



# Enhanced Performance of Natural Polymer Coagulants for Dye Removal from Wastewater: Coagulation Kinetics, and Mathematical Modelling Approach

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## Abstract

This study explores the potentials of *Brachystegia eurycoma* coagulant (BEC) and *Vigna subterranean* coagulant (VSC) as natural organic polymers (NOPs) for the decolourisation of Crystal Ponceau 6R (AR 44) in wastewater. Materials characterisation studies were done on the precursors. A detailed kinetics study was employed. The decolourisation procedures were evaluated through time-dependent reduction in the concentration of particles, with the variation of the independent parameters. The proximate analysis showed protein contents of 19.77% and 18.15% for BEC and VSC, respectively. The functional test showed the presence of –OH, N–H, and C=H. The surface morphological study revealed some rough surfaces, different pores sizes, and compact-net structures. The order of removal efficiency was VSC > BEC with an optimum of 88.8% and 73.3%, respectively. The values of the coagulation rate constant ( $K$ ) and coagulation order ( $\alpha$ ) obtained for BEC and VSC were  $6.38 \times 10^{-4} \text{ L mg}^{-1} \text{ min}^{-1}$ , 1.8 and  $4.03 \times 10^{-3} \text{ L mg}^{-1} \text{ min}^{-1}$ , 1.9, respectively. The coagulation time,  $T_{ag}$  of 31.35 and 26.96 min for BEC and VSC, respectively, disclosed quick coagulation. The coagulation-flocculation kinetics demonstrated that the process conforms to the pseudo-second-order model with  $R^2 > 0.997$ , suggesting that the rate-controlling mechanism is governed by chemisorption. In the mass transfer study, experimental data were well predicted by the cross-validation test, with a percentage mean relative deviation modulus ( $M\%$ ) of 3.26 and 2.54 for BEC and VSC, respectively. These coagulants added meaningful progress in wastewater treatment by coagulation-flocculation while displaying significant adsorption features. Likewise, the usage of kinetics studies and particle behaviour modelling should be a prerequisite in water treatment processes.

**Keywords** Coagulation · Crystal Ponceau 6R · Natural organic polymers · Flocculation kinetics · Adsorption kinetics · Mass transfer

## Article Highlights

- Performance of plant seeds coagulants was investigated for colour removal.
- *Vigna subterranean* coagulant resulted in optimum colour removal of 88.8%.
- *Brachystegia eurycoma* coagulant resulted in optimum colour removal of 73.3%.
- The coagulation-flocculation process conforms to the pseudo-second-order model.

- The rate-controlling mechanism was governed by chemisorption.

## 1 Introduction

Due to the high contaminant contents of dye-containing wastewater, its threat to human health and the aquatic body is already established (Ishak et al. 2020; Obiora-Okafo et al. 2019; Sonal and Mishra 2021). Several works have been carried out on the removal of these pollutants from dye-containing wastewater using natural organic polymers (NOPs) employing the coagulation-flocculation process (Onukwuli et al. 2018). Due to the mission of the world on sustainable development, research interests have shifted to using NOPs (comprising plant-based or animal-based) for wastewater treatment (Obiora-Okafo et al. 2014). These coagulants possess some significant advantages over chemical coagulants due to their low toxicity, low sludge production, cost-effectiveness, and biodegradability (Igwegbe and Onukwuli 2019; Obiora-Okafo et al. 2014; Obiora-Okafo and Onukwuli 2018b).

This work is focused on employing *Brachystegia eurycoma* seed and *Vigna unguiculata* seed as precursors to *Brachystegia eurycoma* coagulant (BEC) and *Vigna unguiculata* coagulant (VUC), respectively. *Brachystegia eurycoma* seed belongs to the *Caesalpinaceae* family with average contents of 15% crude fat, 2.9% crude fiber, 20% protein, 56% carbohydrate, and 4.5% ash (Aviara et al. 2014). *Vigna unguiculata* seed is a legume of West African origin whose seeds are rich in protein and it is widely consumed by poor populations throughout the tropics. *Vigna unguiculata* seed powder has been used in reducing the turbidity of water from 205 NTU to 23 NTU (Edogbanya et al. 2013). Seed extract also shows antimicrobial properties in water. Nutrient contents of mature cowpea seed are protein 19.9%, fat 1.9%, fibre 6.3%, carbohydrate 63.6%, thiamine 0.0074%, riboflavin 0.0042%, niacin 0.00281%, ash 4.4% (Agunbiade and Longe 1999). Hence, this study investigates the novel application of BEC and VSC for effective application in the coagulation-flocculation treatment of Crystal Ponceau 6R dye in an aqueous solution. Coagulation-flocculation applications using natural plant-based coagulants is one of most recently used techniques in industrial treatment plants (Saini and Kumar 2016). One of their major advantages is that they produce lesser sludge which is minimal and cheaper to handle (Choudhary and Neogi 2017; Maurya and Daverey 2018; Onukwuli and Obiora-Okafo 2019).

A good selection of natural coagulants promotes large flocs formation bringing about rapid settling through adsorption of particles, charge neutralisation, sweep floc sizes due to their ability to attract smaller particles, thereby generating larger flocs. These interactions are also flocculation and inter-particle bridging mechanisms (Igwegbe et al. 2021d; Onukwuli et al. 2019; Mumbi et al. 2018). The adsorption mechanism is common when NOPs are used as a coagulant due to their polymeric features (Beltrán-Heredia et al. 2011b). Hence, NOPs encourage enhancement when there is some affinity between polymer segments and particle surfaces. Therefore, particle-particle interaction by adsorption usually occurs through electrostatic forces, hydrogen bonding, as well as ionic bonding. Most NOPs are charge sensitive; naturally, they are anionic, cationic, or non-ionic (Cainglet et al. 2020).

Coagulation-flocculation kinetics study is very important in the realm of colloidal science. It is necessary because it finds application in the analysis of colloidal and hydrodynamic contacts involving particle-particle interactions (Gregory 2009). Coagulation-flocculation kinetics have been investigated using some methods; direct counting of the flocculating col-

loids employing an ultra-microscope, or a particle counter, which yields the most clear-cut results. However, because this method is time-consuming, it is not ideal for routine coagulation kinetics analysis. The bulk technique approach is a regularly employed procedure for coagulation-flocculation kinetics study because it monitors changes in the particle suspension with time (Obiora-Okafo et al. 2020; Trefalt et al. 2020). This time-dependent approach is rapid, easy to use, cost-effective, and suitable for multi-particle determination.

The dynamic nature of the coagulation rate addresses how rapidly or slowly a suspension of particles will flocculate. Coagulation-flocculation processes have been studied by some authors thereby showing how the rate of spherical particles are agglomerated due to Brownian motion, taking diffusion coefficient of particles as constant (Ani et al. 2012; Menkiti et al. 2009; Schick and Hubbard 2005). As a result, the coagulation-flocculation process is always assumed to be a second-order process, therefore, the kinetics data are fitted into a second-order kinetics equation. Brownian mode of collisions of spherical particles would be studied in detail since it captures the crucial kinetics of various mass transfer processes such as coagulation-flocculation, adsorption methods, and advanced oxidation practices.

The possibility of employing active protein components isolated from *Brachystegia eurycoma* (BE) and *Vigna subterranean* (VS) to remove Crystal Ponceau 6R (AR 44) in an aqueous solution is investigated in this study. Coagulation-flocculation functional parameters such as coagulation rate constant and order of reaction were uniquely deduced using Polymath v5.1 software. A mathematical model describing the transient behaviour of the process was adopted to predict the rate of charged spherical particle transmission towards the adsorbing particles during the process.

## 2 Materials and Methods

### 2.1 Preparation and Extraction of Active Coagulant

*Brachystegia eurycoma* and *Vigna subterranean* seeds, as shown in Fig. 1, were purchased from Enugu, Nigeria and milled to sizes of 63–600  $\mu\text{m}$  to accomplish the solubilisation of active constituents. Samples of 2 g each were dispersed in 100 mL of distilled water containing 0.5 M NaCl (2.922 g NaCl / 100 mL) solution (Onukwuli and Obiora-Okafo 2019), agitated for 20 min using a magnetic agitator (Model 78HW, England), and sieved through Whatman, No. 42 and 125 mm diameter. The filtrate is labeled as the crude extract, used as the coagulants at the required dosages. As required, fresh solutions were prepared frequently and kept refrigerated at 20  $^{\circ}\text{C}$  (Onukwuli and Obiora-Okafo 2019; Sonal et al. 2021).

**Fig. 1** Dried seeds of (a) *Brachystegia eurycoma*, and (b) *Vigna subterranean*



## 2.2 Characterisation of the Coagulants

Proximate parameters of the precursors' seed powders were analysed (AOAC 1990). The chemical structure and functional groups were investigated using an FTIR spectrophotometer (IR Affinity, Shimadzu Kyoto, Japan). The spectra ranges were between 4000 and 400  $\text{cm}^{-1}$ . Surface morphology analyses were performed using a scanning electron microscope (Phenom Prox., Eindhoven, Netherlands) and the images were presented after 3D reconstruction via ImageJ v1.53 (Ighalo et al. 2021; Pérez and Pascau 2013) at  $\times 600$  magnification.

## 2.3 Preparation of Synthetic Wastewater

Crystal Ponceau 6R (AR 44) dye, having a molecular structure, as presented in Fig. 2a, was manufactured by May and Baker, England. To obtain the absorption spectrum of the dye, 1000  $\text{mg L}^{-1}$  of AR 44 was dissolved in distilled water (APHA-AWWA-WEF 1999). The solution was scanned against distilled water which is the blank in the range of 200–850 nm using a UV-visible spectrophotometer (Shimadzu, UV-visible, 1800). In addition, a stock solution of 1000  $\text{mg L}^{-1}$  of AR 44 was prepared by dissolving weighed amounts in separate doses. The required concentrations of 10–100  $\text{mg L}^{-1}$  were prepared from the stock solution using the dilution method (Onukwuli et al. 2019). The wavelength obtained at maximum absorbance ( $\lambda_{\text{max}}$ ) is shown in Fig. 2b.

## 2.4 Coagulation Assay

The coagulation action of the seed extracts were experimentally determined by the Jar test (Shankar et al. 2019). The jar test evaluated the coagulation activities of the active protein extracts from the precursors (Obiora-Okafo and Onukwuli 2018a). The jar test procedure was carried out using Phipps and Bird, USA apparatus, equipped with six beakers of 1 L capacity. The procedure involves 4 min of quick mixing speed at 100 rpm and a slow mixing speed of 40 rpm for 25 min. The suspensions were allowed to settle down and after 480 min

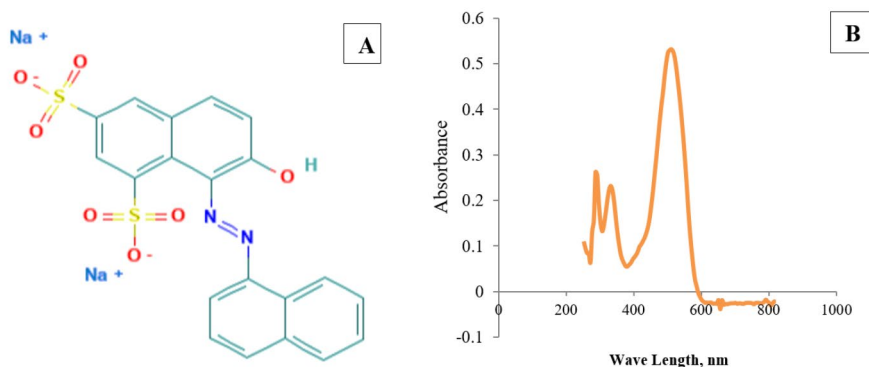


Fig. 2 (a) Structure of AR 44, (b) Spectrum analysis of AR 44

of sedimentation, clarified samples from the beakers were collected for absorbance examination using a UV-visible spectrophotometer, set at  $\lambda_{\max}$  of 511 nm. A preliminary test was conducted to establish the optimum factors including pH, coagulant dosage ( $\text{mg L}^{-1}$ ), dye concentration ( $\text{mg L}^{-1}$ ), settling time (min), and temperature (K) (Onukwuli et al.). Finally, colour concentrations ( $\text{mg L}^{-1}$ ) were measured by comparing absorbance to concentration on a graduation curve (Obiora-Okafo et al. 2018), while the colour removal efficiencies were calculated according to Eq. (1) (Obiora-Okafo and Onukwuli 2018a):

$$\text{Colour removal (\%)} = \left( \frac{c_0 - c}{c_0} \right) \times 100 \quad (1)$$

where,  $C_0$  and  $C$  represent the initial and final colour concentrations ( $\text{mg L}^{-1}$ ) before and after the process, respectively.

The sludge generated from the process was recovered and reused as a coagulant for wastewater treatment (Łukasiewicz 2016). By this, its impact on the environment was limited.

The coagulation kinetics of spherical charged-particle contact was studied following the Brownian diffusion mechanism (Peri-kinetics) (see Supplementary Material (SM) file, Sect. S1). Also, the model equation that can predict the amount of particles transferred in the coagulation system at any given time was derived (see SM file, Sect. S2). The model equation (Eq. S47 in the SM file) was confirmed using MATLAB 9.3 software at different contaminant concentrations during the process occurring at different operating times (McMahon 2007). MATLAB 9.3 proved to be a great code-based mathematical and engineering package used for solving numerous mathematical problems (Carnell 2003; McMahon 2007). The exactness of the model was checked using the percentage mean relative deviation modulus ( $M\%$ ) of Eq. (2), which gives details on the mean deviation of the predicted data from the experimented data (Oke et al. 2014):

$$M\% = \left[ \sum_{n=1}^n \frac{|M_{exp} - M_{pre}|}{M_{exp}} \right] \times \frac{100}{N} \quad (2)$$

where  $M_{exp}$  = experimental data, and  $M_{pre}$  = predicted data.

From the  $M\%$  analysis, values fewer than 5 confirmed an exceptionally good fit;  $M\%$  values between 5 and 10 denote reasonably good fit; and values above 10 showed poor fit (Yousefi et al. 2013). Additionally, some numerical tools, such as the coefficient of determination ( $R^2$ ), Chi-square ( $\chi^2$ ), F-test, and t-test were further applied to the model testing using Microsoft Excel 2010.

### 3 Results and Discussion

#### 3.1 Proximate Study

Proximate analysis of the precursors, as presented in Table 1, shows high moisture values indicating the coagulants' ability to absorb water, as well as, dissolve colour particles sus-

**Table 1** Proximate characteristics of the proposed coagulants

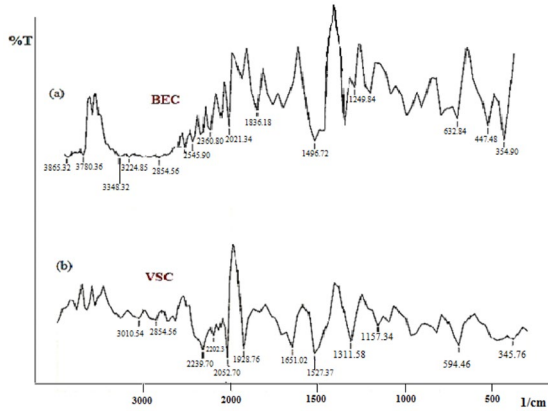
No.	Parameters	Values	
		<i>Brachystegia eurycoma</i> (Black timber)	<i>Vigna subterranean</i> (Bambara nut)
1	Yield	28.31	14.6
2	Bulk density (g mL <sup>-1</sup> )	0.235	0.241
3	Moisture content (%)	7.25	10.0
4	Ash content (%)	3.48	2.97
5	Protein content (%)	19.77	18.15
6	Fibre content (%)	2.20	1.64
7	Carbohydrate (%)	56.76	60.94
8	Fat content (%)	10.53	6.30

pended in water (Obiora-Okafo and Onukwuli 2018a). The reasonable amount of crude protein contents as recorded indicates the presence of active coagulation components. The values obtained agree with the literature that the protein contents of BE and VS are cationic poly-peptides (Igwegbe et al. 2021c; Ikegwu et al. 2009). The fibre content implies that the precursors are biological polymers which have visible fibrous structures when dispersed in an aqueous medium (Bolto and Gregory 2007; Onukwuli et al. 2019; Yin 2010). The proximate results validate the use of the seed extracts as potential coagulants. In addition, other natural coagulants with similar contents exhibit quality coagulation properties (as reported by Igwegbe et al. 2021a; Obiora-Okafo et al. 2019; Ugonabo et al. 2020). Also, a high similarity of the proximate result is shown in the result of Menkiti et al. (2018) due to the same coagulant studied.

### 3.2 FTIR Analysis of the Coagulants

The spectra representation of BEC and VSC are shown in Fig. 3a–b, respectively. In Fig. 3a, there is a slight absorption peak of 3965.52–3780.36 cm<sup>-1</sup> attributed to the stretching vibration of –OH, together with vibration of water absorbed (Igwegbe et al. 2021c). Also, the –OH groups with a peak at 3070.58 cm<sup>-1</sup> were also evidenced in Fig. 3b. The free hydroxyl groups, confirm the occurrence of carboxylic acids, phenols, and alcohols in the coagulants. This band also links to the O-H vibrations of cellulose, pectin, and lignin. This strong O-H band is favorable for adsorbing a large variety of dyes (Chikri et al. 2020; Šćiban et al. 2007). Consequently, there is an agreement between the results of Table 1 and the spectral results indicating the presence of moisture, oil, and carbohydrate. Furthermore, the analysis revealed that the absorption peak for the amines was evidenced in 3348.32 cm<sup>-1</sup> for aliphatic primary amine (N-H) and secondary amine of 3070.58 cm<sup>-1</sup> for BEC and VSC, respectively. Also, the presence of stretching signals, N-H detects the existence of amino compounds, confirming the presence of protein in the powders as demonstrated in Table 1. In addition, a major group in the wider region of 2021.34 cm<sup>-1</sup> and 2052.20 cm<sup>-1</sup> specifies the existence of a C=O group (carbonyl compound) (Igwegbe et al. 2019; Menkiti et al. 2018). There was also a strong adsorption peak at 694.36 cm<sup>-1</sup> and 632.64 cm<sup>-1</sup> for BEC and VSC, respectively, showing the distinguishing occurrence for C-H out of plane deformation which is typically comparative to the position and spatial geometry of the double bond (Coates 2006). Finally, the occurrence of moistures, proteins, and esters is

**Fig. 3** FTIR spectra of (a) BEC and (b) VSC

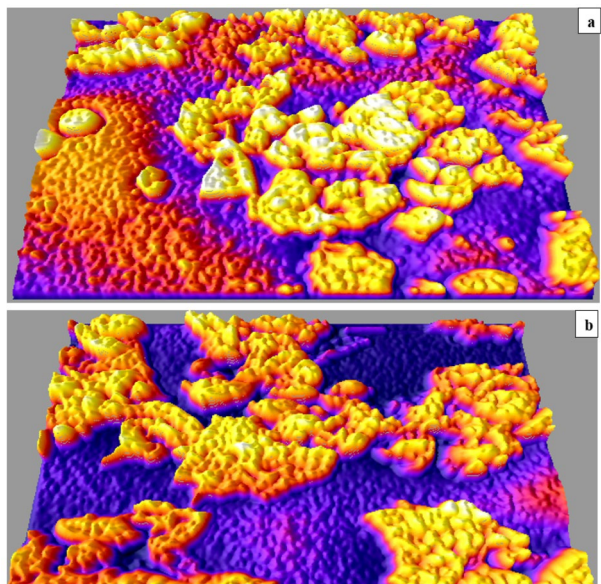


confirmed by the FTIR spectral of BEC and VSC, as well as the proximate analysis provided in Table 1, justifying their usage as good sources of coagulants in this research (Onukwuli and Obiora-Okafo 2019).

### 3.3 Morphological Analysis of the Coagulant

SEM technology was used to examine the external morphologies of the coagulants in this investigation, as shown in Fig. 4a and b at 600x magnifications. The 3D reconstructed SEM images revealed well-developed pores of various sizes and shapes. As a result, pore sizes made up of micro-pores, macro-pores and mesopores, together with their distributions, are confirmed unique features of NOPs (Obiora-Okafo and Onukwuli 2021). Therefore, a major pore size of  $0.41 \mu\text{m}^2$  was revealed in the histograms, as well as fibre lengths between

**Fig. 4** 3D reconstructed SEM micrographs for (a) BEC and (b) VSC (600× magnifications)



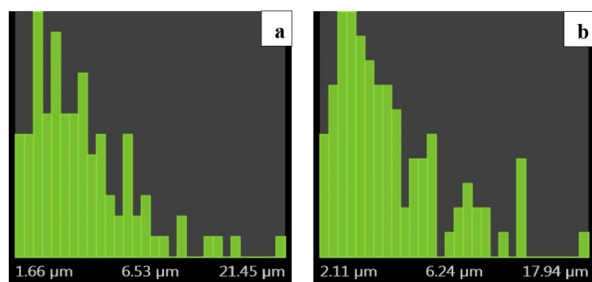


1.66 and 21.45  $\mu\text{m}$  and 2.11–17.94  $\mu\text{m}$  for BEC and VSC, respectively (Fig. 5). Varying fibre lengths are unique features of NOPs that enhance their multifunctional utilization as coagulants and adsorbents (Menkiti et al. 2018; Obiora-Okafo et al. 2018). Rough surfaces disclose that the coagulants are rough fibrous solids primarily made of cellulose and lignin, indicating that they are polymeric (Zhu et al. 2020). The binding of particles to polymer chains via inter-particle bridging or electrostatic interactions improves sweep flocculation. Adsorption as a crucial mechanism in the procedure is also confirmed by small holes and rough surfaces seen on the coagulant morphologies (Igwegbe et al. 2021c; Obiora-Okafo et al. 2018). Furthermore, the structures also retain compact-net arrangements which are more conducive to particle flocculation owing to bridge aggregation. Finally, when compared to the branching structure, the compact-net structure is better for flocculation and particle-bridge creation among flocs (Zhu et al. 2012).

### 3.4 Colour Concentration/Removal Efficiency Dependent on Settling Time

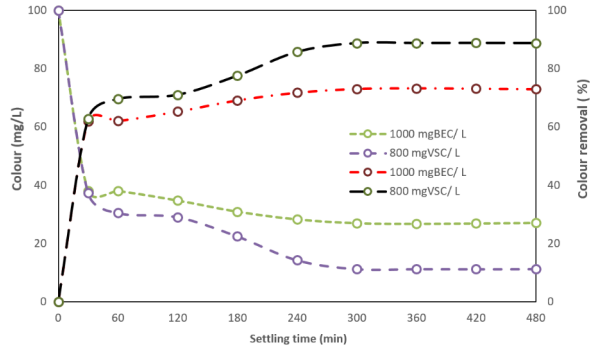
The flocculation process involves particle interactions and a time-dependent interface of coagulant hydroxide formation, following the hydrolysis reaction (Liang et al. 2016; Obiora-Okafo et al. 2018). The time-dependent influence of colour concentration and its reduction efficiency are presented in Fig. 6. The percentage reduction in concentration as observed in 1000 mgBEC/L and 800 mgVSC/L results to 73.3% and 88.8% respectively, at pH 2 (Onukwuli et al.). The higher protein content of BEC, as shown in Table 1, does not mean that it is not efficient, but in this case, higher VSC efficiency is attributed to more fibrous material triggering inter-particle bridging/sweep-flocculation mechanisms. In addition, the sharp time reduction of 30 min specifies a speedy coagulation process that discloses the probable coagulation time ( $T_{ag}$ ). Moreover, this rapid reduction in concentration may perhaps be attributed to either charge neutralisation or its combination with sweep flocculation mechanism (Beltrán-Heredia et al. 2011a). As a result, after 30 min, the amount of particles accessible for flocculation diminishes, showing a gradual drop in colour concentration as the process progresses. This is most likely due to an intricate coagulation-flocculation procedure that may include the development of a net-like structure that does not take a long period. Therefore, the greater flocculation period could be related to the presence of a sorption mechanism that necessitates a longer process time. After 300 min, there was no noticeable change in concentration, indicating that equilibrium has been reached. Consequently, due to the saturation of the active adsorption sites, the aggregate becomes destabilized, preventing further adsorption and, as a result, the settling period is prolonged (Beltrán-

**Fig. 5** Fibre lengths from SEM micrographs for (a) BEC and (b) VSC (600 $\times$  magnifications)





**Fig. 6** Colour removal and removal percentage utilising polymer coagulants as a function of settling time



Heredia et al. 2011a; Onukwuli and Obiora-Okafo 2019). For these reasons, coagulation-flocculation using NOPs in wastewater presents increased removal efficiency at acidic pH conditions, between pH 2 and 4. Analogous to these results have also been reported by Zhu et al. (2011); Onukwuli et al. (2019); Igwegbe et al. (2021a; Trinh and Kang (2011)). In conclusion, successful results have been achieved in the dye/colour removal using various plant-based coagulants (e.g., Bahrodin et al. 2021; Chaibakhsh et al. 2014; Kristanda et al. 2021; Nnajia et al. 2020; Sanghi et al. 2002; Zonoozi et al. 2011).

### 3.5 Coagulation-Flocculation Kinetics Representing Brownian Motion

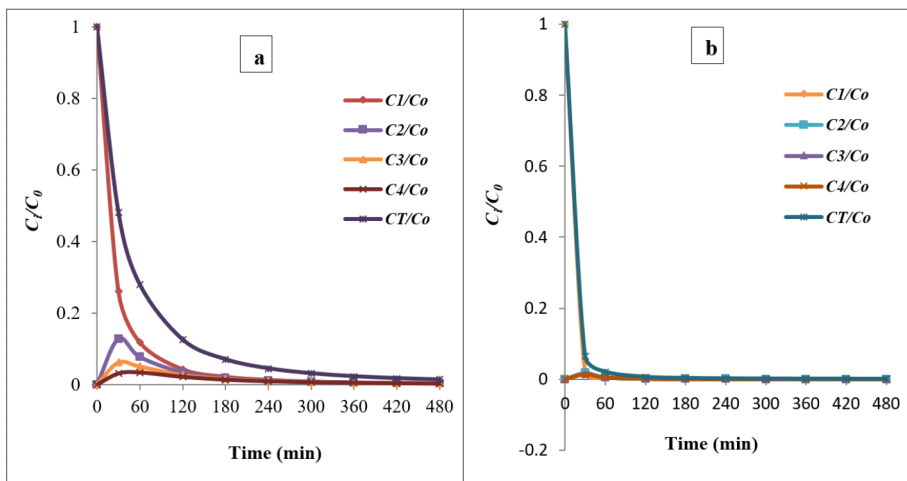
Analysis was performed at a 95% confidence level to determine the order of coagulation-flocculation response. The parameters gotten from the data regression analysis for BEC and VSC are provided in Table 2. The intercept and slope of the equation defining the kinetics of agglomeration were used to calculate the coagulation rate constant  $K$ , and the order of reaction (Eq. S3, see SM file). The coagulation proportionality constant that connects the reaction rate to the concentration of the reacting species is called the coagulation rate constant ( $K$ ) (Schick and Hubbard 2005). This denotes that each minute,  $0.000638 \text{ mg L}^{-1}$  and  $0.00403 \text{ mg L}^{-1}$  of colour particles were consistently attached to the polymer surfaces creating larger aggregates for BEC and VSC, respectively. From the calculation, the reaction order ( $\alpha$ ) obtained was in agreement with the conventional principle of coagulation-flocculation being a second-order process (Menkiti et al. 2011; Schick and Hubbard 2005). Hence, the reaction order gotten confirms the optimum order for the process, showing a second-order reaction. Also, the correlation coefficient ( $R^2$ ) demonstrates good agreement that implies that the studied kinetic data is significant.  $T_{\text{ag}}$  (coagulation time) is inversely proportional to the starting concentration of colour particles, proposing that the higher the contaminant concentration, the shorter the coagulation time required for elimination (Obiora-Okafo et al. 2019). The values of the frequency of collision of the particles ( $\beta$ ) are also provided in Table 2. Furthermore, the collision efficiency ( $E$ ) values explain the attainability assumption that particle collision between contaminants and coagulants is 100% efficient throughout the dispersion, implying that particles will stick together after bimolecular collision and that particle distribution or complex formation distribution will occur during the process (Obiora-Okafo et al. 2019).

**Table 2** Coagulation kinetics parameters from brownian theory

Parameters	1000 mg BEC/L	800 mg VSC/L
$K$ (L/ mgmin)	$6.38 \times 10^{-4}$	$4.03 \times 10^{-3}$
$\alpha$	1.8	1.9
$R^2$	0.981	0.969
Rate Equation (-r)	$6.38 \times 10^{-4} C^2$	$4.03 \times 10^{-3} C^2$
$T_{ag}$ (min)	31.35	26.96
$K_I$ (L/ min)	$3.19 E^{-04}$	$2.02 E^{-03}$
$\beta$ (L/ mgmin)	0.000638	0.00403
$E$ ( $mg^{-1}$ )	1.00	1.00

### 3.6 The Influence of Time on Particle Behaviour

Particle reduction behaviour as a function of time depicts the pattern at which colour concentrations are reduced. Figure 7 depicts the fluctuations in  $C_T$ ,  $C_1$ ,  $C_2$ ,  $C_3$ , and  $C_4$  for initially monodispersed particles obtained using Eqs. S26–S29 (SM file, Sect. S1). With increasing time, both the total colour concentration  $C_T$  and the concentration of the singlet species  $C_1$  drop monotonically. The concentrations  $C_2$ ,  $C_3$ , and  $C_4$  go through a maximum since they are not present at the initial time and concentration. Due to an increase in the number of particle concentrations to the aggregate formation over time, the number of singlets appears to be decreasing faster than the overall number of particles (Igwegbe et al. 2021a; Taitelbaum and Koza 2000). The effect of the bimolecular reaction results in a drop in the total number of particles. Furthermore, we discovered that the lower the  $K$  value, the longer the coagulation time, giving rise to a slow rate and longer coagulation-flocculation process (Menkiti et al. 2009).

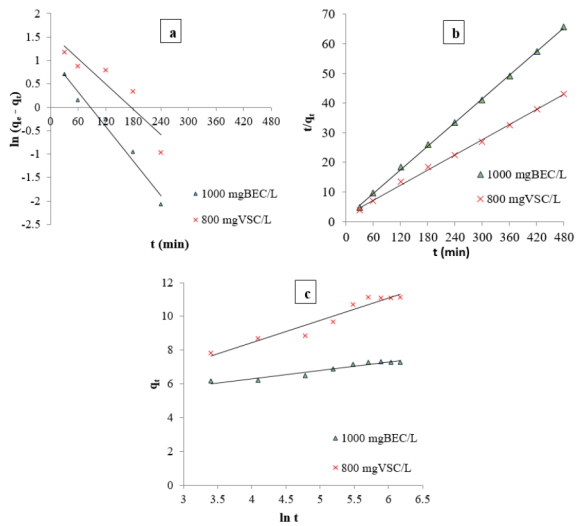


**Fig. 7** The decrease in the normalised number of overall particles with time for colour removal using (a) BEC @ 480 min, and  $6.38 \times 10^{-4}$  mg/L min, (b) VSC @ 480 min and  $K = 4.03 \times 10^{-3}$  mg/L min

### 3.7 Adsorption Models

Some attractions exist between polymer segments and particle surfaces during the flocculation process, which leads to adsorption (Bolto and Gregory 2007). Consequently, some kinetic models such as pseudo-first-order, pseudo-second-order, and Elovich kinetic models (SM file, Sect. S3) were involved to examine the rate at which particles are adsorbed onto polymer surfaces, as presented in Fig. 8. Thus, the kinetic factors obtained are summarised in Table 3. A higher  $R^2$  value indicates that a particular model best suits the data (Mudzielwana et al. 2019; Obiora-Okafo et al. 2019). Consequently, the kinetics data agree more with the pseudo-second-order model due to its higher  $R^2$  values (El-Nemr et al. 2020; Menkiti et al. 2018). Furthermore, the experimental data agree well with the pseudo-second-order kinetic model data, with BEC and VSC having the lowest normalised standard deviation,  $\Delta q$

**Fig. 8** The plot of adsorption kinetics showing (a) pseudo-first-order, (b) pseudo-second-order and (c) Elovich kinetic plots



**Table 3** Adsorption factors for colour removal

<i>Pseudo-first-order kinetics</i>					
	$q_e, exp$ (mg/g)	$q_e, cal$ (mg/g)	$K_{F1}(min^{-1})$	$R^2$	$\Delta q$ (%)
1000 mgBEC/L	7.3	1.95	0.01	0.911	25.911
800 mgVSC/L	11.1	4.899	0.009	0.851	19.75
<i>Pseudo-second-order kinetics</i>					
	$q_e, cal$ (mg/g)	$K_2(g/mg$ $min)$	$R^2$	$h$ (mg/g $min)$	$\Delta q$ (%)
1000 mgBEC/L	7.52	0.0836	0.997	4.73	2.1
800 mgVSC/L	11.76	0.0395	0.999	5.46	1.07
<i>Elovich kinetics</i>					
	$a$	$b$	$R^2$		
1000 mgBEC/L	3362.83	2.028	0.925		
800 mgVSC/L	14.77	0.759	0.933		

(%) values of 2.1% and 1.07%, respectively evaluated using Eq. S54 (SM file). Additionally, the coagulation-adsorption process is confirmed as a second-order process owing to an excellent fit of the second-order kinetic with an  $R^2$  of 0.999. More importantly, the Elovich model’s moderate agreement expanded our knowledge of the adsorption-chemisorption procedure, suggesting selective adsorption without site rivalry, as shown in organic polymers (Feng et al. 2021; Lanan et al. 2021), leading to the position of the Langmuir model in the sorption process (Obiora-Okafo et al. 2018). Thus, chemisorption, which involves valence forces through electron sharing between polymers and pollutants, was found to affect the general rate of the adsorption process (Gheraout et al. 2015; Igwegbe et al. 2021b).

### 3.8 The Expectation of Particles Transfer Rate

The mass transfer rate was verified using particle concentration measurements that showed the investigational and projected transfer rates all through the coagulation-flocculation process, as shown in Fig. 9. The results demonstrated that the actual and expected values are in agreement. Due to this, the anticipated equilibrium point is closer to the experimental equilibrium (Oke et al. 2021).

Table 4 displays the results of statistical data comparing the investigational and projected data. The results indicate that the lower the percentage, the better the prediction. The value of  $M\%$  lesser than 10 specifies a good prediction of investigational data. Also, the correlation coefficient of the predicted results gave positive correlation values of 0.816 and 0.950 for BEC and VSC, respectively. Furthermore,  $\chi^2$  values greater than 0.05 are more signifi-

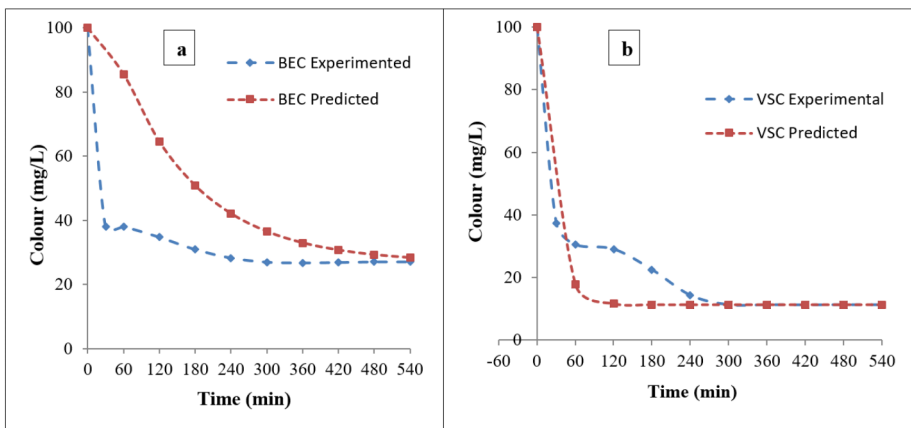


Fig. 9 Particle rate transfer through coagulation-flocculation for: (a) BEC and (b) VSC

Table 4 Modelling verification result

Coagulants	$M\%$	$R^2$	$\chi^2$	F-test	T-test
BEC	3.263	0.816	30.30	0.711	0.0270
VSC	2.536	0.950	23.98	0.0316	0.0316

cant than those less than 0.05. During the coagulation-flocculation, the projected contaminant particle decline pattern is likewise similar to Oke et al. (2021) earlier study.

### 3.9 Process Cost Management

In this study, the main process cost will be centered on two main items such as: raw material cost and cost of sludge handling and disposal. The cost of treating 1 L of BEC and VSC was calculated by taking into account the cost of preparing 1000 mg/L BEC and 800 mg/L VSC of the coagulant dosages and the energy cost. The preparation of 1000 mg/L of BEC and 800 mg/L VSC costs 1 EUR (462 NGN) and 0.8 EUR (370 NGN), respectively. The cost of energy for the preparation of the two coagulants is 3.0 EUR (1386 NGN). The total cost was computed as 4.8 EUR (2,218 NGN). Then, compared to the use of conventional coagulants mostly used in Nigeria such as aluminium sulphate (alum), whose present cost for 1 g is 5 NGN, i.e., far less than 1 EUR. This makes the use of bio-coagulants in wastewater management an expensive application. However, chemical coagulants have greater dosage requirements as compared to natural coagulants (Igwegbe et al. 2021a; Moghaddam et al. 2010). In addition, the usage of these two coagulants for wastewater treatment may pose future food depletion. However, the use of natural coagulants is still more acceptable to avoid the disadvantages that chemical coagulants appear to bring (Obiora-Okafo et al. 2014).

Analyzing the costs of disposal and handling the huge quantities of sludge created from this process can account for an enormous part of the operating costs of the wastewater treatment plant (WWTP). Also, the restricted land available for sludge disposal makes this a substantial concern for water purification authorities (Heil and Barbarick 1989; Viraraghavan and Ionescu 2002). Therefore, recovering and reclaiming the wastewater sludge (WWS) as a coagulant in the WWTP for dye/colour removal could offer great advantages such as cost reduction in sludge disposal sites, high removal efficiency, and impact on economic savings on the overall treatment plant operating cost (Łukasiewicz 2016; Moghaddam et al. 2010). In addition, reusing the WWS as a low-cost material (almost free of charge) can provide a considerable cost benefit with fresh coagulant reserves in WWTP. In conclusion, it is balanced to suggest that WWS generated from this procedure can be fruitfully employed as a low-cost coagulant for the removal of dye from aqueous solutions.

## 4 Conclusions

Natural organic polymers were found to be effective at removing colour from AR 44 dye effluent. The proximate, FTIR and SEM analyses done on the coagulants showed that *Brachystegia eurycoma* (BE) and *Vigna subterranean* (VS) have the characteristics of possible coagulants. The characterisation results also revealed the coagulant's capability to disrupt contaminant particles due to their cationic nature, adsorb particles on its surfaces, improve floc formation due to their polymer features, and then enhance large settleable flocs due to particle linking and sweep flocculation mechanisms. The obtained values of coagulation rate constant ( $K$ ) and coagulation order ( $\alpha$ ) agreed with the traditional assumption that rapid coagulation shows a second-order process. The adsorption procedure was more of a second-order process, demonstrating that the rate is proportional to the square of the particle concentration. These findings further suggested that in general, coagulation and adsorption

processes were second-order processes governed by the chemisorption mechanism. The model investigated could be used to control colour particle transfer at any given condition and forecast the rate at which particles are transferred in a process without needing an experimental technique. It could also be utilized to extrapolate space and time that are not stated by the experimental results. In this study, the coagulation-flocculation and adsorption capabilities of *Brachystegia eurycoma* coagulant (BEC) and *Vigna subterranean* coagulant (VSC) were credited with their efficiency. Generally, this research has demonstrated the utilization of kinetics research in the large field of wastewater treatment and other mass-transfer processes. In addition, BEC and VSC are promising coagulants to be applied in WWTP because of their various advantages over chemical coagulants such as environmental friendliness, and easy sludge handling and reuse operation.

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## Disclosure statements

**Conflict of Interest** The authors proclaim no conflicts of interest.

**Compliance with Ethical Standards** There is no research using human or animal subjects in this article.

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