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Coagulation-Flocculation of Aquaculture Wastewater Using Green Coagulant from *Garcinia kola* Seeds: Parametric Studies, Kinetic Modelling and Cost Analysis

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Abstract: To achieve sustainability, it is necessary to use proper treatment methods to reduce the pollutant loads of receiving waters. This study investigates the coagulative reduction of turbidity, COD, BOD and colour from aquaculture wastewater (AW) using a novel *Garcinia kola* seeds coagulant (GKC). This coagulant was obtained from extraction of *Garcinia kola* seeds and analysed for its spectral and morphological characteristics through FTIR and SEM. The kinetics of coagulation-flocculation were also investigated in terms of total dissolved and suspended solids (TDSP). The seeds had 11.27% protein and 68.33% carbohydrate, showing usability in adsorption/charges neutralisation as a coagulant to reduce particles. Maximal turbidity reduction = 81.93%, COD = 75.03%, BOD = 72.84% and colour = 56.69% at 0.3 g GKC/L, pH 2, 60 min and 303 K were achieved. Von Smoluchowski's second-order peri-kinetics theory was used to fit the results, giving $R^2 > 0.9$. At a coagulation order (α) of 2, the reaction rate (K_C) and half-life ($\tau_{S1/2}$) were 0.0003 L/g·min and 25.3 min at the optimal conditions. The sorption data better fit the Lagergren compared to the Ho adsorption model. Furthermore, the net cost of using GKC to handle 1 L of AW (including electricity and material costs) was calculated to be 1.57 EUR, and the costs of 0.3 g/L GKC preparation and energy were 0.27 and 1.30 EUR, respectively. In summary, these seeds can be used to pre-treat AW.

Keywords: *Garcinia kola*; aquaculture; coagulation; water treatment; adsorption; turbidity

1. Introduction

Unused feedstuff, faeces and biological floc leached off culture facility surfaces and containers provide biosolids in fish processing systems [1–3]. All aquaculture locations inject wastes into the receiving ecosystem as a point means of pollution [4]; as a result, the key benefit of aquaculture is that wastewater treatment can reduce the overall concentration of dissolved pollutant particles [4]. It is necessary to use proper treatment to optimise this valuable resource to achieve sustainability [5,6], and to reduce the burden on coastlines while still producing huge quantities of fish in inland aquaculture systems. Aquaculture waste depends on the feed composition and feeding technology. It is important to know the system that is applied for aquaculture production and also the composition of wastewater generated by the particular fish production facility for the development of any technology for its effluent treatment [7].

The primary benefit of aquaculture is that wastewater treatment can lower the overall load of dissolved nutrients and particulates [3]. Aquaculture effluents have been handled by researchers using different conventional water mitigation procedures, including physical processes such as sand and mechanical filters, and aerobic/anaerobic processes

(using microalgae culture and macrophytes). These treatment systems have the drawbacks of producing large amounts of sludge, using a lot more energy and requiring frequent maintenance [3]. Coagulation-flocculation, on the other hand, has not been widely used in the aquaculture business.

Coagulation is the process of causing stable colloidal particles in suspension to agglomerate into settleable flocs by introducing Al and Fe salts or synthesised polymeric materials. Chemical coagulants are extremely powerful and extensively used, but they have a number of drawbacks, including a detrimental influence on humans, a high metallic content in sludge, as well as a great impact on water pH [8–11]. Therefore, it is desirable to gradually replace these chemical coagulants (inorganic and organic) with alternative novel natural coagulants to avoid the disadvantages that chemicals appear to bring [11]. Coagulant dosages used typically range from 0.5 to 20 mg/L. Inorganic coagulants have a greater dosage required compared to polymeric coagulants.

The use of green coagulants is more acceptable to overcome the main limitations of conventional coagulants since they prevent the generation of toxic sludge. Additionally, green coagulants (natural polymers or polyelectrolytes) are renewable, highly degradable, eco-friendly and not likely to generate water with intense pH after treatment [8–10]. Coagulant extraction, on the other hand, is typically time consuming. As a result, initiatives should be created to reduce costs by using cost-effective extraction procedures in order to scale up the use of natural coagulants in the future. Polyelectrolytes work in two ways: charge neutralisation and particle bridging. Since effluents' particulates are usually negatively charged, the cationic polyelectrolytes (since they contain –OH, –COOH and –NH groups) can serve as coagulants, reducing or neutralising the negative charge to speed-up particles' settling, similar to the effect of aluminium sulphate [11,12]. Natural coagulants are usually comprised of lipids, protein and carbohydrates [9]. Polysaccharides and amino acids polymers are mostly used by researchers [9,10].

Garcinia kola (bitter cola) seeds (Figure 1), the material of interest for the production of the coagulant for the coagulation-flocculation (CF) process, belong to the *Clusiaceae* or *Guttiferae* family. Tropical and subtropical wet lowland forests are their natural home. The seeds are readily found and cultivated in abundance in Ghana, Nigeria, Liberia, Sierra Leone, Senegal, etc. [13]. Historically, *Garcinia kola* has been believed to have purgative, anti-parasitic and antimicrobial properties [14]. These seeds contain polysaccharides and can form a gel in a solution, so they can act as a coagulant. However, there is no published work on the utilisation of the popular *Garcinia kola* seeds for wastewater purification. The significance of this work is in determining the efficacy of a new bio-coagulant in wastewater treatment, with the hope that by employing a locally available material, the treatment costs might be decreased and the effects of using chemical coagulants will be reduced.



(a)



(b)

Figure 1. Unshelled *Garcinia kola* seeds (a), shelled *Garcinia kola* seeds (b).

This study investigated the percentage reductions in water pollutants such as turbidity (TURB), COD, BOD and colour (COL) from aquaculture effluent using a green coagulant, *Garcinia kola* seeds coagulant (GKC). The *Garcinia kola* seeds' physicochemical characteristics were obtained. FTIR (Fourier transform infrared) and SEM (scanning electron microscopy) spectroscopy were used to observe the coagulant extracted from the seeds for its morphological and spectral properties. The coagulation kinetics and particles' time evolution were also considered. The sorption kinetics were also studied. In addition, the cost of using GKC to treat 1 L of AW was calculated.

2. Materials and Methods

2.1. Aquaculture Wastewater (AW) Collection

Aquaculture wastewater (AW) was brought from a local aquaculture pond business in Agu-Awka, Nigeria (Figure 2), using a gravity pump. The AW was kept in containers at 277 K ahead of treatment to elude deterioration of its properties (Table 1), as assessed by the acceptable procedures [11,15].

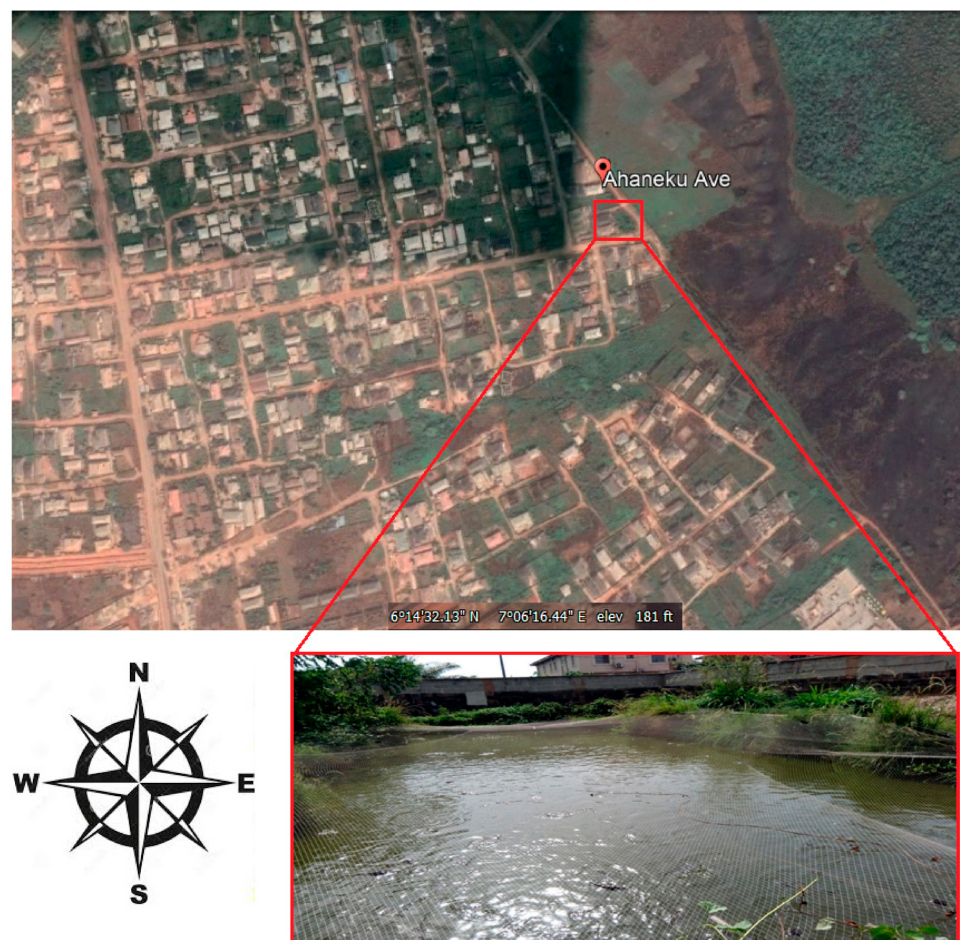


Figure 2. Point of collection of the AW (Latitude: $6^{\circ}14'32.13''$ N, Longitude: $7^{\circ}06'16.44''$ E).

Table 1. Characteristics of AW.

Parameter	Value
Absorbance at 275 nm	0.842
Ammoniacal nitrogen	0.829 mg/L
Appearance	Yellowish green
Biochemical oxygen demand (BOD ₅)	317 mg/L
Biodegradability index (BI)	0.42
Calcium	5.40 mg/L
Chemical oxygen demand (COD)	758 mg/L
Chloride	2.44 mg/L
Dissolved oxygen	9.6 mg/L
Conductivity	1963 μ S/cm
Iron	0.425 mg/L
Nitrogen	0.829 mg/L
pH	7.9
Potassium	5.45 mg/L
Temperature	303.2 K
Total dissolved solids	650 mg/L
Total phosphorus	0.91 mg/L
Total solids	695 mg/L
Total suspended solids	45 mg/L
TURB	404 NTU

2.2. Preparation of the GKC

To limit the inclusion of unwanted material, the active coagulant (GKC) was isolated from the coagulant precursor, *Garcinia kola* seeds [16]. This was also carried out to maximise the efficiency of pollution removal. The *Garcinia kola* seeds were collected from a local market in Onitsha, Nigeria, on 16 April 2015, and certified by the Department of Botany, Nnamdi Azikiwe University, and the voucher specimen was made available in the herbarium of the same department. The seeds were cleaned with deionised water, dried at 27 ± 2 °C, crushed, sieved by a sieve of 75 μ m and refrigerated until they were used. *Garcinia kola* powder was analysed for its proximate composition. Soxhlet extractor was used to remove fat from the seeds by adding 30 g of the seeds to 250 mL of n-hexane at 70 °C for 6 h. The 10 g seeds were mixed with 250 mL salt solution prepared by mixing 4.0 g MgCl₂, 25 g NaCl, 0.75 g KCl and 1.0 g CaCl₂ in 1000 mL of distilled water. Then, the mixture was shaken at 323 K for 60 min and filtered through a Whatman no. 90 mm, and the filtrate (the coagulant) was left to harden at 27 ± 2 °C. The coagulant yield was determined following Menkiti and Ezemagu [17].

The functional groups present in the GKC were determined via a Buck M520 infrared spectrophotometer to ascertain the groups available and taking part in the coagulation experiment from 4000 to 400 cm⁻¹. SEM was performed via a Carl Zeis Analytical SEM Series MA 10.EVO-10-09-49. A 3D reconstruction of the adsorbent surface based on SEM images was performed using ImageJ v1.53 [18,19].

2.3. Coagulation-Flocculation Procedure

A jar test flocculator apparatus was employed for the coagulation-flocculation tests. A summary of the experiment is shown in Figure 3. To ensure that the AW concentration was uniform, it was agitated before collecting the samples for the experiments. The effects of GKC dosage, pH, temperature and settling time on TURB, COD, TDS, COL and BOD changes were investigated. A measuring cylinder was used to measure 500 mL of AW, which was then poured into various 1000 mL beakers. Then, their pH was attuned to a specified pH using HCl or NaOH 1M solutions. A known GKC dose was added to each beaker, which was then agitated for 5 min with a magnetic stirrer at a steady speed of 120 rpm, supported by 20 min of shaking at a reduced speed of 30 rpm at a given temperature and left for various settling times. A syringe was used to extract 20 mL of the samples at a 0.02 m depth for each of the

1000 mL beakers and tested for the coagulation efficiency (%CE) in terms of TURB, COD, BOD and COL. The %CE was evaluated using (1):

$$\%CE = \frac{CE_i - CE_f}{CE_i} \times 100 \quad (1)$$

where CE_i and CE_f are the original and final TURB, COD, BOD and COL.

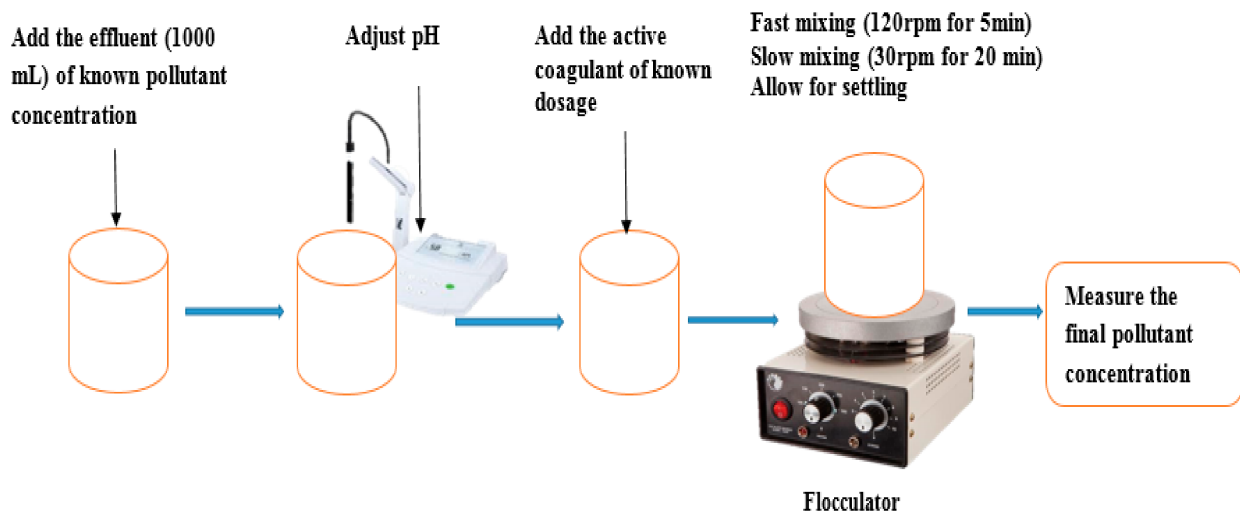


Figure 3. The jar test coagulation-flocculation process used in this study.

2.4. Coagulation-Flocculation Kinetics Study

The coagulation data were fitted into (2) and (3) [20,21] to determine if the coagulation-flocculation treatment of AW with GKC adheres to the peri-kinetics concept [22,23] using the regression coefficient (R^2) as the criterion [15,24]. The aggregation kinetics were investigated by plotting $\ln C_t$ with time (t) (using (2)) and $\frac{1}{C_t}$ with t (using (3)) [25,26]. Turbidity particle concentration was calculated by converting TURB (in NTU) to TURB (in mg/L) using a conversion factor of 1.0912 [27].

$$\frac{1}{C_t} - \frac{1}{C_0} = K_C t \quad (2)$$

(when $\alpha = 1$).

$$\ln C_t = -K_C t + \ln C_0 \quad (3)$$

(when $\alpha = 2$), where C_0 and C are the initial TURB (in mg/L) and TURB (in mg/L) at any period, t , K_C is reaction rate constant and α is the reaction order. In general, the particle distribution graph for coagulation with time may be depicted as (4) [23]:

$$\frac{C_w(t)}{C_0} = \frac{\left[\frac{1}{\tau_S}\right]^{w-1}}{\left[1 + \frac{t}{\tau_{S1/2}}\right]^{w+1}} \quad (4)$$

where w is 1, 2 or 3 for singlets, doublets and triplets respectively, and τ_S is the swift coagulation period and swift coagulation half-life ($\tau_{S1/2}$) evaluated using (5) and (6) [21,28–30]:

$$\tau_S = \frac{1}{C_0 K_C} \quad (5)$$

$$\tau_{S1/2} = \frac{1}{0.5 C_0 K_C} \quad (6)$$

2.5. Cost Estimation

The total cost for the treatment of 1 L of the AW was evaluated using the expression shown in (7). The energy consumption (E_C) was evaluated as 1.3 EUR using (8) [31]:

$$\text{Total cost} = \text{Cost of coagulant production} + \text{Cost of energy} \quad (7)$$

$$E_C = P_C (f \times t \times C) \quad (8)$$

where P_C is the power utilised by the device (40 kW), f is a load factor (in a full mode, so $b = 1$), t is the time of usage of the device (0.25 h) and C is the energy cost (0.13 EUR/KWh) in Nigeria on 27 May 2021.

3. Results

3.1. Physio-Chemical Characteristics of the *Garcinia kola* Seeds

The physio-chemical characteristics of the *Garcinia kola* seeds are provided in Table 2. The high protein content of 11.7%, the carbohydrate content of 68.33% and the coagulant yield of 80.46% are a sign of the probability of the seeds being good active coagulants in the treatment of AW [17,32]. The neutralisation of colloidal particles requires proteins that activate the bridging coagulation process, which facilitates floc formation [24]. Additionally, their high levels of carbohydrates (celluloses and polysaccharides) mean that they can be used as wastewater coagulants [33]. This natural polymer-based coagulant promotes the creation of particle aggregates, which can aid in the reduction of pollution levels. Bridging is a coagulation process that happens when threads or fibres from coagulants are applied to numerous colloids, trapping and connecting them [11,34].

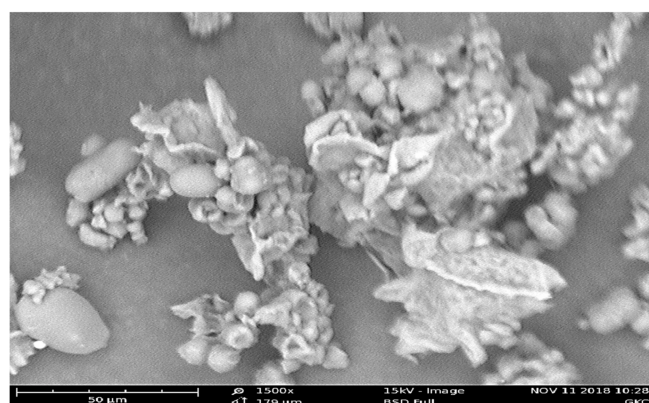
Table 2. Physio-chemical characteristics of the *Garcinia kola* seeds.

Parameters	Unit	Values %	Procedure
Ash content	%	4.147	AOAC method 942.05 [35]
Bulk density	g/mL	0.22	AOAC method PA 105 [36]
Carbohydrate	%	68.33	FAO [11]
Fibre	%	3.940	AOAC method 978.10 [37]
Protein	%	11.27	AOAC method 945.18-B [38]
Fat	%	3.030	AOAC method 920.39 [39]
Moisture	%	9.280	AACC method 44-15A [40]
Yield of coagulant	%	80.46	Menkiti and Ezemagu [17]

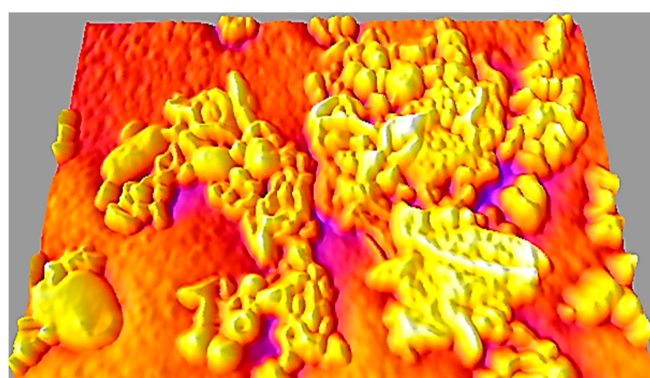
3.2. SEM and FTIR Characterisation of the GKC

The SEM image (at 1500× magnification) of the GKC is displayed in Figure 4a. Diverse sized and irregular shaped particles (thread-like and granular) are displayed by the GKC which are important for the adsorption and bridging of the AW particles, thereby promoting fast particles' settling [11,34,41,42]. The 3D SEM micrograph of GKC is shown in Figure 4b at a magnification of 1500×. Uneven-sized lumps can be observed on an otherwise smooth surface morphology. These lumps are scattered and singularised, while there are agglomerations observed in some areas. These heterogeneous features are consistent with those of other materials for water treatment obtained from biomass sources [43].

Figure 5 depicts the FTIR spectrum of GKC. The existence of amine groups is indicated by the N-H stretching (3389.364 cm^{-1}) in GKC. The amino (N-H) and hydroxyl (O-H) groups with H_2 bonding are the preferential groups for the CF process [44–46]. The medium C-H stretch (2883.547 and 3000.239 cm^{-1}) and C–Cl (alkyl halides) stretch (828.92 cm^{-1}) were present on the GKC. The strong and sharp band of O-H stretch (2458.096 , 2594.338 , 3186.246 , 3262.94 , 3389.364 and 3532.273 cm^{-1})—free hydroxyl of alcohols and phenols—was observed on the GKC, which is very important for most treatment processes, including coagulation, adsorption, advanced oxidation, etc. [11,47,48].



(a)



(b)

Figure 4. SEM image (a) and 3D SEM micrograph (b) of GKC at 1500× magnification.

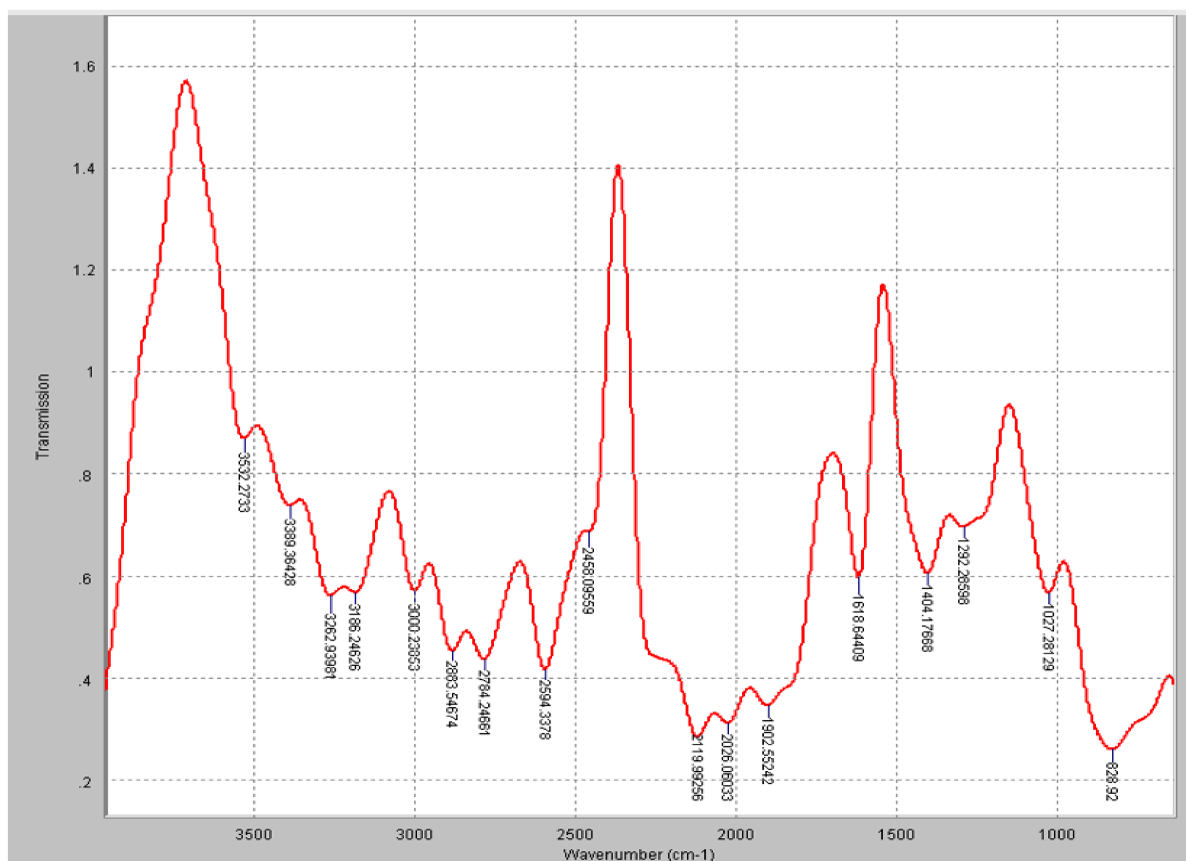


Figure 5. FTIR spectra on the GKC.

3.3. Effect of Process Factors

3.3.1. Effect of GKC Dose

The improved knowledge of the scientific concepts behind coagulation-flocculation and the process allows for the optimisation of coagulant doses. This ensures that a sufficient amount of coagulant is supplied to achieve charge neutralisation. There is an ideal bio-coagulant dose sufficient to generate satisfactory bridging between particles and the dose of bio-coagulant likely to cause saturation on the colloidal surfaces, inhibiting bridging [49].

The effect of GKC dose on pollutant reduction (TURB, COD, BOD and COL) on AW was investigated by varying the GKC dosages from 0.1 to 0.5 g/L at a time of 60 min and effluent pH 7.9. The effect of GKC dose on TURB, COD, BOD and COL removals is revealed in Figure 6. Maximum TURB, COD, BOD and COL reductions of 68.32%, 62.87%, 58.62% and 47.02% on AW were achieved at GKC dosages of 0.3 g/L, with the lowest performance at the highest studied GKC dosage of 0.5 g/L. Excess coagulant was added above the optimal dosage, which reversed the surface charges of the particles and reduced their elimination efficiency [50–52]. This might be attributable to the increased kinetic energy caused by the Brownian motion of the suspended particles [21] or more positive charges conferred by the GKC on the particles' surface (a positive zeta potential), thus redispersing the particles [15,17]. It is known that an increase of coagulant dosage would either increase or decrease the zeta potential, which will stabilise or destabilise, respectively, the suspended particles. The relationship between optimum dose and reduction (%) sheds light on the role of the sweep flocculation process mechanism [53,54]. Furthermore, the low optimal dosage obtained with GKC suggests that the neutralisation and adsorption mechanism is the primary mechanism in the treatment process [54,55].

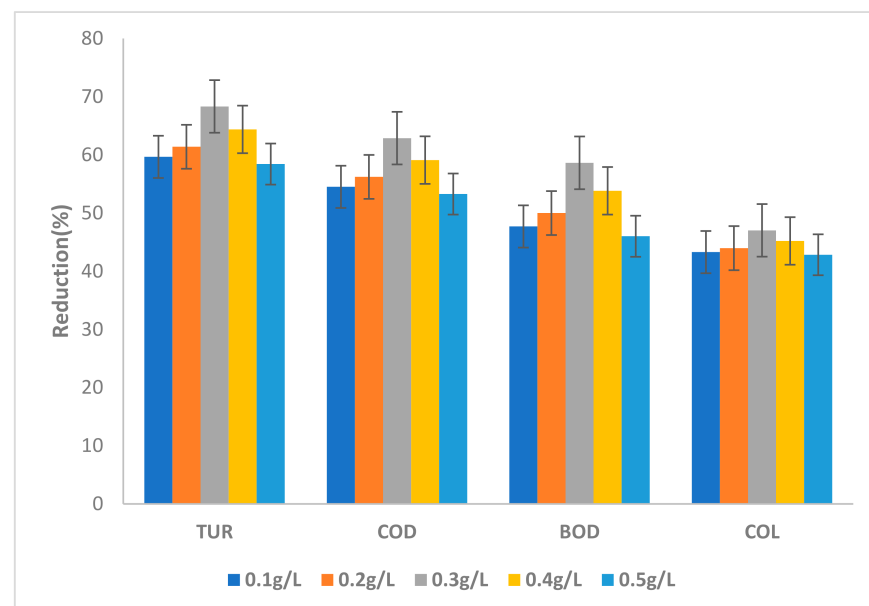


Figure 6. Effect of GKC dose on pollutants' elimination on AW (time of 60 min and effluent pH 7.9).

3.3.2. Effect of AW pH

The efficiency of GKC for TURB, COD, BOD and COL reduction in AW was inspected by adjusting the AW pH from 2 to 10 over a 60 min settling time and GKC dose of 0.3 g/L (Figure 7). Maximum TURB, COD, BOD and COL elimination rates of 81.93%, 75.03%, 72.84% and 55.69% were observed, respectively. The removal was most effective in acidic conditions. Furthermore, pH 6 produced the poorest results due to a poor influence on particle electrophoretic mobility, resulting in minimal surface charge neutralisation [40]. Increasing the pH above the optimum caused a rise in electrostatic repulsion of the AW particles and GKC owing to a comparable charge (with more availability of OH^-), resulting in a low decrease and stability of the suspended contaminants [21,56]. As a result, lower

pH was advantageous for this process. Furthermore, particle agglomeration was enhanced at low pH due to decreased repulsions [57,58]. The charge neutralisation mechanism, with polymeric material bridging, adsorption and floc-trapping mechanisms, was responsible for the lowering of TURB, COD, BOD and COL concentrations in AW.

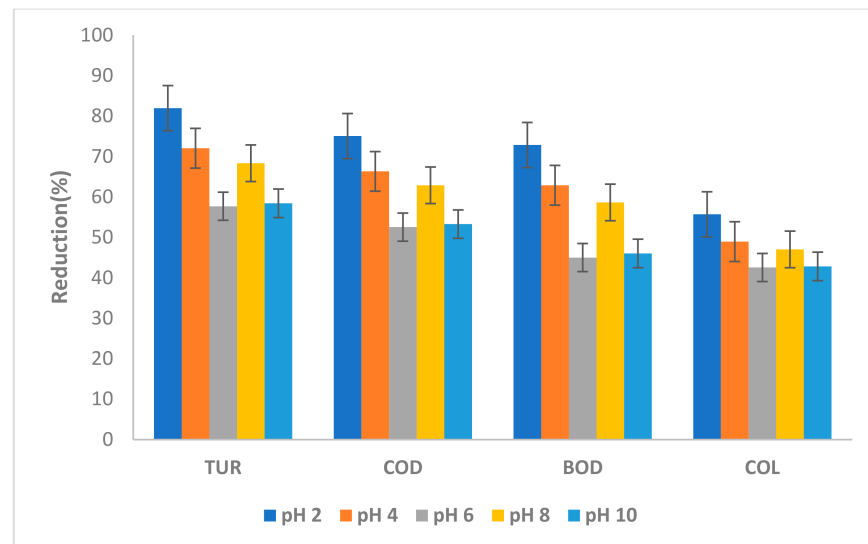


Figure 7. Effect of AW pH on pollutants' elimination (at 60 min and 0.3 g/L GKC).

3.3.3. Effect of Temperature on TURB, COD, BOD and COL Reduction

Temperature influences the removal effectiveness of contaminants during coagulation-flocculation processes [59]. To find the best temperature for the coagulation-flocculation process, the impact of temperature on TURB, COD, BOD and COL reductions on AW utilising GKC was tested at 303, 313 and 323 K, and the optimal dose and pH. At 303 K, maximum TURB, COD, BOD and COL elimination rates of 81.93%, 75.03%, 72.84% and 55.69% were attained (Figure 8). Furthermore, TURB, COD, BOD and COL reductions by GKC performed the worst at the temperature of 323 K. The TURB, COD, BOD and COL decreased with increased temperature; hence, the ideal temperature was determined to be 303 K for future tests. The decrease in TURB, COD, BOD and COL with growing temperature might be attributed to the haphazard movement of pollutant particles produced by increased kinetic energy, which might obstruct the particles' trapping to the GKC to form flocs and lead to a reduction in floc size [60]. As a result, the particles spread widely apart rather than agglomerating together to create bigger flocs, preventing the particles from settling quicker [57,61]. The floc strength was ultimately deteriorated and became readily broken [56]. In addition, less large flocs were developed. The viscosity of AW was altered as the temperature rose, reducing treatment efficiency [62]. Furthermore, an increase in temperature may impair the coagulant's coagulating capability along with its structure (functional groups).

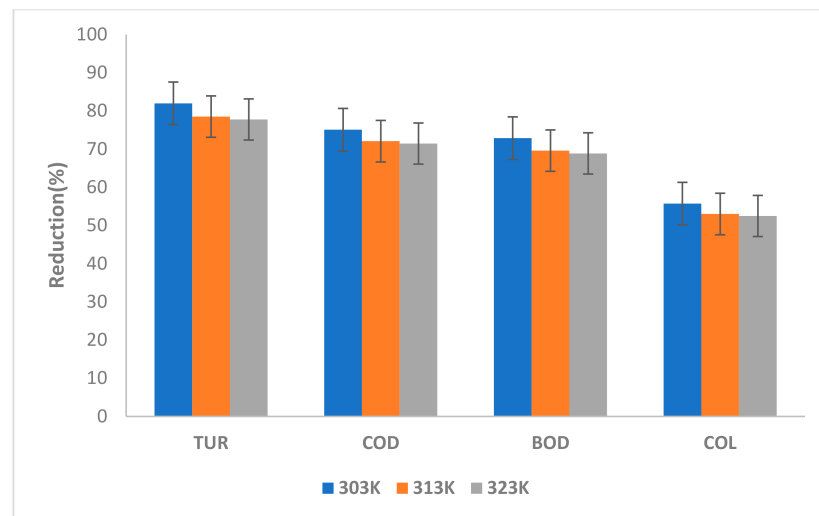


Figure 8. Temperature effect on pollutants' reduction on AW at a settling period of 60 min, 0.3 g/L and pH 2.

3.3.4. Effect of Settling Time on TURB, COD, BOD and COL Reduction

The impact of the period of settling on the coagulation-flocculation process on the pollutants (TURB, COD, BOD and COL) was investigated by altering the settling time from 0 to 60 min. This investigation was carried out at the optimal dose and temperature at various pH levels. Figure 9 depicts the influence of settling time on the reduction of TURB, COD, BOD and COL on AW utilising GKC. Pollutant elimination improved as settling time increased and stayed stable after a while, with little or no increase. This means that once equilibrium is attained, no additional increase in settling time is required. The rapid settling speed was aided by the production of bigger and denser flocs as a result of the biopolymer chain's adhesion to the particles [56]. For all contaminants removed, equilibrium was attained after 40 min. At the optimal dose (0.3 g/L) and equilibrium settling time, maximum TURB, COD, BOD and COL removals of 80.44%, 74.40%, 72.15% and 55.07% (at pH 2) respectively, were achieved. Igwegbe et al. [33] and Ugonabo et al. [63] made a similar observation while employing *Picralima nitida* seeds and *Mucuna pruriens* seeds to treat generated water. GKC was used to achieve delayed coagulation (optimum settling time > 30 min) in the current investigation. Furthermore, when the TURB was lowered, the COD, BOD and COL were lowered concurrently, as seen in Figure 9a–d.

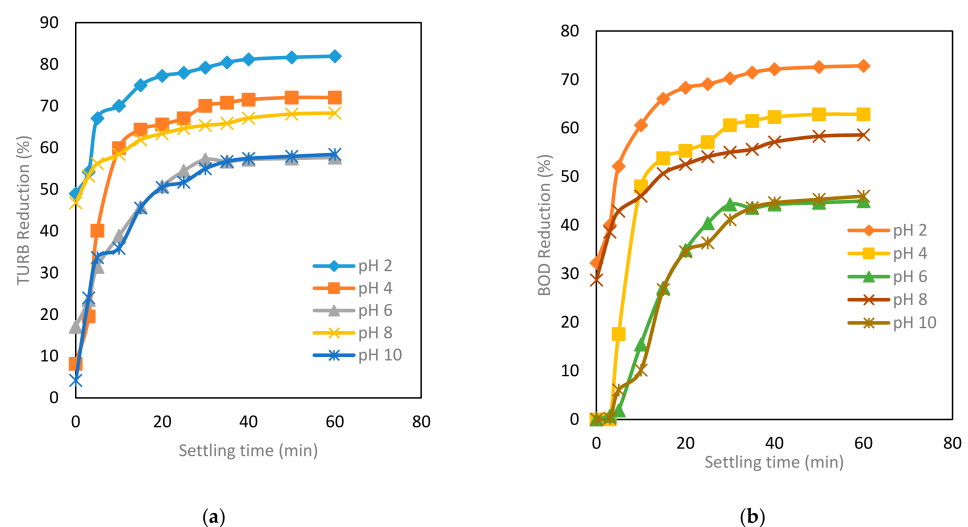


Figure 9. Conts.

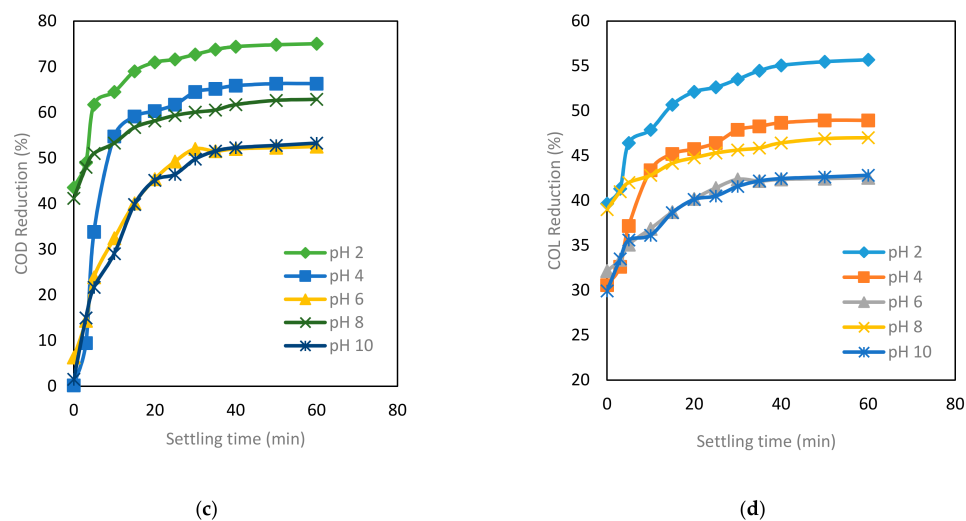


Figure 9. Effect of settling time on (a) TURB, (b) BOD, (c) COD and (d) COL elimination on AW at 0.3 g/L GKC, pH 2 and 303 K.

3.4. Brownian Coagulation-Flocculation Kinetics on the Process

The K_C and C_0 were obtained from Figure 10a,b comparing (2) and (3), respectively. The kinetic parameters are provided in Tables 3 and 4. The kinetic data obeyed the second-order kinetic model (peri-kinetics flocculation theory, when $\alpha = 2$) rather than the first-order kinetics; for this reason, the other kinetic parameters (Table 4) were estimated using the second-order kinetics data.

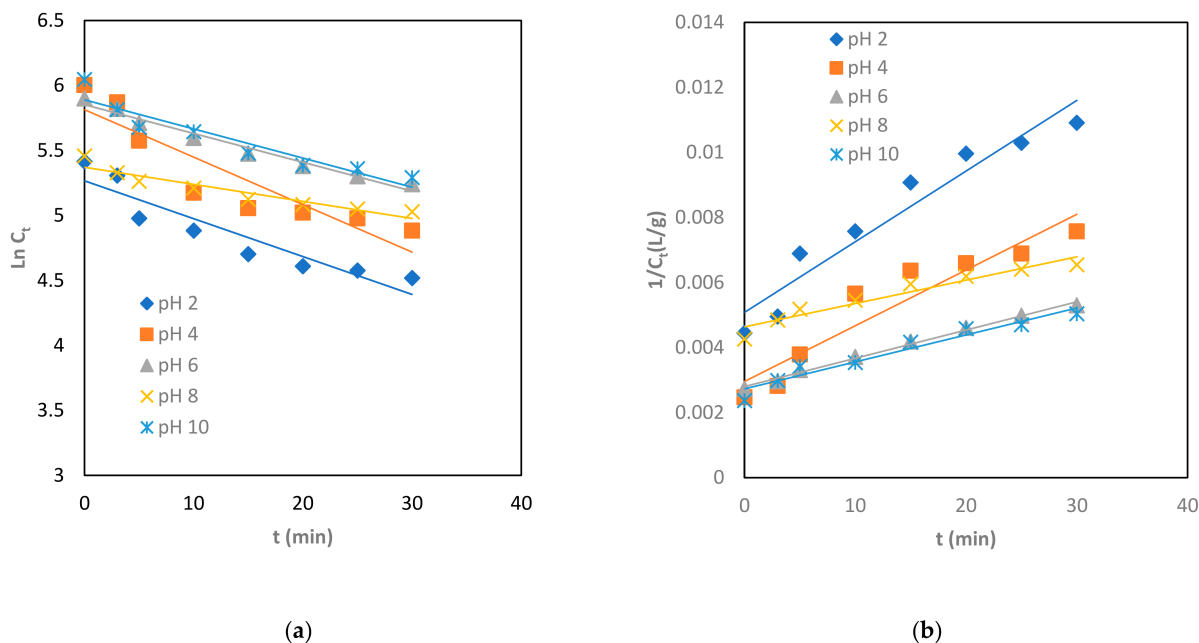


Figure 10. First-order (a) and second-order (b) coagulation-flocculation kinetics at 303 K and 0.3 g/L GKC.

The kinetics parameters B_F , ε_{ce} , K_{SC} , D^1 , τ_S and $\tau_{S1/2}$ were evaluated using Equations (S1), (S3)–(S5), Equations (5) and (6), respectively (see Supplementary Materials, Section S1). The K_{SC} values remained unchanged at all pH levels due to negligible changes in temperature and viscosity of the coagulation-flocculation medium [64]. The rate of coagulation ($-r_p$), which accounts for the rate of particle concentration depletion, is derived from Supplementary Equation (S2). The negative values in the rate equation reflect the reduction in TURB (in mg/L) as time increases [21]. The values of ε_{ce} and $\tau_{S1/2}$ are

used to determine the degree of coagulation. A higher ϵ_{ce} (collision efficiency) value was observed for pH 2 (the optimum pH) and pH 4, which is in agreement with the statement by Hunter [65] and Menkiti and Ezemagu [17], that a high ϵ_{ce} value results in a high energy of kinetics, which have a tendency to lower the zeta potential, leading to colloidal destabilisation at short $\tau_{S1/2}$ to produce optimum coagulation-flocculation efficiency [66]. Finally, the values of τ_S and $\tau_{S1/2}$ are presented in Table 4. The value $\tau_{S1/2}$ is an important parameter since it is linked to ion or particle aggregation [67].

Table 3. Brownian kinetics at 303 K and 0.3 g/L GKC at $\alpha = 1$.

Factor	pH 2	pH 4	pH 6	pH 8	pH 10
R ²	0.8679	0.8321	0.973	0.8991	0.8933
K_C (L/mg min)	0.0291	0.0365	0.0221	0.0131	0.0224
C_0 (mg/L)	193.78	334.82	348.14	214.99	361.41
r_p (mg/min)	$-0.0291C_t^2$	$-0.0365C_t^2$	$-0.0221C_t^2$	$-0.0131C_t^2$	$-0.0224C_t^2$

Table 4. Brownian kinetics at 303 K and 0.3 g/L GKC at $\alpha = 2$.

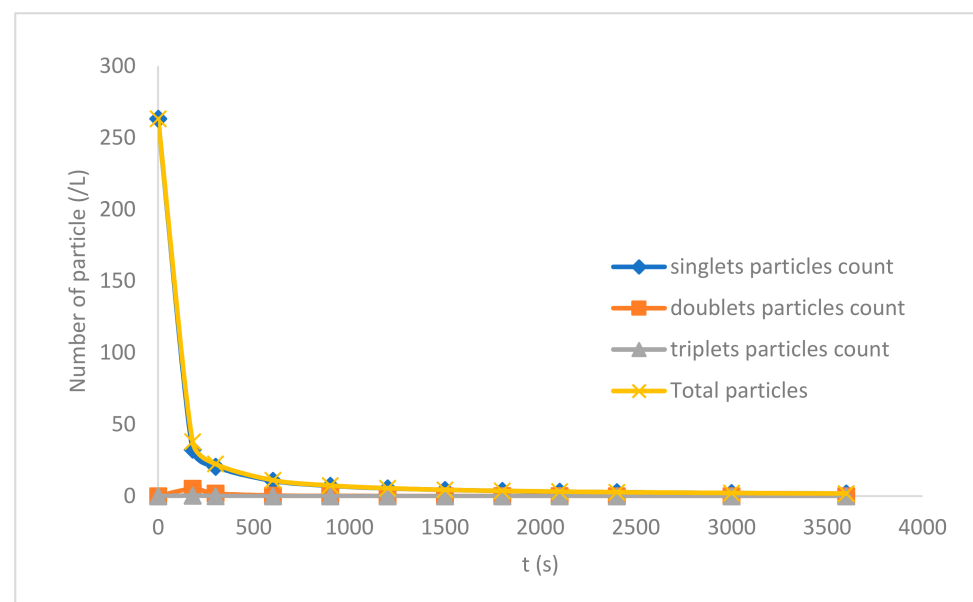
Factor	pH 2	pH 4	pH 6	pH 8	pH 10
R ²	0.9292	0.8975	0.9931	0.9313	0.9457
K_C (L/mg min)	0.0002	0.0002	0.0001	0.0001	0.0001
C_0 (mg/L)	196.08	333.33	357.14	217.39	217.39
r_p (mg/min)	$-0.0002C_t^2$	$-0.0002C_t^2$	$-0.00009C_t^2$	$-0.00007C_t^2$	$-0.00007C_t^2$
$\tau_{S1/2}$ (min)	51	30	62.222	131.43	131.43
τ_S (min)	102	60	124.44	262.86	262.86
B_F (L/mg min)	0.0004	0.0004	0.0002	0.0002	0.0001
K_C (L/min)	2.14×10^{-18}	2.15×10^{-18}	2.15×10^{-18}	2.15×10^{-18}	2.15×10^{-18}
ϵ_{ce} (L/mg)	9.32×10^{13}	9.32×10^{13}	4.20×10^{13}	3.26×10^{13}	1.88×10^{-9}
D^1	0.0082	0.0082	0.0037	0.0029	0.0003

3.5. Particle Distribution Behaviour of the Process

Equation (4) was employed to forecast the time development of aggregating species: singlets, doublets and triplets, based on particles' variation behaviour as time changes (Table 5). The particle distribution pattern in terms of particle concentration was investigated using $\tau_{S1/2}$, C_0 and K_C values derived from second-order kinetics under the optimal conditions (Table 5). Table 5 shows the computed singlet, doublet and triplet particle counts, as well as the overall particle counts, and Figure 11 shows the plots with time. Since the formation of doublet and triplet particles is driven by the quick destabilisation of singlets, the singlet particle count dropped faster than the overall number of particles [63]. This distribution was explained by a combination of charge neutralisation and sweep flocculation [17]. The fundamental particles are dominated by Brownian (peri-kinetic) coagulation (Figure 11) [68]. A similar pattern can be seen throughout all plots. These demonstrate the application of (4) in particle size distribution. The number of singlet, doublet and triplet particles dropped systematically over time. The protonated amine groups often destabilise the negative particles and the zeta potential, lowering or eliminating the DLVO energy barrier and allowing for more species interactions [17]. While charge neutralisation happened, the majority of the pollutant particulates were cleaned up from the wastewater by gravity after being entwined in the protein complex.

Table 5. Particle evolution with time for the AW/GKC process at $\tau_{51/2} = 0.85$ s, $C_0 = 196.08$ g/L and $K_C = 0.0002$ L/g·min.

Time (s)	Singlet Particles Count	Doublet Particles Count	Triplet Particles Count	Total Particles
0	263.16	0	0	263.16
180	32.468	5.1981	0.4332	38.099
300	20.492	1.8754	0.1146	22.482
600	10.661	0.4691	0.0168	11.147
900	7.2046	0.2085	0.0053	7.4184
1200	5.4407	0.1173	0.0023	5.5603
1500	4.3706	0.0751	0.0012	4.4469
1800	3.6523	0.0521	0.0007	3.7051
2100	3.1368	0.0383	0.0004	3.1755
2400	2.7488	0.0293	0.0003	2.7784
3000	2.2036	0.0188	0.0002	2.2225
3600	1.8389	0.0130	0.0001	1.8520

**Figure 11.** Particle evolution graph for the AW/GKC process at $\tau_{51/2} = 0.85$ s, $C_0 = 196.08$ g/L and $K_C = 0.0002$ L/g·min.

3.6. Coagulation-Adsorption Kinetics Studies

The COL was considered for the study of the adsorptive constituent of the bio-coagulation-flocculation process since adsorption is known to be more effective for colour removal from effluents [69,70]. The experimental data were also fitted into the adsorption kinetic models. Coagulation phenomena can be modelled theoretically considering them as adsorption-like processes [71]. The sorption mechanisms in CF processes has been discussed by other researchers [72].

To analyse the adsorption kinetics of the process, the nonlinear Lagergren [73,74] and Ho [75–77] kinetic models were tested (see Supplementary Materials, Section S2).

The correlation coefficient, R^2 , was used as the basis to determine the model that best fits the data. A higher R^2 value indicates that a particular model best suits the data [78,79]. To further validate the models, the chi-square error (X^2), Marquardt's percent standard deviation (MPSD), sum average relative error (ARE), the sum of absolute errors (SAE), normalised standard deviation ($\Delta q_e(\%)$) and the sum of squares error (SSE) values were also evaluated (see Supplementary Materials, Section S2).

The adsorption kinetics plots are presented in Figure 12. The q_t values were plotted against time. Table 6 shows the adsorption non-linear kinetic parameters obtained for AW using GKC. The estimated parameters, R^2 , MPSD, ARE, EABS, χ^2 , $\Delta q_e(\%)$ and SSE, are presented in Table 6. The model with the minimum MPSD, ARE, EABS, χ^2 , $\Delta q_e(\%)$ and SSE values best fits the coagulation-adsorption data. The kinetic data for COL removal on AW using GKC conformed more to the Lagergren model in comparison to the Ho model's R^2 , MPSD, ARE, EABS, χ^2 , $\Delta q_e(\%)$ and SSE.

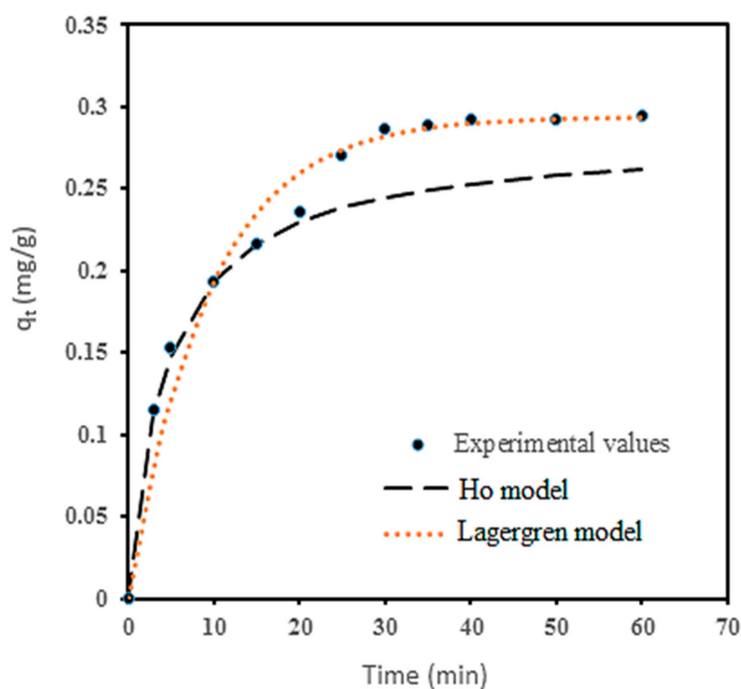


Figure 12. Coagulation-adsorption nonlinear kinetics plots for COL removal on AW at pH 2 and 0.3 g/L.

Table 6. Non-linear coagulation-adsorption kinetic parameters at optimum conditions for colour removal on AW using GKC.

Model	Parameter	Value	Unit
Lagergren	q_e	0.2938	mg/g
	K_1	0.1075	min^{-1}
	h_0	0.0316	mg/g/min
	R^2	0.9987	-
	χ^2	0.0905	-
	MPSD	5.8045	-
	ARE	0.2793	-
	SAE	0.0905	-
	$\Delta q_e(\%)$	5.5196	-
	SSE	0.0082	-
Ho	q_e	0.2818	mg/g
	K_2	0.7774	g/mg/min
	h_0	0.0617	mg/g/min
	R^2	0.9856	-
	χ^2	0.2968	-
	MPSD	19.040	-
	ARE	0.9161	-
	SAE	0.2968	-
	$\Delta q_e(\%)$	9.9967	-
	SSE	0.0881	-

3.7. Cost Analysis on the Process

Cost analysis is a typical decision-making tool. The cost of the coagulation-flocculation operation is based on the cost of the coagulant used to remove contaminants. Wastewater handling, on the other hand, necessitates the use of low-cost materials [80,81]. The cost of treating 1 L of AW was calculated by taking into account the cost of preparing 0.3 g/L (optimal dose) of the bio-coagulant dosage, the cost of energy and the cost of labour. The preparation of 0.3 g/L of GKC costs 0.27 EUR. The overall cost was computed as 1.57 EUR by including the costs of 0.3 g/L GKC preparation and energy (1.30 EUR).

The cost of preparing 1 g of GKC is 0.9 EUR. Compared to the use of conventional coagulants, for example, aluminium polychloride (which costs less than 1 EUR), this is extremely costly. This is one of the main limitations of using green coagulants in wastewater management. However, according to the present study, using a dosage above 0.3 g/L will reduce coagulation efficiency in AW. Other limitations may include competition with the food chain. Nevertheless, the use of natural coagulants is more acceptable to avoid the disadvantages that chemicals appear to bring. In addition, inorganic coagulants have a greater dosage required compared to polymeric coagulants.

4. Conclusions

The present study focused on the use of *Garcinia kola* seeds coagulant (GKC). The data were analysed through the sorption and flocculation kinetics equations. The GKC possesses the amino (N-H) and hydroxyl (O-H) groups, which are very beneficial for coagulation-flocculation. Maximal turbidity reduction = 81.93%, COD = 75.03%, BOD = 72.84% and colour = 56.69% at a 0.3 g/L dose of GKC, pH 2, 60 min and 303 K were achieved. Von Smoluchowski's second-order peri-kinetics fit the results better than the first-order equation. At a coagulation order (α) of 2, the reaction rate (K_C) and half-life ($\tau_{S1/2}$) were 0.0003 L/g·min and 25.3 min at the optimal conditions. The sorption data better fit the Lagergren compared to the Ho adsorption model. The cost of using GKC to handle 1 L of AW was 1.57 EUR, including the costs of 0.3 g/L GKC preparation (0.27 EUR) and energy (1.30 EUR). The GKC was found to be an effective green coagulant that can pre-treat AW.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/su13169177/s1>, Section S1: Coagulation-flocculation kinetics study, Section S2: Coagulation-adsorption kinetics studies. These two sections contain Equations (S1)–(S16).

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References

- Sharrer, M.J.; Rishel, K.; Summerfelt, S. Evaluation of geotextile filtration applying coagulant and flocculant amendments for aquaculture biosolids dewatering and phosphorus removal. *Aquacult. Eng.* **2009**, *40*, 1–10. [[CrossRef](#)]
- Ebeling, J.M.; Timmons, M.B. *Recirculating Aquaculture*; Cayuga Aqua Ventures: Freeville, NY, USA, 2010.
- Ermukdakul, T.; Chawaloephonsiya, N.; Boonchayaanant, B.; Pungrasmi, W.; Painmanakul, P. Different Approaches for the Separation of Suspended Solids in Aquaculture System. *J. Water Environ. Technol.* **2013**, *11*, 59–70. [[CrossRef](#)]
- Walker, S. *Scoping Science Assessment of the Impacts of Freshwater Aquaculture on the Canadian Environment*; National Water Research Institute, Environment Canada: Burlington, ON, Canada; Saskatoon, SK, Canada, 2003.
- Ighalo, J.O.; Igwegbe, C.A.; Aniagor, C.O.; Oba, S.N. A Review of Methods for the Removal of Penicillins from Water. *J. Water Process. Eng.* **2021**, *39*, 101886. [[CrossRef](#)]
- Ighalo, J.O.; Adeniyi, A.G.; Marques, G. Internet of Things for Water Quality Monitoring and Assessment: A Comprehensive Review. In *Artificial Intelligence for Sustainable Development: Theory, Practice and Future Applications*; Hassanien, A.E., Bhatnagar, R., Darwish, A., Eds.; Springer Nature: Basingstoke, UK, 2021; Volume 912, pp. 245–259.
- Ighalo, J.O.; Adeniyi, A.G.; Eletta, A.A.O.; Ojetimi, N.I.; Ajala, O.J. Evaluation of Luffa Cylindrica Fibers in A Biomass Packed Bed for The Treatment of Fish Pond Effluent Before Environmental Release. *Sustain. Water Resour. Manag.* **2020**, *6*. [[CrossRef](#)]
- Sahu, O.; Chaudhari, P. Review on chemical treatment of industrial waste water. *J. Appl. Sci. Environ. Manag.* **2013**, *17*, 241–257. [[CrossRef](#)]
- Kumar, V.; Othman, N.; Asharuddin, S. Applications of natural coagulants to treat wastewater—A review. In Proceedings of the ISCEE 2016 MATEC Web of Conferences, Melaka, Malaysia, 5–6 December 2016.
- Adinolfi, M.; Corsaro, M.M.; Lanzetta, R.; Parrilli, M.; Folkard, G.; Grant, W.; Sutherland, J. Composition of the coagulant polysaccharide fraction from Strychnos potatorum seeds. *Carbohydr. Res.* **1994**, *263*, 103–110. [[CrossRef](#)]
- Igwegbe, C.A.; Onukwuli, O.D.; Ighalo, J.O.; Menkiti, M.C. Bio-coagulation-flocculation (BCF) of municipal solid waste leachate using picralima nitida extract: RSM and ANN modelling. *Curr. Res. Green Sustain. Chem.* **2021**, *4*, 100078. [[CrossRef](#)]
- Teh, C.Y.; Wu, T.Y. The potential use of natural coagulants and flocculants in the treatment of urban waters. In Proceedings of the Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction (PRES 2014), Crete, Greece, 20–23 October 2014; pp. 1603–1608.
- Olajide, O.J.; Adeniyi, P.A. Studies on effects of aqueous Garcinia kola extract on the lateral geniculate body and rostral colliculus of adult Wistar rats. *Med Pract. Rev.* **2011**, *2*, 23–28.
- Iwu, M.W.; Duncan, A.R.; Okunji, C.O. *New antimicrobials of plant origin. Perspectives on New Crops and New Uses*; ASHS Press: Alexandria, VA, USA, 1999; pp. 457–462.
- Igwegbe, C.A. Evaluation of Bio- and Electro- Coagulants' Activities on Fish Pond Wastewater and Solid Waste Leachate. Ph.D. Thesis, Department of Chemical Engineering, Faculty of Engineering, Nnamdi Azikiwe University, Awka, Nigeria, 2019.
- Ghebremichael, K.A.; Gunaratna, K.; Henriksson, H.; Brumer, H.; Dalhammar, G. A simple purification and activity assay of the coagulant protein from Moringa oleifera seed. *Water Res.* **2005**, *39*, 2338–2344. [[CrossRef](#)]
- Menkiti, M.C.; Ezemagu, I.G. Sludge characterization and treatment of produced water (PW) using Tympanotonus fuscatus coagulant (TFC). *Petroleum* **2015**, *1*, 51–62. [[CrossRef](#)]
- Collins, T.J. ImageJ for microscopy. *BioTechniques* **2007**, *43*, S25–S30. [[CrossRef](#)]
- Ighalo, J.O.; Adeniyi, A.G.; Igwegbe, C.A. 3D Reconstruction and Morphological Analysis of Electrostimulated Hyperthermophile Biofilms of Thermotoga neapolitana. *Biotechnol. Lett.* **2021**, *43*, 1303–1309. [[CrossRef](#)]
- Nwabanne, J.T.; Obi, C.C. Coagulation-Flocculation Performance of Snail Shell Biomass in Abattoir Wastewater Treatment. *J. Chem. Technol. Metall.* **2019**, *54*, 1177–1188.
- Mageshkumar, M.; Karthikeyan, R. Modelling the kinetics of coagulation process for tannery industry effluent treatment using Moringa oleifera seeds protein. *Desalination Water Treat.* **2016**, *57*, 14954–14964. [[CrossRef](#)]
- Smoluchowski, M. Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen. *Z. Phys. Chem.* **1917**, *92*, 129–168. [[CrossRef](#)]
- Igwegbe, C.A.; Onukwuli, O.D.; Ighalo, J.O.; Umembamalu, C.J.; Adeniyi, A.G. Comparative analysis on the electrochemical reduction of colour, COD and turbidity from municipal solid waste leachate using aluminium, iron and hybrid electrodes. *Sustain. Water Resour. Manag.* **2021**, *7*, 1–18. [[CrossRef](#)]
- Menkiti, M. Studies on Coagulation and Flocculation of Coal Washery Effluent: Turbid Metric Approach. Master's Thesis, Nnamdi Azikiwe University, Awka, Nigeria, 2007.
- Ugonabo, V.I.; Emembolu, L.N.; Igwegbe, C.A. Bio-Coag-Flocculation of Refined Petroleum Wastewater using Plant Extract: A Turbidimetric Approach. *Int. J. Emerg. Eng. Res. Technol.* **2016**, *4*, 19–26.
- Emembolu, L.N.; Igwegbe, C.A.; Ugonabo, V.I. Effect of Natural Biomass Treatment on Vegetable Oil Industry Effluent via Coag-Flocculation. *Saudi J. Eng. Technol.* **2016**, *1*, 172–179.
- Igwegbe, C.A.; Onukwuli, O.D.; Ighalo, J.O.; Umembamalu, C.J. Electrocoagulation-flocculation of aquaculture effluent using hybrid iron and aluminium electrodes: A comparative study. *Chem. Eng. J. Adv.* **2021**, *6*, 100107. [[CrossRef](#)]
- Ugonabo, V.I.; Emembolu, L.N.; Igwegbe, C.A.; Olaitan, S.A. Optimal evaluation of coag-flocculation factors for refined petroleum wastewater using plant extract. In *International Conference 2016 Proceedings*; Faculty of Engineering, Nnamdi Azikiwe University: Awka, Nigeria, 2016; pp. 548–557.

29. Menkiti, M.C.; Ejimofor, M.I. Experimental and artificial neural network application on the optimization of paint effluent (PE) coagulation using novel Achatinoidea shell extract (ASE). *J. Water Process. Eng.* **2016**, *10*, 172–187. [[CrossRef](#)]
30. Okey-Onyesolu, C.; Onukwuli, O.; Ejimofor, M.; Okoye, C. Kinetics and mechanistic analysis of particles decontamination from abattoir wastewater (ABW) using novel Fish Bone Chito-protein (FBC). *Heliyon* **2020**, *6*, e04468. [[CrossRef](#)]
31. Ahmadi, S.; Mohammadi, L.; Rahdar, A.; Rahdar, S.; Dehghani, R.; Igwegbe, C.A.; Kyzas, G.Z. Acid Dye Removal from Aqueous Solution by Using Neodymium (III) Oxide Nanoadsorbents. *Nanomaterials* **2020**, *10*, 556–582. [[CrossRef](#)]
32. Bouaouine, O.; Bourven, I.; Khalil, F.; Baudu, M. Identification of functional groups of *Opuntia ficus-indica* involved in coagulation process after its active part extraction. *Environ. Sci. Pollut. Res.* **2018**, *25*, 11111–11119. [[CrossRef](#)] [[PubMed](#)]
33. Igwegbe, C.A.; Onukwuli, O.D. 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. *Pharm. Chem. J.* **2019**, *6*, 32–45.
34. Coruh, H.A. Use of Calcium Alginate as a Coagulant in Water treatment. Master's Thesis, Middle East Technical University, Ankara, Turkey, 2005.
35. AOAC. *Official Method of Analysis. Method 935.14, 942.05 and 992.24*, 18th ed.; AOAC: Washington, DC, USA, 2005.
36. AOAC. *Official Methods of Analysis*, 14th ed.; Association of Official Analytical Chemists International Publisher: Arlington, VA, USA, 1984.
37. AOAC. *Total, Soluble, and Insoluble Dietary Fiber in Foods: Enzymatic Gravimetric Method, MES-TRIS Buffer*, 17th ed.; Association of Official Analytical Chemists International Publisher: Arlington, VA, USA, 2000.
38. AOAC. *Determination of Protein Content in Food, Method 945.18-B*; AOAC International Publisher: Gaithersburg, MD, USA, 2005.
39. AOAC. *Oil in Cereal Adjuncts: Petroleum Ether Extraction Method*, 17th ed.; Association of Official Analytical Chemists International Publisher: Arlington, VA, USA, 2000.
40. AACC. *AACC Method 44-15A. Approved Methods of the American Association for Clinical Chemistry (AACC)*, 10th ed.; AACC: Washington, DC, USA, 2000.
41. Li, G.; Huang, Y.; Lin, J.; Yu, C.; Liu, Z.; Fang, Y.; Xue, Y.; Tang, C. Effective capture and reversible storage of iodine using foam-like adsorbents consisting of porous boron nitride microfibers. *Chem. Eng. J.* **2020**, *382*, 122833. [[CrossRef](#)]
42. Sharma, B.; Dhuldhoya, N.; Merchant, U. Flocculants—An ecofriendly approach. *J. Polym. Environ.* **2006**, *14*, 195–202. [[CrossRef](#)]
43. Ighalo, J.O.; Adeniyi, A.G. A Mini-Review of the Morphological Properties of Biosorbents Derived from Plant Leaves. *SN Appl. Sci.* **2020**, *2*, 509. [[CrossRef](#)]
44. Zhang, Z.; Xia, S.; Zhao, J.; Zhang, J. Characterization and flocculation mechanism of high efficiency microbial flocculant TJ-F1 from *Proteus mirabilis*. *Colloids Surf. B. Biointerfaces* **2010**, *75*, 247–251. [[CrossRef](#)]
45. Assaad, E.; Azzouz, A.; Nistor, D.; Ursu, A.; Sajin, T.; Miron, D.; Monette, F.; Niquette, P.; Hausler, R. Metal removal through synergic coagulation–flocculation using an optimized chitosan–montmorillonite system. *Appl. Clay Sci.* **2007**, *37*, 258–274. [[CrossRef](#)]
46. Zhang, D.; Crini, G.; Lichtfouse, E.; Rhimi, B.; Wang, C. Removal of Mercury Ions from Aqueous Solutions by Crosslinked Chitosan-based Adsorbents: A Mini Review. *Chem. Rec.* **2020**, *20*, 1220–1234. [[CrossRef](#)] [[PubMed](#)]
47. Ahmadi, S.; Rahdar, A.; Igwegbe, C.A.; Mortazavi-Derazkola, S.; Banach, A.M.; Rahdar, S.; Singh, A.K.; Rodriguez-Couto, S.; Kyzas, G.Z. Praseodymium-doped cadmium tungstate (CdWO₄) nanoparticles for dye degradation with sonocatalytic process. *Polyhedron* **2020**, *190*, 114792. [[CrossRef](#)]
48. Igwegbe, C.A.; Onukwuli, O.D.; Onyechi, K.K.; Ahmadi, S. Equilibrium and Kinetics Analysis on Vat Yellow 4 Uptake from Aqueous Environment by Modified Rubber Seed Shells: Nonlinear modelling. *J. Mater. Environ. Sci.* **2020**, *11*, 1424–1444.
49. Nharingo, T.; Zivurawa, M.; Guyo, U. Exploring the use of cactus *Opuntia ficus indica* in the bio-coagulation–flocculation of Pb (II) ions from wastewaters. *Int. J. Environ. Sci. Technol.* **2015**, *12*, 3791–3802. [[CrossRef](#)]
50. Ejimofor, M.I.; Menkiti, M.C.; Ezemagu, I.G. Comparative Studies on Removal of Turbid-Metric Particles (Tdsp) Using Animal Based Chito-Protein And Aluminium Sulfate On Paint Wastewater (Pww). *Sigma J. Eng. Nat. Sci./Mühendislik Fen Bilimleri Dergisi* **2020**, *38*, 1143–1159.
51. Bhandari, V.M.; Ranade, V.V. Advanced physico-chemical methods of treatment for industrial wastewaters. *Ind. Wastewater Treat. Recycl. Reuse* **2014**, 81–140. [[CrossRef](#)]
52. Loganathan, P.; Gradzielski, M.; Bustamante, H.; Vigneswaran, S. Progress, challenges, and opportunities in enhancing NOM flocculation using chemically modified chitosan: A review towards future development. *Environ. Sci. Water Res. Technol.* **2020**, *6*, 45–61. [[CrossRef](#)]
53. Fedala, N.; Lounici, H.; Drouiche, N.; Mameri, N.; Drouiche, M. physical parameters affecting coagulation of turbid water with *Opuntia ficus-indica* cactus. *Ecol. Eng.* **2015**, *77*, 33–36. [[CrossRef](#)]
54. Cruz, D.; Pimentel, M.; Russo, A.; Cabral, W. Charge neutralization mechanism efficiency in water with high color turbidity ratio using aluminium sulfate and flocculation index. *Water* **2020**, *12*, 572. [[CrossRef](#)]
55. Obiora-Okafo, I.; Onukwuli, O.; Eli-Chukwu, N. Evaluation of bio-coagulants for colour removal from dye synthetic wastewater: Characterization, adsorption kinetics, and modelling approach. *Water SA* **2020**, *46*, 300–312.
56. Teh, C.Y.; Wu, T.Y.; Juan, J.C. Potential use of rice starch in coagulation–flocculation process of agro-industrial wastewater: Treatment performance and flocs characterization. *Ecol. Eng.* **2014**, *71*, 509–519. [[CrossRef](#)]
57. Shak, K.P.Y.; Wu, T.Y. Coagulation–flocculation treatment of high-strength agro-industrial wastewater using natural *Cassia obtusifolia* seed gum: Treatment efficiencies and flocs characterization. *Chem. Eng. J.* **2014**, *256*, 293–305. [[CrossRef](#)]

58. Zuki, N.M.; Ismail, N.; Omar, F.M. Evaluation of zeta potential and particle size measurements of multiple coagulants in semiconductor wastewater. In Proceedings of the 6th International Conference on Environment (ICENV2018), Penang, Malaysia, 11–13 December 2018; p. 020036.
59. Zhou, Z.; Yang, Y.; Li, X.; Wang, W.; Wu, Y.; Wang, C.; Luo, J. Coagulation performance and flocs characteristics of recycling pre-sonicated condensate sludge for low-turbidity surface water treatment. *Sep. Purif. Technol.* **2014**, *123*, 1–8. [[CrossRef](#)]
60. Phalakornkule, C.; Mangmeemak, J.; Intrachod, K.; Nuntakumjorn, B. Pretreatment of palm oil mill effluent by electrocoagulation and coagulation. *Sci. Asia* **2010**, *36*, 142–149. [[CrossRef](#)]
61. Marriott, N.G.; Robertson, G. *Essentials of Food Sanitation*; Springer Science & Business Media: Berlin, Germany, 1997.
62. Bhatia, S.; Othman, Z.; Ahmad, A.L. Pretreatment of palm oil mill effluent (POME) using Moringa oleifera seeds as natural coagulant. *J. Hazard. Mater.* **2007**, *145*, 120–126. [[CrossRef](#)]
63. Ugonabo, I.V.; Onukwuli, O.; Ezechukwu, C. Deturbidization of Pharmaceutical Industry Wastewater Using Natural Coagulant: Response Surface Methodology Applied. *Int. J. Progress. Sci. Technol.* **2020**, *22*, 258–267.
64. Okolo, B.I.; Nnaji, P.C.; Menkiti, M.C.; Ugonabo, V.I.; Onukwuli, O.D. Application of single angle turbidimetry on coag-flocculation effect of *Detarium microcarpum* seed in brewery effluent. *Mater. Sci. Appl.* **2014**, *5*. [[CrossRef](#)]
65. Hunter, R. *Introduction to Modern Colloid Science*; Oxford University Press: Oxford, UK, 1993.
66. De Oliveira Reis, G. Study of the Mechanism of Acid Coagulation of Hevea Latex and of the Rheological Properties of Resulting Gels. Ph.D. Thesis, Université de Montpellier, Montpellier, France, 2015.
67. Ifeanyi, U.V.; Chukwudi, M.M.; Okechukwu, O.D. Effect of coag-flocculation kinetics on telfairia occidentalis seed coagulant (TOC) in pharmaceutical wastewater. *Int. J. Multidiscip. Sci. Eng.* **2012**, *3*, 22–33.
68. Park, S.; Kruis, F.; Lee, K.; Fissan, H. Evolution of particle size distributions due to turbulent and Brownian coagulation. *Aerosol. Sci. Technol.* **2002**, *36*, 419–432. [[CrossRef](#)]
69. Balarak, D.; Zafariyan, M.; Igwegbe, C.A.; Onyechi, K.K.; Ighalo, J.O. Adsorption of Acid Blue 92 Dye from Aqueous Solutions by Single-Walled Carbon Nanotubes: Isothermal, Kinetic, and Thermodynamic Studies. *Environ. Process.* **2021**, *8*, 869–888. [[CrossRef](#)]
70. Iwuozor, K.O.; Ighalo, J.O.; Ogunfowora, L.A.; Adeniyi, A.G.; Igwegbe, C.A. An Empirical Literature Analysis of Adsorbent Performance for Methylene Blue Uptake from Aqueous Media. *J. Environ. Chem. Eng.* **2021**, *9*, 105658. [[CrossRef](#)]
71. Beltrán-Heredia, J.; Sánchez-Martín, J.; Gómez-Muñoz, C. Performance and characterization of a new tannin-based coagulant. *Appl. Water Sci.* **2012**, *2*, 199–208. [[CrossRef](#)]
72. Miller, S.M.; Fugate, E.J.; Craver, V.O.; Smith, J.A.; Zimmerman, J.B. Toward understanding the efficacy and mechanism of *Opuntia* spp. as a natural coagulant for potential application in water treatment. *Environ. Sci. Technol.* **2008**, *42*, 4274–4279. [[CrossRef](#)]
73. Lagergren, S.; Svenska, B.K. On the theory of so-called adsorption of dissolved substances. *R. Swed. Acad. Sci. Doc. Band* **1898**, *24*, 1–13.
74. Oba, S.N.; Ighalo, J.O.; Aniagor, C.O.; Igwegbe, C.A. Removal of ibuprofen from aqueous media by adsorption: A comprehensive review. *Sci. Total Environ.* **2021**, *780*, 146608. [[CrossRef](#)] [[PubMed](#)]
75. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465. [[CrossRef](#)]
76. Aniagor, C.O.; Igwegbe, C.A.; Ighalo, J.O.; Oba, S.N. Adsorption of doxycycline from aqueous media: A review. *J. Mol. Liq.* **2021**, *334*, 116124. [[CrossRef](#)]
77. Mohamed, L.A.; Aniagor, C.O.; Hashem, A. Isotherms and kinetic modelling of mycoremediation of hexavalent chromium contaminated wastewater. *Clean. Eng. Technol.* **2021**, *4*, 100192. [[CrossRef](#)]
78. Igwegbe, C.A.; Ighalo, J.O.; Onyechi, K.K.; Onukwuli, O.D. Adsorption of Congo red and malachite green using H₃PO₄ and NaCl-modified activated carbon from rubber (*Hevea brasiliensis*) seed shells. *Sustain. Water Resour. Manag.* **2021**, *7*, 63. [[CrossRef](#)]
79. Ahmadi, S.; Igwegbe, C.A. Kinetic Studies on penicillin G removal from aqueous environments by cupric oxide nanoparticles. *Arch. Hyg. Sci.* **2021**, *10*, 86–96.
80. Igwegbe, C.A.; Ighalo, J.O.; Ghosh, S.; Ahmadi, S.; Ugonabo, V.I. Pistachio (*Pistacia vera*) Waste as Adsorbent for Wastewater Treatment: A Review. *Biomass Convers. Biorefinery* **2021**, 1–18. [[CrossRef](#)]
81. Hevira, L.; Ighalo, J.O.; Aziz, H.; Zein, R. Terminalia catappa shell as low-cost biosorbent for the removal of methylene blue from aqueous solutions. *J. Ind. Eng. Chem.* **2021**, *97*, 188–199. [[CrossRef](#)]