shell extract and Sibiya et al. [20] in coagulation treatment of industrial wastewater.

3.5 Effect of variation of effluent initial pH

According to Ejimofor [21], the ideal pH for any coagulation process is determined by the type of coagulant used, since it influences the coagulant's solubility in the aquatic medium and affects colloidal particle stabilization. The effect of the initial pH (2 – 10) of the abattoir effluent was studied using 4g of GSC and a settling time of 20 min. From Fig. 5, varying the initial pH has minimal effect on the reduction efficiency of the GSC and the optimum initial pH was pH 8 with a removal efficiency of 83.45%, similar result was obtained by Menkiti et al.[7] in the use of extract from *Brachystegia Eurycoma* in the coagulation treatment of paint effluent.

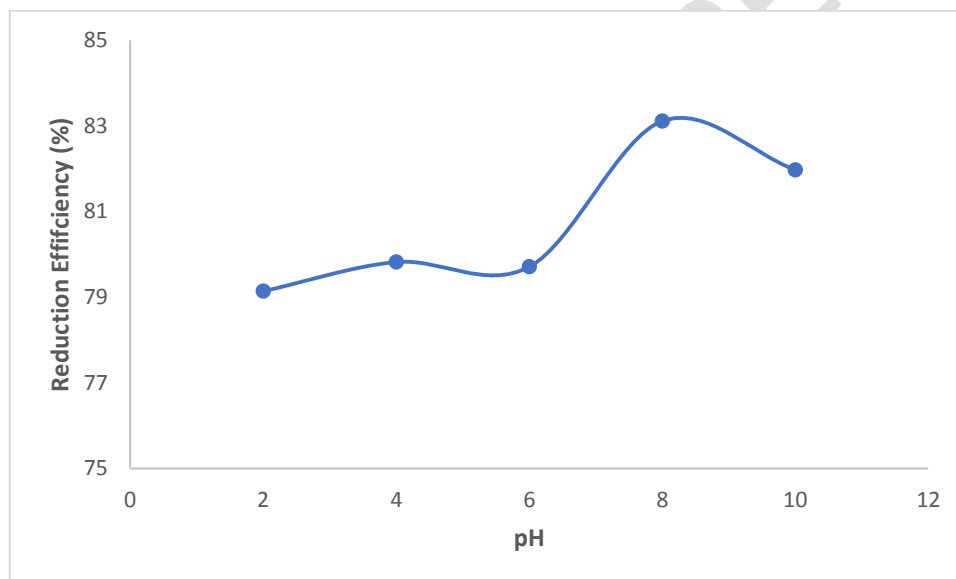


Fig. 5. Effect of pH variation on percentage turbidity reduction efficiency

3.6 Effect of Temperature variation on turbidity reduction efficiency

The plot of the effect of varying temperature from 298 K to 318 K at pH 8 and optimum dosage of 4g/l was presented in Fig. 6. It was observed that an increase in temperature from 298 K to 318 K increases the turbidity reduction efficiency of the coagulant from 89.80% at 298 K to 92.06% at 308 K and then to 94.90 at 318 K. According to Ejimofor [21] increasing the temperature of the coagulation process generally increases the kinetic energy of the particles leading to efficient collision and coagulation.

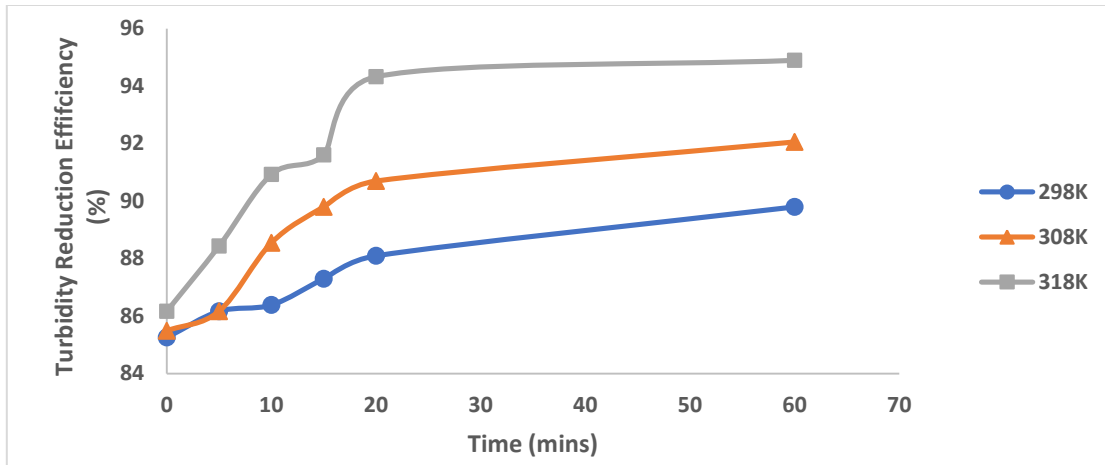


Fig.6. Effect of ABW Temperature variation on percentage turbidity reduction efficiency

3.7 Von Smoluchowski coagulation kinetics studies

The experimental data in turbidity were converted to concentration in mg/L using a factor of 2.35 (Nicholls, 1979 as cited in Menkiti, [14]) and fitted into the second-order kinetic theory (equation 3) at temperatures of 293 K, 308 K and 318 K, it can be observed from Fig. 7 that the experimental data fitted best in the second-order kinetics equation at 298 K with a correlation coefficient of 0.952.

It can be depicted from Table 2, that increasing the temperature from 298 K to 318 K, led to a corresponding increase in coagulation rate constant from 0.00002 to 0.00008 L/(mg.min) and collision efficiency (equation 4) from 8.703×10^{12} to $3.255 \times 10^{13} \text{ mg}^{-1}$ which correspond to high kinetic energy supplied to overcome the repulsive forces of the colloidal particles [22] thereby resulting to decrease in coagulation time from 48.24 min at 298K to 12.06 min at 318 K. Also from Table 2 the high coagulation time and time for the formation of aggregates ($t_{\max 2}$, $t_{\max 3}$, and $t_{\max 4}$) at 298 K suggests that charge neutralisation is the dominate mechanism while lower coagulation time and time for formation aggregates at 308 and 318 K suggests that colloidal entrapment that results in floc sweep is the dominate mechanism [14].

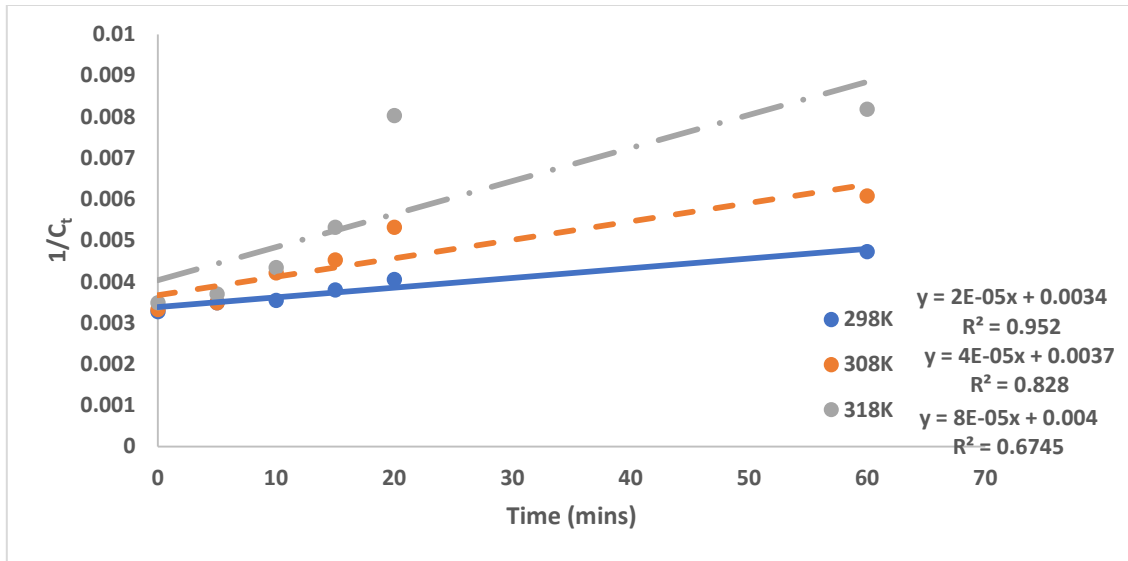


Fig.7. Second-order Kinetics of ABW Coagulation using 4g of GSC, pH of 8 and at 298 K, 308 K and 318 K

Table 2: Kinetics Parameters for coagulation of ABW using GSC

Kinetics Parameter	298K	308K	318K
R^2	0.952	0.828	0.675
K (L/(mg.min))	0.00002	0.00004	0.00008
C_o (mg/L)	294.12	270.27	250
k_s (L/min)	2.298×10^{-18}	2.380×10^{-18}	2.458×10^{-18}
ε_p (mg ⁻¹)	8.703×10^{12}	1.681×10^{13}	3.255×10^{13}
$-r$ (mg(Lmin) ⁻¹)	$0.00002C_t^2$	$0.00004C_t^2$	$0.00008C_t^2$
T_{aq} (min)	48.24	24.12	12.06
t_{max2} (min)	24.12	12.06	6.03
t_{max3} (min)	48.24	24.12	12.06
t_{max4} (min)	72.36	36.18	18.09

4. Conclusion

The research has shown that coagulants extracted from groundnut shells using NaCl solution can be used in the coagulation treatment of Abattoir wastewater, thereby minimizing dependence on chemical coagulants. The optimum concentration of NaCl salt for the extraction of the active component from the groundnut shell is 2M, with an optimum dosage of 4g/l, pH of 8 and 20 mins settling time, from the kinetics studies, the experimental data fitted Von-Smoluchowski's second-order coagulation kinetic at 298 K than at 308 K and 318 K. To be able to meet sustainable development goal, target 6.3; onsite treatment of Abattoir wastewater should be encouraged. Also, groundnut shell coagulant which is seen as a waste, readily available, biodegradable, less expensive and not harmful to human health can be used for turbidity reduction of Abattoir wastewater instead of the chemical coagulants.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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