The Pharmaceutical and Chemical Journal, **2019, 6(4):32-45**

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

Removal of Total Dissolved Solids (TDS) from Aquaculture Wastewater by Coagulation-flocculation Process using Sesamum indicum extract: Effect of Operating Parameters and Coagulation-Flocculation kinetics

Chinenye Adaobi Igwegbe*, Okechukwu Dominic Onukwuli

Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria
Corresponding author: ca.igwegbe@unizik.edu.ng; +2348036805440; ORCID: 0000-0002-5766-7047

Abstract The aim of this study was to investigate the reduction of total dissolved solids (TDS) from aquaculture wastewater using *Sesamum indicum* seeds extract (SIC). The physicochemical properties (protein content, carbohydrate content, etc) of the seeds were determined. The coagulant was obtained from the seeds using the salt extraction technique. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were done the coagulant (SIC) to determine its morphology and functional groups present, respectively. The effects of SIC dosage (0.1-0.5 g/L), pH (2-4), temperature (303-323 K) and settling time (0-60 min) on the reduction of TDS using SIC were examined. The coagulation-flocculation kinetics of the process was also studied. *Sesamum indicum* seeds were found to contain 30.6 % protein and 7.58 % carbohydrate which implies that it can be used as a coagulant for solids/particles removal. Maximum removal of 82 % was obtained at the optimum conditions of dosage: 0.4 g/L, pH: 2, temperature: 303 K and settling time: 60 min. The coagulation-flocculation parameters were successfully determined using the first-order (where reaction order, α = 1) and second-order (α = 2) reactions at the optimum conditions. The regression coefficient, R^2 values indicated that the removal of TDS using SIC fitted into the second-order reaction (R^2 = 0.9837) than the first-order reaction (R^2 =0.9314). This implies that the order of the coagulation reaction, α is 2. At these conditions, the reaction rate (K_m) and coagulation-flocculation half-life ($\tau_{1/2}$) were evaluated as 0.0002 L/g.min and 20 min, respectively. From this study, it can be concluded that *Sesamum indicum* seeds can be applied for the pretreatment of aquaculture effluents.

Keywords Coagulation-flocculation, *Sesamum indicum* seeds, Total dissolved solids, Aquaculture wastewater, Wastewater treatment, von Smoluchowski model

Introduction

The disposal of polluted water with suspended solids have led to the pollution of surface water, groundwater, and natural water bodies [1]. Recycling of wastewaters will help to reduce pressure (including organic loads, loads of dissolved nutrients and particulate matter) on the receiving waters. Aquaculture or fish farming is an activity that could contribute to environmental pollution such as water and soil pollution. Due to the high demand for fish consumption, aquaculture systems normally create environmental problems such as wastewater containing high organic pollutants including suspended solids, nitrogen, and phosphorus [2, 3]. However, the load of waste is directly proportional to fish production [3].

The coagulation-flocculation process is a proven technology for the safety of environmental and human health with extensive applications in water and wastewater management facilities [4]. However, coagulation-flocculation has not been extensively applied in the aquaculture industry because of the dilute nature of most aquaculture wastes. Coagulation is defined as the process through which colloidal particles and very fine solid suspensions are destabilised so that they can begin to agglomerate if conditions are suitable [5]. Flocculation is the aggregation of particles in suspension into visible flocs that sediment under gravity [6, 7]. Coagulants are useful in disabling or decreasing electrostatic barriers in order to allow closer contact between individual particles [8]. A coagulant is a material that can be added to destabilize colloidal particles. They may include inorganic coagulants (salts), synthetic and natural organic polymers [4, 6]. The development of flocs can take place spontaneously only through the successive collisions between the several particles, if the system has enough energy to do so, as a result of the agitation of the system. On the other hand, extreme agitation can disaggregate the flocs [6].

Many studies have emphasized the feasibility of coagulants made from proteins, polysaccharides, and starches in decreasing suspended solids in water through physical processes [9, 10]. Natural coagulants (biopolymers) would be of great interest since they are natural low-cost products, characterized by their environmentally friendly behaviour, and presumed to be safe for human health [11]. They are also readily available especially those of the plant origin than animal-based coagulants, thus suggesting that they could be potential replacements to chemical coagulants and have since gained continuing impact over the years [12]. These chemical coagulants also have some drawbacks, which include pH alteration, large volume of sludge resulting in huge disposal cost, not being effective in low-temperature water, and high procurement cost [13, 14].

Sesamum indicum (Fig. 1) is a flowering plant of *Sesamum* genus, also called beniseed [15]. Sesame seed is one of the oldest oilseed crops known, domesticated well over 3000 years ago [16]. Sesame seeds have also been found to possess numerous medicinal properties. The authors, Jibril et al. [17] used sesame seed as a coagulant for the removal of turbidity from surface water. They obtained maximum turbidity removal of 97.6% at the optimum coagulant dose of 12 g/L at the pH of 6.8 and coagulation time of 10 min.

This aim of this study is to examine the reduction of total dissolved solids (TDS) from aquaculture effluent using *Sesamum indicum* seeds extract (SIC). The influence of coagulant dosage, pH, temperature and settling time on the reduction of TDS from aquaculture wastewater (AW) using SIC was examined and their optimum conditions determined. The coagulation-flocculation kinetics of the process was also studied.

Theoretical principles and coag-flocculation kinetics

The perikinetics of the coagulation-flocculation process was studied using the first-order and second-order reactions. The perikinetics of particles coagulation is influenced by Brownian motion [18, 19]. The kinetics of coagulation of particles controlled by Brownian motion can be described by Eq. 1:

$$\frac{dC_z}{dt} = \frac{1}{2}\sum_{i=j} K_{ij}\, C_i C_j - C_z \sum_{i=1} K_{iz} C_i \qquad (1)$$

Where the $K_{ij}$is a second order coagulation rate constant, t is the time, and C_z is the total particle concentration of z-fold clusters.

The kinetics of Brownian coagulation of single dispersed particles at the early stage ($t < 30min$) is generally described by the rate equation [19, 20]:

$$-r = -\frac{dC_t}{dt} = K_m C_t^{\alpha} \qquad (2)$$

Where $-r$ is the rate of reduction of particles concentration, K_m = Menkonu coagulation rate constant, α = order of coagulation reaction, C_t= concentration of particles (TDSP) at time, t.

Linearizing Eq. 2 gives:

$$\mathrm{Ln}\left[-\frac{dC_t}{dt}\right] = \alpha\, LnC_t + Ln\, K_m \qquad (3)$$

The values of α and K_m could be determined from Eq. (3). This constant, K_m is the product of collision efficiency (ε_p) and the Smoluchowski rate constant for rapid coagulation (K_r). It is given as:

$$K_m = \varepsilon_p\, K_r \qquad (4)$$

von Smoluchowski rate constant for rapid coagulation, K_r is given by:

$K_r = 8\pi R D^1$ (5)

and $R = 2a$ (6)

Where a and D^1 is the particle radius and particle diffusion coefficient, respectively.

From Einstein's equation, diffusivity is given as [21, 22]:

$D^1 = \frac{K_B T}{B}$ (7)

From Stoke's equation:

$B = 6\pi\eta a$ (8)

$a = \frac{R}{2}$ (9)

Where K_B is the Boltzmann's constant (1.38064852 x 10^{-23} JK^{-1}), B is the friction factor, η is the viscosity of the fluid (effluent); T = absolute temperature in Kelvin.

Substituting Eq. 9 into Eq. 8 gives:

$B = \frac{6\pi\eta R}{2} = 3\pi\eta R$ (10)

Also, substituting Eq. 10 into Eq. 7 for B leads to:

$D^1 = \frac{K_B T}{3\pi\eta R}$ (11)

Putting Eq. 11 into Eq. 5 gives:

$K_r = \frac{4K_B T}{3\eta}$ (12)

Again, substituting Eq. 12 into Eq. 4 produces:

$K_m = \varepsilon_{P[\frac{4K_B T}{3\eta}]C^{\alpha}}$ (13)

Combining Eqs.13 and 2 leads to:

$\frac{dC_t}{dt} = -\varepsilon_{p[\frac{4K_B T}{3\eta}]C^{\alpha}}$ (14)

WST [23] and Menkiti [24] stated that in real practice, $1 \le \alpha \le 2$. Based on this, what is required to evaluate K_m is to determine the line of better fit between α = 1 and 2, while the experimental data are fitted into the linearised form of Eq. 2.

For a first-order reaction kinetics (where α =1), Eq. 2 gives

$Ln\, C_t = -K_m t + Ln\, C_0$ (15)

For α = 2 (second-order reaction kinetics), Eq. 2 becomes:

$\frac{1}{C_t} - \frac{1}{C_0} = K_m t$ (16)

Where C_o is the initial particle concentration and Ct is the concentration at any time, t; K_m is the reaction rate constant.

Let coagulation-flocculation time, $\tau = \frac{1}{C_0 K_m}$ (17)

Solving Eq. 17, the coagulation-flocculation half-life, $\tau_{1/2}$ is obtained as

$\tau_{1/2} = \frac{1}{0.5 C_0 K_m}$ (18)

According to Smoluchowski theory where the coagulation of spherical particles is controlled entirely by Brownian diffusion, Eq. 18 can be solved to obtain [25, 26]:

$\frac{C_z\,(t)}{C_0} = \frac{\left[\frac{1}{\tau}\right]^{n-1}}{\left[1 + \frac{t}{\tau_{1/2}}\right]^{n+1}}$ (19)

Equation 19 represents the general expressions of a particle of any ith order.

For primary particles, of singlets (when $i = 1$):

$C_1(t) = C_0 \left[\frac{1}{\left[1 + \frac{t}{\tau_{1/2}}\right]^2}\right]$ (20)

For doublets(when $i = 2$):

$$C_2(t) = C_0 \left[\frac{(\frac{t}{\tau_{1/2}})}{\left[1+\frac{t}{\tau_{1/2}}\right]^3} \right] \quad (21)$$

For triplets(when $i = 3$):

$$C_3(t) = C_0 \left[\frac{(\frac{t}{\tau_{1/2}})^2}{\left[1+\frac{t}{\tau_{1/2}}\right]^4} \right] \quad (22)$$

Materials and Method

Sample Collection

Collection of aquaculture wastewater

The aquaculture wastewater (AW) was collected from an aquaculture pond in the Agu-Awka, Anambra state, Nigeria on January 18, 2017. The water sample was stored in containers at 4^0C prior to use to avoid degradation or changes to their characteristics. The wastewater was analyzed for its physicochemical parameters such as pH, total dissolved solids (TDS), turbidity, total solids (TS), total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), nitrogen, phosphorus, etc. by using the standard methods [27]. The effluents were also characterized after treatment and compared with the World Health Organisation (WHO) standards for water quality.

Coagulant precursor collection and processing

The coagulant precursor, *Sesamum indicum* seeds sample (Fig. 1) was purchased from Awka main market, Anambra state, Nigeria. The seeds were sorted to remove bad ones, washed with de-ionized water to remove dirt and impurities to avoid its interference with the coagulation-flocculation experiments. The sample was dried at room temperature for 2 weeks at room temperature to preserve the physiochemical properties of the samples. The dried sample was ground with a local grinder to a particle size of approximately 300 µm. The ground samples were then stored in an airtight container in a refrigerator until use. The sample was analyzed for its proximate composition such as bulk density, moisture content, crude fat, crude protein, carbohydrate content, crude fiber, ash content using the methods described by Menkiti and Ezemagu [28]. Its specific gravity was also determined.

Figure 1: Sesamum indicum seeds

Preparation of the coagulant extract

The extraction method for coagulant preparation is aimed at improving the material's coagulation performance and therefore reduces the rate of coagulant consumption to make pollutants removal more cost-effective [29]. 500ml of n-Hexane was used to extract oil from the ground seed in the column. Complex salts (25g of NaCl, 4g of $MgCl_2$, 1g of $CaCl_2$, 0.75g of KCl) were dissolved in 1000ml of distilled water. 10g of the cake was dissolved in 250ml of the prepared salt solution and stirred continuously for 1 h at a temperature of 70^{o}C, using a magnetic stirrer to promote extraction of the coagulant. This was then passed through a sack to obtain the filtrate which was dried at room temperature, ground and stored in an airtight container for further use.

The functional groups and the morphological properties of the coagulant were obtained using the Fourier transform infrared (FTIR) machine (Buck M520 Infrared spectrophotometer) and scanning electron microscopy (Carl Zeis Analytical SEM Series. MA 10. EVO-10-09-49).

Coagulation-Flocculation Experiment (Jar Test)

The effect of coagulant dosage, pH, temperature and settling time on the reduction of TDS from AW using SIC was studied using the one-factor-at-a-time (OFAT) method. At first, to obtain the optimum dosage, 250ml of the sample were poured into five beakers, dosed with 0.1, 0.2, 0.3, 0.4 and 0.5 g/L of the coagulant and stirred using magnetic stirrers. After stirring at high speed (120 rpm) for 5 min, the speed was reduced to 30 rpm and stirred further for 20 min. When the stirring has been completed, the hot plates were turned off simultaneously and 20ml of the samples were withdrawn from each of the beakers and their respective TDS were measured using the TDS meter (HANNA instruments) at settling time, t= 0, 3,5,10,20,30,40, 50 and 60 min. Secondly, the optimum pH was studied in the range of pH 2-10 at the optimum dosage. The pH was adjusted by adding 1M HCl or NaOH solutions. Subsequently, the optimum temperature was determined by varying the solution temperature from 303 – 323 K at the optimum coagulant dosage and pH. The percentage of TDS removal was evaluated using Eq. 23:

$$\%TDS = \frac{TDS_i - TDS_f}{TDS_i} \times 100 \quad (23)$$

where TDS_i and TDS_f are the initial and final values of TDS.

Results and Discussion

Aquaculture wastewater characteristics

The characteristics of the untreated aquaculture wastewater and treated effluent are presented in Table 1. Aquaculture wastewater is treated for sustainability and water conservation [3]. pH of 7.9 makes the wastewater basic. The pH values were within the permissible limit (6.5-8.5) of WHO standard before discharge or reuse. It shows that the existence of total dissolved solids (TDS) and total suspended solids (TSS) which caused the water to be turbid which shows the need for its treatment [25]. The wastewater also possessed very high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The reduction of the pollutants levels of the wastewater after treatment confirmed the efficacy of coagulation-flocculation process [30]. Also, the BOD/COD ratio (BI) was 0.42 for the raw wastewater, which after treatment with SIC at the optimum conditions improved to 0.52. This shows that the biodegradability of the AW was improved and the pretreated wastewater can be subjected to biological treatment [31].

Table 1: Characteristics of aquaculture wastewater before and after treatment using SIC

Parameter	**Unit**	**Before treatment**	**After coagulation**	**WHO standard, 2002**
pH		7.9	6.9	6.5-9.2
Temperature	℃	30.2	30.4	-
Appearance		yellowish green	clear	-
Odour	-	Positive	Negative	-
Biological oxygen demand (BOD)	mg/L	317	95	-
Chemical oxygen demand (COD)	mg/L	758	182	250
Dissolved oxygen (DO)	mg/L	9.6	7.8	-
Biodegradability index (BI)	-	0.42	0.52	-
Electrical conductivity (EC)	µS/cm	1963	938	1000
Turbidity	NTU	404	65.12	50
Total solids (TS)	mg/L	695	142	250

Total suspended solids (TSS)	mg/L	45	30	-
Total dissolved solids (TDS)	mg/L	650	112	-
Nitrogen	mg/L	0.829	0.577	-
Total phosphorus	mg/L	0.91	0.53	-
Nitrate	mg/L	0.829	0.577	-
Chloride	mg/L	2.44	1.53	2.5
Calcium	mg/L	5.40	2.43	150
Potassium	mg/L	5.45	3.57	-
Iron	mg/L	0.425	0.37	0.1-1.0

Physiochemical characteristics of the coagulant precursors

Table 2 shows the proximate composition of the coagulant precursor, *Sesamum indicum* seeds. The relatively high protein content of 30.6 % obtained for *Sesamum indicum*, is an indication of the good performance of the seeds as a precursor for the treatment of effluents [12, 28, 32, 33]. This is essential for neutralization (the adsorption of an oppositely charged coagulant on the colloidal surface) of the colloidal particles; these, in turn, induces the process of coagulation via bridging, which stimulates the flocs development [12]. Other researchers suggest that polysaccharides such as carbohydrate are active coagulating agents too [34]. The high carbohydrate content (Table 2) also suggests that it is a potential coagulant for wastewater treatment.

Table 2: Proximate analysis of the coagulant precursor

Parameters	Unit	Value
Bulk density	g/mL	0.26
Ash content	%	4.91
Moisture content	%	2.53
Crude fiber	%	4.41
Fat content	%	52.63
Crude protein	%	30.6
Carbohydrate content	%	7.58
Specific gravity	%	3.22

Instrumental characterization of the coagulant

Fourier transform infrared spectroscopy (FTIR) on the biopolymers

FTIR is used to identify the functional groups that are actively taking part in the coagulation-flocculation processes [35]. The spectrum was collected from 4000 to 400 cm^{-1}. The FTIR spectra of the SIC spectrum is shown in Fig. 2. The presence of N-H stretching (1619.794 cm^{-1}) in the FTIR spectra of the coagulant indicates the presence of amino compounds. The carboxyl, C=O (1858.74 cm^{-1}), and hydroxyl, O–H (2472.144, 2588.339, 3208.179, 3283.442 cm^{-1}) groups can be observed; these groups including amino or amide (N-H) are the preferred groups for the coagulation-flocculation processes [36]. The medium alkane group, C–H stretch (2852.209) was present on the coagulant. The O–H stretch of alcohols and phenols (, 3433.98, 3676.286, 3821.958), which is a strong band was observed. Strong bonds of =C–H bend of alkenes (767.637, 903.5788), and C–C stretch of aromatics (1410.927) were also seen. These strong bands took an active part in the treatment process. Also, the presence of –C≡C– stretch of alkynes (2030.862) and H–C=O: C–H stretch of aldehydes (2716.548) were dictated.

Scanning electron microscopy (SEM) on the biopolymers

The SEM image (at 500x) of the coagulant, SIC is shown in Fig. 3. The irregular and rough granular structures observed on the coagulant indicates that the coagulant possesses features of a good coagulant with respect to the adsorption and bridging of colloidal particles thereby promoting the sedimentation of particles. Also, the particles appear fibrous and compact in nature forming clusters. The bridging coagulation process will occur when coagulants containing threads or fibers are applied, which will attach to several colloids, capturing and binding them together [37].

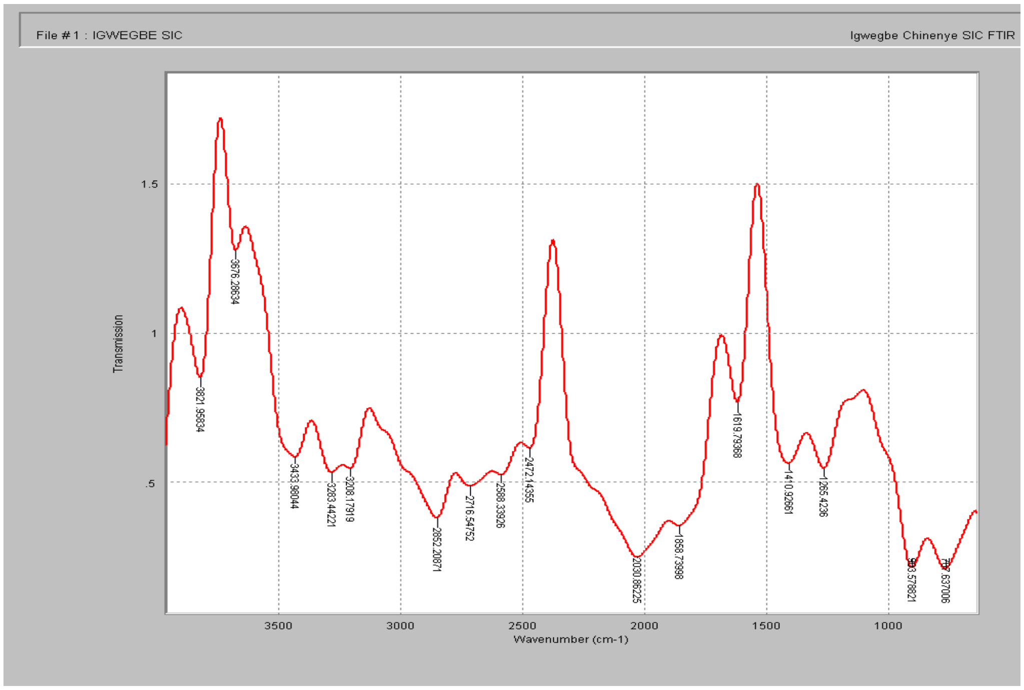

Figure 2: FTIR spectra on SIC

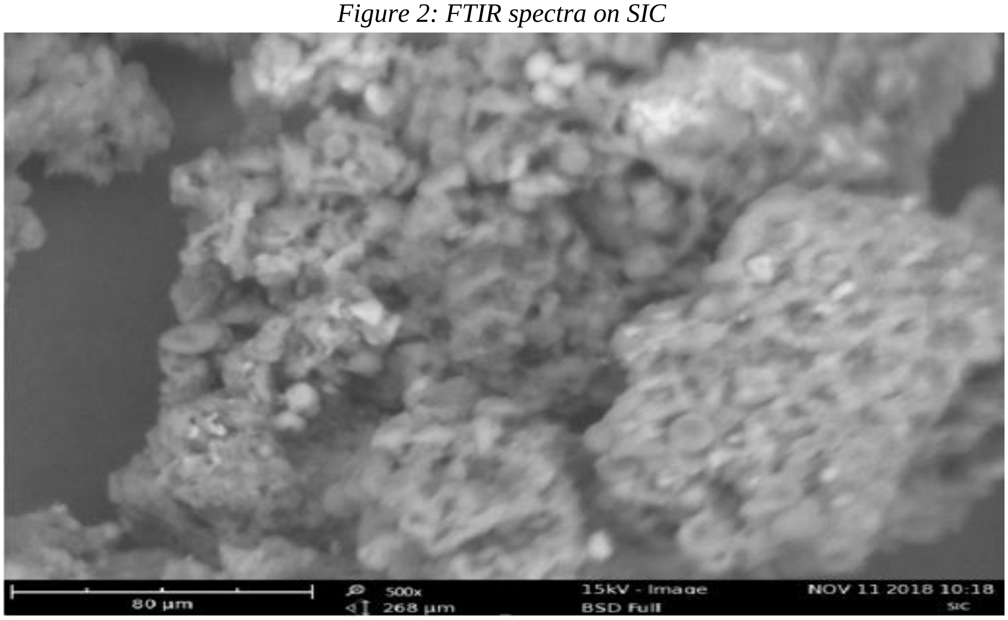

Figure 3: SEM image of SIC

Effect of operating parameters on TDS reduction

Effect of coagulant dosage on TDS reduction

Dosage is one of the most important parameters that must be considered to determine the optimum condition for the performance of any coagulant for removal of pollutants because coagulant alters or destabilizes negatively charged particulate, dissolved, and colloidal contaminants.Insufficient dosage or overdosing would result in poor performance in flocculation [38]. It is important to determine the optimal dose for coagulation; insufficient doses will not effectively destabilize the particles and adding excess dose can cause detrimental effects such as restabilization and excessive sludge production. The coagulant dosages were varied between 0.1 to 0.5 g/l. The effect of different dosages on TDS reduction (%) at the initial wastewater pH of 7.9is shown in Fig. 4. It can be observed that the removal of TDS increases progressively as the coagulant dosage increases from 0.1 to 0.4 g/L.The positively charged coagulant adsorbed on the surface negatively charged colloid particles by charge neutralization because increasing the dosage would provide more coagulants to be contacted with AW colloidal particles in order to form aggregates, resulting to higher formation of flocs [39]. However, TDS removal decreased when the dosage was further increased to 0.5 g/L; more than the optimum dosage would destabilize the particles due to surface saturation which resulted to decline in TDS removal [40]. The mechanism of coagulation-flocculation has been assumed to have great effects on the influence of coagulant dosage on the aggregation of particles [6].

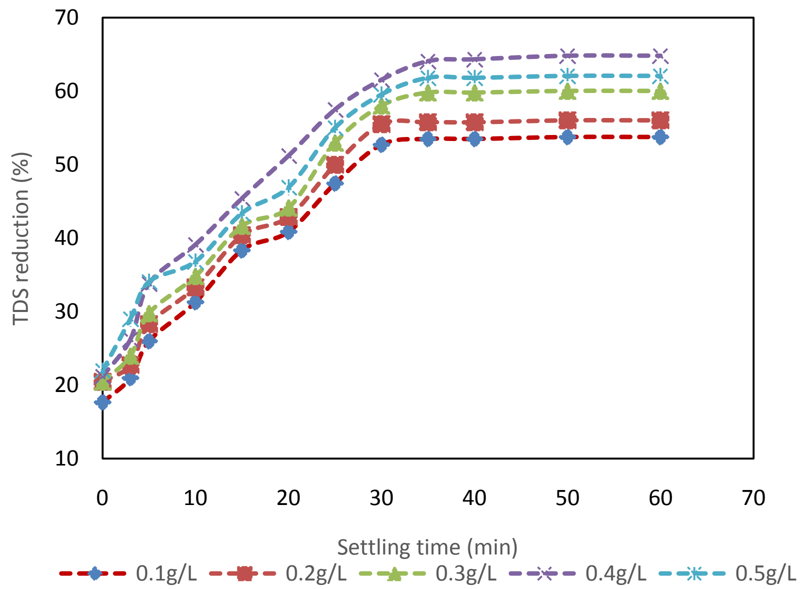

Figure 4: Effect of coagulant dosage on TDS reduction (%) using Sesamum indicum seed extract (pH = 7.9; temperature = 303 K).

Effect of solution pH and settling time on TDS reduction

pH plays a vital part in biological and chemical reactions. It affects the ionization of pollutants [41]. The rate of pollutants elimination from an aqueous environment is mainly dependent on the pH of the effluent [42]. The pH effect on pollutants reduction is related to the pH of the solution and functional groups present in the coagulants which affect its surface charge. These pollutants cannot agglomerate unless the pH is adjusted to the isoelectric point [43]. Fig. 5 shows the TDS removal at different pH (2, 4, 6, 8 and 10) at the optimum the dosage of 0.4 g/L. The reduction of TDS using SIC gave better results in the acidic medium than in the alkaline medium, having pH 2 as the optimum which was adopted for further experiments. At this pH, precipitation of flocs was more and better than the other pH. The coagulation activity was poorer at pHof 10. This shows that the degree of solubility is higher in the acidic medium than the alkaline medium. It has been noted that the higher the solubility of a coagulant, the greater the collision of its total dissolved solid particles [44]. From Fig. 5, it can be seen that pH has a great effect on the removal efficiency of TDS. According to Tarleton and Wakeman [45], at lower pH values, non-ionic polymers and polymers with few ionized groups often produce the best performance.

Figure 5 also shows the TDS removal using SIC at different settling time at varying pH and optimum SIC dosage of 0.4 g/L. From Fig. 5, it can be seen that the percentage removal of TDS increases with increasing settling time. The removal efficiency was rapid between 0 – 35 min but slowed down after 30 min. Equilibrium time was observed at settling time of 35 min; there was a little or no significant increase in TDS removal after the equilibrium settling time (35 min). This suggests that no further increase in settling time is necessary after equilibrium has been achieved.

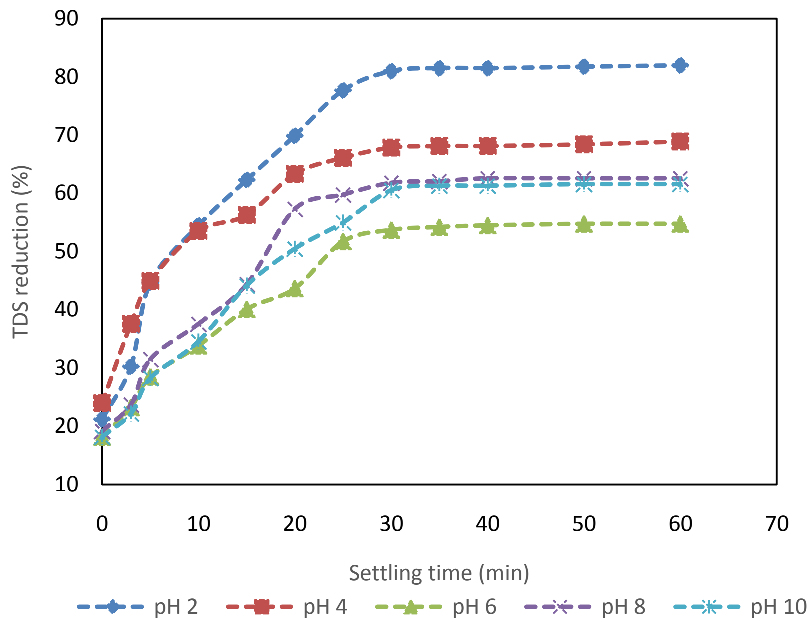

Figure 5: Effect of solution pH on TDS reduction (%) using Sesamum indicum seed extract (SIC dosage = 0.1 g/L; temperature = 303 K).

Effect of Temperature on the TDS reduction

The TDS removal was studied at different temperatures of 303, 313 and 323 K at pH of 2 and SIC dosage of 0.4 g/L (Fig. 6). Highest removal efficiency (82 %) was obtained at the lowest temperature (303 K) as can be seen in Fig. 6. The reduction in pollutants reduction with increasing temperature may be due to of random motion of colloidal particles caused by the increase of kinetic energy which interfere the attachment of particles onto the biopolymers to form flocs and reduction in flocs sizes [46].

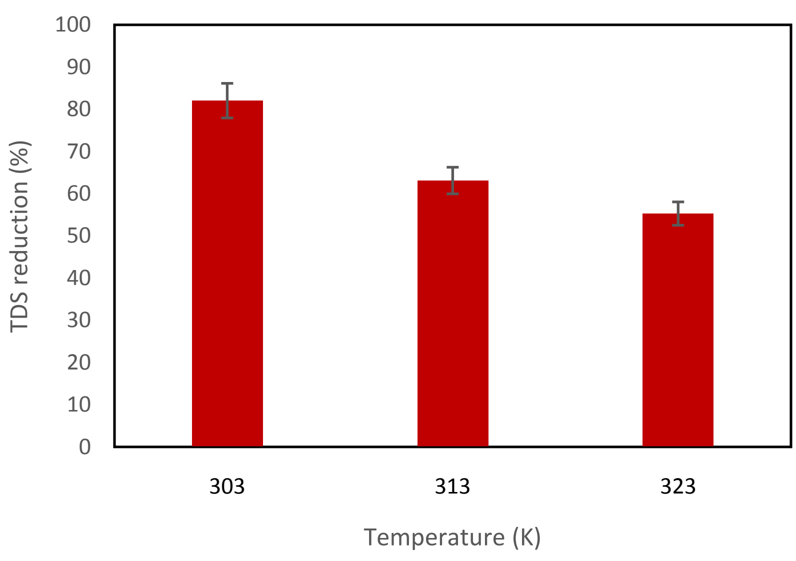

Figure 6: Effect of solution temperature on TDS reduction (%) using Sesamum indicum seed extract (pH = 7.9; SIC dosage = 0.4 g/L).

Coag-flocculation kinetics

The coagulation-flocculation kinetic data were fitted into the first-order (where α =1) and second-order (where α =2) coagulation-flocculation reaction equations. The coagulation-flocculation parameters at the optimum conditions: SIC dosage of 0.4 g/L, pH of 2, temperature of 303 K and settling time of 60 min are presented in Table 3. K_m for first-order was obtained from the slope of the linear plot of $Ln\ C_t$ versus time, *t* (Fig. 7a) using Eq. 15 while K_m for second-order was obtained from the slope of the straight line plot of $\frac{1}{C_t}$ versus *t* (Fig. 7b) using Eq. 16. K_m is a constant that affects the rate of aggregation of particles [28]. The coefficient of regression, R^2 was used to establish the level of accuracy of fit of the experimental data to the models expressed as Eqs. 15 and 16 and the model that best fits the process. The R^2 values of 0.9314 and 0.9837 for first-order and second-order, respectively are moderately high and reveals the effectiveness of both equations in describing the coagulation-flocculation processes. Thus the coagulation-flocculation kinetic data follows the perikinetic flocculation theory. But the data fitted best into the second-order coagulation-flocculation equation with K_m value of 0.0002 L/g.min and coagulation-flocculation half-life, $\tau_{1/2}$of 20 min (Table 3) suggesting very fast coagulation. This implies that the order of the reaction (α) is 2. High ε_p results in high kinetic energy to overcome the repulsive forces [4].

Table 3: Brownian coagulation-flocculation kinetics and regression parameters for TDS reduction on AW using SIC at pH 2 and coagulant dosage of 0.4 g/L.

Kinetic parameter	First-order	Second-order
R^2	0.9314	0.9837
K_m (L/g min)	0.0502	0.0002
C_o (g/L)	426.45	500.00
$-r$ (g/min)	$0.0502C_t$	$0.0002C_t^2$
$\tau_{1/2}$ (min)	0.0934	20
τ (min)	0.1868	40
β (L/ g min)	0.1004	0.0004
K_r (L/min)	2.14532E-18	2.14532E-18
ε_p (L/g)	2.33998E+16	9.32264E+13
$(N_p)_0$	2.56809E+23	3.011E+23
D^1	4.1667E-20	1.65159E-24
A	1	2

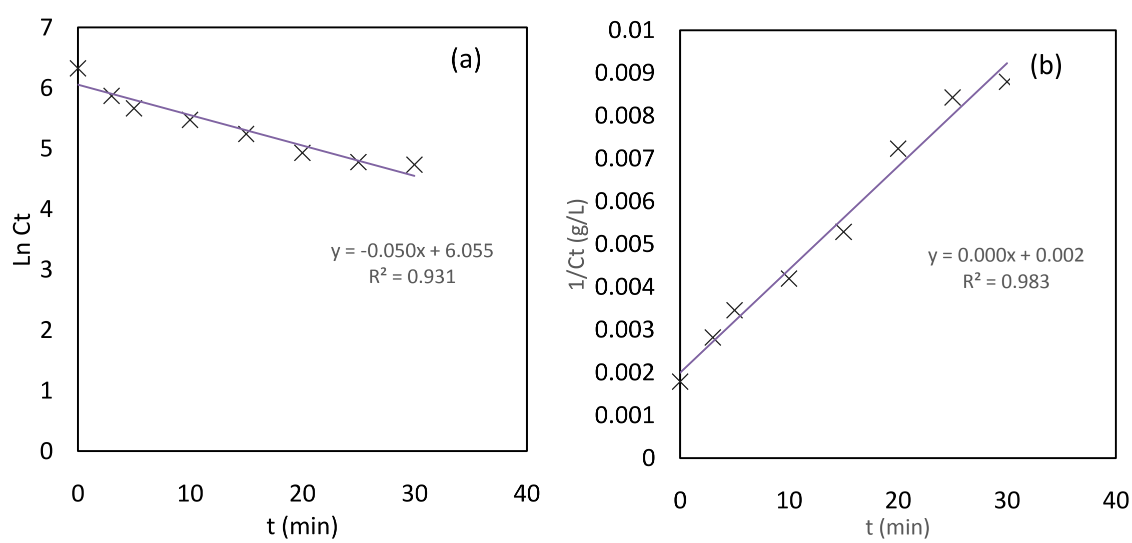

Figure 7: Particle concentration versus time graph for TDS reduction on AW using (a) coagulation-flocculation first-order kinetics and (b) coagulation-flocculation second-order kinetics

Particle distribution plots

To predict the time evolution of three aggregating particles or species -singlets, doublets, and triplets (for n = 1, 2 and 3 respectively), Eq. 19(which is from Smoluchowski's model) was used. The plots of the aggregating particles and the total aggregate against time are shown in Fig. 8. The number of primary particles (singlets) declined more swiftly than the total number of particles (ΣC) since doublets and triplets are formed because of the rapid destabilization of singlets which aided the coagulation process [4, 25]. These brought to limelight the suitability of Eq. 19 in particle size distribution.

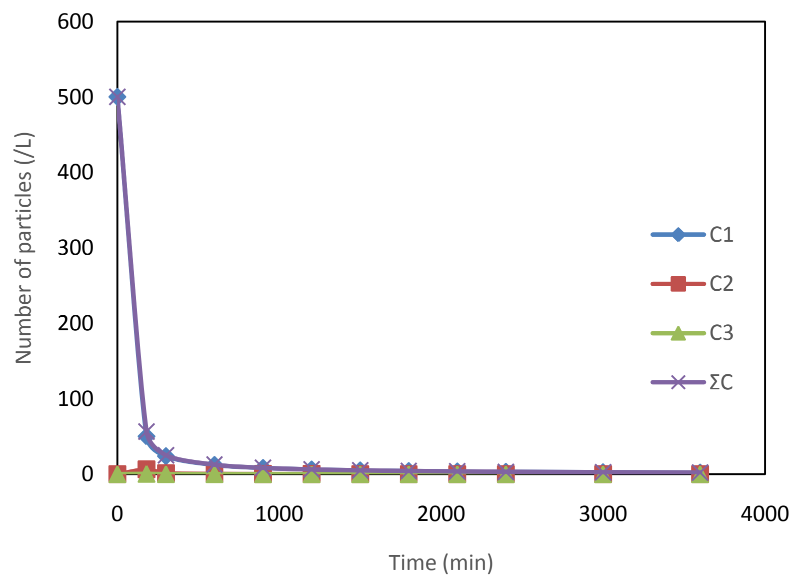

Figure 8: Particle variations behaviour and total aggregate against time on AW using SIC on AW (at pH = 2, coagulant dosage = 0.4 g/L, $\tau_{1/2}$=0.333333s, C_0=500g/L and K_m= 0.0002L/g.min).

Conclusion

The present study showed that total dissolved solids (TDS) can be removed effectively from aquaculture wastewater with the use of *Sesamum indicum* seeds extract as coagulants. The process was found to be dependent on the dosage of coagulant, settling time, temperature and pH of the effluent. Optimum TDS removal of 82 % was obtained at pH of 2, dosage of 0.4 g/L, solution temperature of 303 K and settling time of 60min. The coagulation-flocculation kinetic data followed the second-order coagulation-flocculation model (R^2 = 0.9837) than the first-order coagulation-flocculation reaction equation (R^2 = 0.9314) which implies that the order of the coagulation reaction, α is 2. At these conditions, the coagulation-flocculation half-life ($\tau_{1/2}$) and reaction rate (K_m) were evaluated as 20 min and 0.0002 L/g min, respectively. The process was found to follow the perikinetic flocculation theory. These coagulants are environmentally friendly, readily available and cheap to obtain. Thus, the use of this material in wastewater treatment could be more suitable and advantageous when compared to chemical coagulants that are normally expensive and also have a lot of undesirable environmental and health impacts.

Acknowledgments

The authors wish to thank the Department of Chemical Engineering for their support during the course of this research.

Conflict of Interest

There is no conflict of interest associated with this work.

References

[1]. Kumar, M. S., Krishna, G. V. T. G., & Sivasankar, V. (2015) Coagulation Performance Evaluation of Natural and Synthetic Coagulants in Waste Water Treatment. *ARPN Journal of Engineering and Applied Sciences*, 10(6):2714-2717.

[2]. Darwin, D., Sarbaini, S. P., Dhiauddin, F., Ilham, M., & Fazil, A. (2017). Wastewater Treatment for African Catfish (*Clarias gariepinus*) Culture by using Anaerobic Process. *AGRITECH* 37(4):462-470.

[3]. Turcios, A. E & Papenbrock, J. (2014). Sustainable Treatment of Aquaculture Effluents-What can we learn from the past for the future? *Sustainability*, 6:836-856.

[4]. Menkiti, M.C, Nwoye, C. I., Onyechi, C. A., & Onukwuli, O. D. (2011).Factorial Optimization and Kinetics of Coal Washery Effluent Coag-Flocculation by *Moringa Oleifera* Seed biomass. *Advances in Chemical Engineering and Science*, 1:125-132.

[5]. Rytwo, G. (2012). The Use of Clay-Polymer Nanocomposites in Wastewater Pretreatment. *The Scientific World Journal*, Article ID 498503, 7 pages.

[6]. Menkiti, M. C., Onyechi, C. A., & Onukwuli, D. O. (2011). Evaluation of Perikinetics Compliance for the coagflocculation of Brewery Effluent by *Brachystegia eurycoma* Seed Extract. *International Journal of Multidisciplinary Sciences and Engineering*, 2(6):73-80.

[7]. Oladoja A, N., & Aliu, Y.D. (2009). Snail Shell as Coagulant Aid in the Alum Precipitation of Malachite Green from Aqua System. *Journal of Hazardous Materials*, 164 (2-3):1496-1502.

[8]. AhmadI, S., Mostafapour, F. K. & Bazrafshan, E. (2017). Removal of Aniline and from Aqueous Solutions by Coagulation/Flocculation–Flotation. *Chemical Science International Journal* 18(3):1-10.

[9]. Silva, M. J. M., Pateriani, J. E. S. & Francisco, A. R. (2013). Application of *Moringa olifera* Natural Coagulant for Clarification and Disinfection of Treated Wastewater in Wetlands and Multistage Filtration. *African Journal of Agricultural Research*, 8(24): 3102-3106.

[10]. Di Bernardo, L. (1993). *Metodos e Tecnicas de Tratamento de Agua*, 1 & 2. ABES, Rio de Janeiro.

[11]. Binayke, R. A., &Jadhav, M.V. (2013) Application of Natural Coagulantsin Water Purification. *International Journal of Advanced Technology and Civil Engineering*, 2:118-123.

[12]. Choy, S. Y., Prasad, K. M. N., Wu, T. Y., & Ramanan, R. N. (2015). A Review on Common Vegetables and Legumes as Promising Plant-Based Natural Coagulants in Water Clarification. *Int. J. Environ. Sci. Technol.*, 12:367–390.

[13]. Shan, T. C., Al Matar, M., Makky, E. A., &Ali, E. N. (2017). The Use of *Moringa oleifera* Seed as a Natural Coagulant for Wastewater Treatment and Heavy Metals Removal. *Appl. Water Sci.*, 7: 1369–1376.

[14]. Menkiti, M.C., Ejimofor, M.I., Ezemagu, I. G., Uddameri, V. (2016). Turbid-Metric Approach on the Study of Adsorptive Component of Paint Effluent Coagulation using Snail Shell Extract. *Arab J. Sci. Eng.*, 41:2527-2543.

[15]. Nwobasi, C.S, & Attamah, C.G. (2017). Proximate Analysis and Phytochemical Properties of Sesame (*Sesamum indicum* L.) Seeds Grown and Consumed in Abakaliki, Ebonyi State, Nigeria. *International Journal of Health and Medicine*, 2(4):1-4.

[16]. Ram, R., Catlin, D., Romero, J. & Cowley, C. (1990). *Sesame: New approaches for crop improvement*. Purdue University Press.

[17]. Jibril, A., Giwa, S. O., & Giwa, A. (2015). The Use of Sesame Seed as a Coagulant for the Treatment of Turbid Surface Water. *Journal of Environmental Science, Computer Science and Engineering & Technology*, Sec. A 4(2):543-554.

[18]. von Smoluchowski, M. (1917). Verscuheiner Mathematischen Theory der koagulations kinetic kolloider lousungen. *Z Phys Chem* 92:129-168.

[19]. Menkiti, M. C., Igbokwe, P. K., Ugodulunwa, F. X. O. & Onukwuli, O. D. (2008). Rapid Coagulation/Flocculation Kinetics of Coal Effluents with High Organic Content using Blended and Unblended Chitin Derived Coagulants (CSC). *Research Journal of Applied Sciences*, 3(4):317-323.

[20]. Ugonabo, V. I., Menkiti, M. C. & Onukwuli, O. D. (2012). Effect of Coag-Flocculation Kinetics on *Telfairia occidentalis* Seed Coagulant (TOC) in Pharmaceutical Wastewater. *Proceedings of the National Conference on Infrastructural Development and Maintenance in the Nigerian Environment*, Faculty of Engineering, Nnamdi Azikiwe University, Awka, Nigeria, 179-190.

[21]. Fridrikhsberg, D. A. (1984). *A course in colloidal chemistry*, Mir Publishers Moscow, Russia.

[22]. Danov, D. K., Kralchevsky, P. A. & Ivanov, I. B. (2001). *Dynamic process in surfactants stabilized emulsion*, Faculty of Chemistry, University of Sofia.

[23]. Water Specialist Technology (WST) (2003). *About coagulation and flocculation*: Information Bulletins 22-29. U.S.A.

[24]. Menkiti, M.C. (2007). *Studies on Coagulation and Flocculation of Coal Washery Effluent: Turbid Metric Approach*, M.Sc. thesis, Nnamdi Azikiwe University, Awka, Nigeria.

[25]. Ugonabo, V. I., Emembolu, L. N., & Igwegbe, C. A. (2016). Bio-Coag-Flocculation of Refined Petroleum Wastewater using Plant Extract: A Turbidimetric Approach. *International Journal of Emerging Engineering Research and Technology* 4(11):19-26.

[26]. Emembolu, L. N., Igwegbe, C. A., & Ugonabo, V. I. (2016). Effect of Natural Biomass Treatment on Vegetable Oil Industry Effluent via Coag-Flocculation. *Saudi Journal of Engineering and Technology*, 1(4):172-179.

[27]. *American Public Health Association, American Water Works Association, Water Environment Federation (APHA, AWWA, WEF) (*2012)*. Standard Methods for the Examination of Water and Wastewater, 22th edition,* American Public Health Association, *Washington, D.C., USA.*

[28]. Menkiti, M. C. & Ezemagu, I. G. (2015). Sludge Characterization and Treatment of Produced Water (PW) using *Tympanotonus fuscatus* Coagulant (TFC). *Petroleum* 1:51-62.

[29]. Ramavandi, B. (2014). Treatment of water turbidity and bacteria by using a coagulant extracted from *Plantago ovata*. *Water Resources and Industry*, 6:36-50.

[30]. Nur, A. A. A. & Zawawi, D. (2012). *Electrocoagulation of palm oil mill effluent using aluminum electrodes* 3, Faculty of Civil and Environmental Engineering, University of Tun Hussein Onn Malaysia.

[31]. Verma, S., Prasad, B., & Mishra I. M. (2010) Pretreatment of Petrochemical Wastewater by Coagulation and flocculation and The Sludge Characteristics. *Journal of Hazardous Materials* 178:1055–1064.

[32]. Ghebremichael, K.A., Gunaratna, K.R., Henriksson, H., Brumer, H., & Dalhammar, G. A. (2005). Simple Purification and Activity Assay of the Coagulant Protein from *Moringa oleifera* Seed. Water Research 39:2338–2344.

[33]. Ndabigengesere, A., Narasiah, K.S., Talbot, B. G. (1995).Active Agents and Mechanism of Coagulation of Turbid Waters using *Moringa oleifera, Water Research*29(2):703-710.

[34]. Okuda, T., Baes, A. U., Nishijima, W., Okada, M. (2001). Coagulation Mechanism of Salt Solution Extracted Active Components in *Moringa oleifera* Seeds. Water Research 35:830–4.

[35]. Nharingo, T., Zivurawa, M. T., & Guyo, U. (2015) Exploring the Use of Cactus *Opuntia ficus indica* in the Biocoagulation–Flocculation of Pb(II) ions from Wastewaters. *Int. J. Environ. Sci. Technol.,* 12:3791–3803.

[36]. Zhang, Z., Xia, S., Zhao, J., & Zhang, J. (2010) Characterization and Flocculation Mechanism of High Efficiency Microbial Flocculant TJ-F1 from *Proteus mirabilis*. *Colloids Surf. B Biointerfaces* 75:247–251.

[37]. Çoruh, H.A. (2005).*Use of Calcium Alginate as a Coagulant in Water Treatment*. A Thesis Submitted To The Graduate School of Natural and Applied Sciences of Middle East Technical University, In Partial Fulfillment of the Requirements for the Degree of Master of Science in Department of Environmental Engineering.

[38]. Daud, Z., Nasir, N., Awang, H. (2013). Treatment of Biodiesel Wastewater by Coagulation and Flocculation using Polyaluminum Chloride. *Australian Journal of Basic and Applied Sciences*, 7(8):258-262.

[39]. Teh, C.Y., Wu, T.Y., &Juan, J.C. (2014). Potential Use of Rice Starch in Coagulation-Flocculation Process of Agro-Industrial Wastewater: Treatment Performance and Flocs Characterization. *Ecological Engineering* 71:509–519.

[40]. Sharma, B.R., Dhuldhoya, N.C., &Merchant, U. C.(2006). Flocculants—An Ecofriendly Approach. *J. Polym. Environ.*,14: 195–202.

[41]. Ahmadi, S., Mohammadi, L., Igwegbe, C.A., Rahdar, S., & Banach, A.M. (2018) Application of Response Surface Methodology in the Degradation of Reactive Blue 19 using H_2O_2/MgO Nanoparticles Advanced Oxidation Process. *Int. J. Ind. Chem.,* 9: 241.

[42]. Ahmadi, S., Rahdar, A., Rahdar, S., & Igwegbe, C. A. (2019). Removal of Remazol Black B from Aqueous Solution using P-γ-Fe_2O_3Nanoparticles: Synthesis, Physical Characterization, Isotherm, Kinetic and Thermodynamic Studies. *Desalination and Water Treatment,* 152: 401–410.

[43]. Amor, C., Lucas, M. S., Pirra, A. J., & Peres, J. A. (2012). Treatment of Concentrated Fruit Juice Wastewater by the combination of biological and chemical processes. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.,* 47(12):1809-17.

[44]. Nwaiwu, N.E. & Bello, A.A. (2011). Effect of *Moringa oleifera*-Alum Ratios on Surface Water Treatment in North East Nigeria. *Research Journal of Applied Sciences, Engineering and Technology,* 3(06): 505-512.

[45]. Tarleton, E.S. & Wakeman R. J. (2006). *Solid/Liquid Separation: Equipment Selection and Process Design,* Elsevier, Oxford.

[46]. Phalakornkule, C., Mangmeemak, J., Intrachod, K., & Nuntakomjorn, B. (2010). Pretreatment of Palm Oil Mill Effluent by Electrocoagulation and Coagulation. *Sci. Asia* 36:142–149.