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Application of kinetics and mathematical modelling for the study of colour removal from aqueous solution using natural organic polymer

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ABSTRACT

The potential of using *Moringa oleifera* coagulant (MOC) as a coagulant in colour concentration reduction from Crystal Ponceau 6R dye using spectrophotometric method has been studied. The kinetics and mathematical modelling were employed to study the particle transfer rate during coagulation-flocculation process. The proximate composition, structure, and surface morphology of the coagulant were analysed using standard official methods, Fourier-Transform Infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM), respectively. The removal process was evaluated through time-dependent decrease in particle concentrations and consequently, flocs growth formations. Effects of the process parameters including pH, coagulant dosage, dye concentration, settling time, and temperature were tested and the best ranges were determined experimentally. The best operating conditions established were pH 2, 800 mg MOC/L coagulant dosage, 20 mg/L dye concentration, 420 min, and 303 K. The best colour removal was achieved at 93.8%. The values of rate constant, K and order of reaction, α obtained were 8.09E-04 L/mg min and 2, respectively. The coagulation time, of 87.72 min showed a rapid coagulation process. Coagulation-adsorption kinetics showed a high agreement of the process to pseudo-second order model implying that chemisorption is the rate controlling step. Adsorption of particles on the polymer surfaces occurred mostly as a mono-molecular layer according to chemisorption mechanism. Model equation was verified using experimental data and coagulation kinetics parameters in MATLAB environment. Cross validation test showed good prediction of the experimental data. The precursor extracts have potential for application as a coagulant while showing significant part of adsorptive phenomenon. Applying kinetics and modelling in wastewater treatment study is a requirement in separation processes that involves particle transfer.

Keywords: Coagulation-flocculation; Colour removal; Organic polymer coagulant; Kinetics study; Particle transfer; Modelling

1. Introduction

Industrial operations generate high volumes of waste waters with high contaminant contents. Textile industry is one of the sectors posing pollution traits to the world considering its wastewater contents and high volume of discharges into the environment. Presently, about 10,000 commercial dyes and pigments are being used and over 7.11×10^7 kg/y of them are produced worldwide [1]. Dye containing wastewater, when discharged to the aquatic body could be toxic to aquatic life, slows down self-purification of streams by reducing light penetration, retards photosynthetic activity, and inhibits the growth of aquatic biota [2]. On this note, dye containing wastewater generated from industrial processes has to be treated properly in accordance with the standard discharge able limit.

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Studies have been done on colour removal by coagulation-flocculation [3–5]. Due to the world quest for sustainable development, research on wastewater treatment is gradually re-focused on the use of natural coagulants (either plant-based or animal-based) because of their abundant source, cost-effectiveness, eco-friendly, multi-functional, biodegradability in water purification, low sludge volume production, and they do not alter the pH of the treated wastewater [6]. Good choice of natural coagulant (organic polymer) enhances the aggregation of particles for large flocs formation which are capable of rapid settling through particle adsorption mechanism, charge neutralization mechanism, enmeshment in a precipitate, and inter-particle bridging mechanism. The adsorptions of particle behaviours in water are common when natural organic polymers (NOCs) of high molecular weight are used as coagulants. Particles interaction by adsorption occurs when there are some affinity between polymer segments and particle surfaces. Adsorption interactions are possible by electrostatic forces, hydrogen bonding and ionic bonding [5]. NOCs might be anionic, cationic or nonionic in nature [4].

Coagulation-flocculation will be incomplete without an adequate knowledge of its process kinetics. The study of coagulation kinetics is employed to investigate the hydrodynamic interactions involving particle-particle transfer [7]. Various methods such as bulk techniques, and single particle techniques (Coulter counter, flow cytometer, single particle light scattering) have been employed in monitoring the reduction of particle concentrations. Bulk technique is widely used procedure for coagulation-flocculation kinetics study because it monitors particle concentration transfer with time i.e. a time-dependent operation [8]. The dynamics of coagulation rate addresses how rapidly or slowly suspended particles will coagulate. Coagulation rate has an immense practical implications and it plays an important role in the mathematical modelling, design and control of water treatment plants. Von Smoluchowski [9] was the first to study the rate of coagulation of particles due to Brownian motion with the diffusion coefficient of particles taken as constant.

Mathematical model describes the time-dependent behaviour of a process. It is a set of equations (including necessary input data to solve the equations) that predicts the behaviour of a process. It is suitable for simulating the dynamic behaviour and studying control strategies of a process. Process modelling of coagulation-flocculation improves and optimizes design of equipment and develops a better insight on the process operation. In the theoretical study of coagulation-flocculation process, the prediction of particle reduction in response to a set of coagulation conditions is an area of interest. Brownian bi-molecular collisions of particles on a spherical target are analysed in detail because it captures the essential kinetics of many mass transfer processes including coagulation-flocculation of colloidal particles, diffusion growth, and diffusion-controlled chemical reactions [8]. Coagulation kinetics is a complex phenomenon that requires adequate models to predict the mass transfer behaviour of particles during the process. Jimoda et al. [10] model adequately predicted the particle transfer rate during the coagulation-flocculation process.

This paper investigates the performance of active protein agents from natural coagulant in colour removal from aqueous solution. Detailed physicochemical characterisations of the precursor were conducted. The novel approach of extracting active coagulant agent was adopted in the coagulation-flocculation process. Spectrophotometry method was used to monitor the dynamic behaviour of particle concentrations at best conditions. The study also explores the kinetics of particle transfer and modelling predicting the real-time particle transfer rate during the coagulation-flocculation process.

2. Materials and methods

2.1. Coagulant preparation and extraction of active content

Dried seeds of *Moringa oleifera* were purchased from local market of Enugu city, Nigeria. Matured seeds showing no signs of discolouration were used. The dry seeds of the sample were ground to fine powder (63–600 µm) using an ordinary food processor (Model BL 1012, Khind) to achieve solubilisation of active ingredients. The active proteins from coagulant were extracted by preparing a stock solution of 20000 mg of powdered samples in 1 L distilled water. Magnetic stirrer (Model 78HW-1, U-Clear England) stirred the stock solution vigorously for 20 min at room temperature to promote adequate extraction of the coagulant proteins. Filter paper (Whatman 42, 125 mm diameter) was used to filter the suspension to enable nano, micro, and macro-particles to be present in the filtrate for an enhanced polymer adsorption process. The resultant filtrate was used as coagulant at required dosages. Dilution formula was employed to get the required working coagulant dosages of 200–1000 mg/L. Fresh solutions were prepared daily and kept refrigerated to prevent any ageing effects such as change in pH, viscosity, and coagulation activity. Before each experiment, solutions were shaken vigorously and used immediately for each sequence of experiment.

2.2. Characterization of the coagulant

Yield, bulk density, moisture content, ash content, protein content, fat content, carbohydrate content, and fibre content of the seed powder were determined by the standard official methods of analysis [11]. Fourier Transformed Infra-Red (FTIR) spectrophotometer supplied by IR Affinity-1, Shimadzu Kyoto, Japan, was used to study the chemical structure and functional groups present in the sample. The spectra were measured in the range of 4000–400 cm^{-1}. Surface structures and morphologies of the seed powders were studied using scanning electron microscopy (SEM) supplied by Phenom Prox., world Eindhoven, Netherlands

2.3. Decolourisation procedure

2.3.1. Absorption spectrum and preparation of stock solution

Crystal Ponceau 6R (AR 44), water soluble dye used in this study was provided by May & Baker, England. Dye with commercial purity was used without further purification. The absorption spectrum of the dye was obtained by dissolving 1000 mg/L of AR 44 in distilled water. A sample of the solution was scanned against the blank in the range of 200–850 nm using UV-Vis spectrophotometer (Shimadzu, Model UV-1800). The maximum wavelength (λ_{max}) of 511 nm was obtained [13]. Stock solution of 1000 mg/L of dye was prepared by dissolving accurately weighed amounts of AR 44 in separate doses of 1 L distilled water. The desirable experimental concentrations of 10–100 mg/L were prepared by diluting the stock solution with distilled water when necessary using general dilution formula [12]. The wavelength at maximum absorbance (λ_{max}) and its calibration curves at λ_{max} of the dye were determined. The colour concentrations (mg/L) were determined through the calibration analysis with respect to absorbance reading [12].

2.4. Coagulation studies

A conventional jar test apparatus supplied by Phipps and Bird, VA, USA, equipped with six beakers of 1 L capacity and six paddle stirrers was used to perform the coagulation-flocculation experiment. The jar test was conducted to evaluate the performance of the active agent extracted based on the methods adopted by Obiora-Okafo and Onukwuli [13] and also to establish the best operating condition for the process. The jar test procedure involved 4 min of rapid mixing at 100 rpm. The mixing speed was reduced to 40 rpm for another 25 min. All the suspensions were left for settling (30–480 min). The supernatant samples were withdrawn (after settling) for absorbance analysis using UV-Vis spectrophotometer (Shimadzu, model 1800) at 511 nm. The preliminary studies were conducted by varying experimental factors including pH, coagulants dosages (CD), dye concentration (DC), settling time (ST), and temperature. These were done to establish the optimum ranges of operating conditions. The final experiments were carried out at varying operating conditions as shown in Table 1. Colour concentration (mg/L) measurement was determined by comparing absorbance to concentration on a calibration curve [13]. Buffered solutions were prepared by the standards established according to the National Bureau of Standards (NBS, US) and standardized using a digital HANNA pH meter. The solution pH was adjusted to the desired value using 0.1 M HCl and 0.1 M NaOH. Coagulant dosages and dye concentrations were prepared by using standard dilution formula [12]. Solution temperatures were attained using magnetic stirrers with hot plate supplied by 78HW-1, U-Clear England. The colour removal efficiency was obtained according to Eq. (1) as:

$$\text{Colour removal } (\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100 \tag{1}$$

where C_0 and C are the initial and final colour concentration (mg/L) in dye solutions before and after coagulation-flocculation treatment, respectively.

2.5. Theoretical principles guiding coagulation-flocculation kinetics

The study of kinetics is very important in the topic of particles flocculation. It is used as a means of investigating the colloidal and hydrodynamic interactions involved in particle-particle transfer. When two particles of comparable size collide with each other, the collision may lead to the formation of doublet and the process involved is termed coagulation-flocculation [14]. In this study, coagulation kinetics of spherical particle interaction is studied following Brownian-controlled diffusion mechanism (Peri-kinetics coagulation). The equations in Smoluchowski's model have formed the basis of almost all subsequent research in coagulation-flocculation modelling [9,15].

Coagulation of two particles to form a single new aggregate may not be described fully as a second-order rate process as recorded by some authors without obtaining the other of reaction [15,16]. Von Smoluchowski theory and Brownian kinetics equation of mono-disperse particles at early stage were used to determine the coagulation rate constant and order of coagulation-flocculation reaction using POLYMATH software. The equation describing the kinetics of aggregation is given in Eq. (2):

$$\frac{-dC}{dt} = -kc^{\alpha} \tag{2}$$

where C is the primary particles concentration at time t, α is the order of coagulation-flocculation reaction, K is the α^{th} order rate constant or absolute coagulation rate constant. Putting Eq. (2) in a linear form gives:

Table 1
Factor variations involved in the process

Operational parameters	pH	Coagulant dosages (mg/L)	Dye concentration (mg/L)	Settling time (min)	Temperature (K)
Effect of pH	2, 4, 6. 8, 10 and 12	800	20	420	303
Effect of coagulant dosage (CD)	2	200, 400, 600, 800, and 1000.	20	420	303
Effect of dye concentration (DC)	2	800	20, 40, 60, 80, and 100.	420	303
Effect of settling time (ST)	2	800	20	60, 120, 180, 240, 300, 360, 420, and 480.	303
Effect of temperature	2	800	20	420	303, 313, 323, 333, 343, and 353.

$$\ln\left(\frac{-dc}{dt}\right) = \ln k + \alpha \ln C \tag{3}$$

Hence, a plot of ($\frac{-dC}{dt}$) against (*ln C*) yields a straight line, from which *K* (rate constant) and α (order of reaction), can be determined from the intercept and slope, respectively.

The rate constant (first derived by Smoluchowski) has remarkable features that for mono-disperse particles it is independent of particle size and for the total formation. The rate constant could be calculated from Brownian hydrodynamics [17] as:

$$k = \frac{8K_B T}{3\mu} \tag{4}$$

where k_B is the Boltzmann's constant (*J/ K*), *T* is absolute temperature (K) and *μ* is viscosity of the medium.

The equation describing the timed-based evolution of the cluster of kind *K* is as follows:

$$\frac{dC_k}{dt} = \frac{1}{2}\sum\nolimits_{i=1}^{k-1} k_{ij} C_i C_j - C_k \sum\nolimits_{i=1}^{\infty} k i_k C_i \tag{5}$$

where $\frac{-dC_k}{dt}$ is the rate of change of concentration of particle size *k*, k_{ij} is the coagulation constant which depends on details of the collision process between i-mers and j-mers = *(k–i)* mer. This kernel embodies the dependence on *i* and *j* of the meeting of i-mer and j-mer, including the mutual diffusion coefficient (D_{ij}) and collision radius of the sphere R_{ij}. By this means, the coagulation constant, $k_{ij} = k_1$ assuming a constant kernel, is:

$$k_1 = 8\pi RD \tag{6}$$

where K_1 is the Von Smoluchowski rate constant for rapid coagulation, *R* is the particles radius and *D* is the Brownian diffusion coefficient of the particles.

Von Smoluchowski rate constant for rapid coagulation is related to Stokes-Einstein (SE) diffusion coefficient for translational sphere diffusion [18], with the following expression:

$$k_1 = \frac{4}{3}\frac{K_B T}{\mu} \tag{7}$$

Eqs. (4) and (7) show that second-order rate constant and Von Smoluchowski constant with:

$$k = 2k_1 \tag{8}$$

Particle collisions lead to flocculation and hence a reduction in the total number of particles and an increase in the particle average size. The rate of flocs growth was determined by the frequency of these collisions. Based on the work of Von Smoluchowski [9], it is shown that the frequency f_{ij} of binary collision between particles of type *i* and *j* is given as:

$$f_{ij} = \beta\left(v_i, v_j\right) C_i C_j \tag{9}$$

where C_i and C_j are the respective number of concentrations of two particle types. β (v_i, v_j) is the collision frequency factor. The rate of particles of size forming per unit volume by collision of particles of size *i* and *j* is given by:

$$\frac{1}{2}\sum\nolimits_{i+j=k} f_{ij} \tag{10}$$

The factor *1/2* in Eq. (10) is present because each collision is counted twice in the summation. Eq. (10) is due to the generation of the k^{th} species. In turn, particle *k* collides with other particles leading to particle volumes larger than v_k. The disappearance term is given by:

$$\sum\nolimits_{i=1}^{\infty} f_{1k} \tag{11}$$

The total balance equation for k_{th} species is given by:

$$\frac{dC_k}{dt} = \frac{1}{2}\sum\nolimits_{i=1;i+j=k}^{i=k-1} f_{ij} - \sum\nolimits_{i=1}^{\infty} f_{1k} \; for\, k = 1,2,3,.......\infty \tag{12}$$

Using Eq. (9), the above equation becomes:

$$\frac{dC_k}{dt} = \frac{1}{2}\sum\nolimits_{i=1;i+j=k}^{i=k-1} \beta_{ij} \mathrm{C_i C_j} - C_k \sum\nolimits_{i=1}^{\infty} \beta_{ik} C_i \tag{13}$$

where $\beta ij = \beta\left(vi, vj\right)$

Inclusion of an efficiency factor, Eq. (9) is replaced by:

$$f_{ij} = E_{ij} \beta C_i C_j \tag{14}$$

where E_{ij} is the efficiency factor for collision between *i* and *j* particles or flocs, f_{ij} is the rate of collisions between particles of size *i* and *j*. Taking note of the collision efficiency, the collision frequency function for Brownian motion (Peri-kinetic aggregation), is given as [9,15]:

$$\beta\left(v_i = v_j\right)\frac{8K_B T}{3\mu} = k \tag{15}$$

and

$$\beta\left(v_i = v_j\right)\frac{E 8K_B T}{3\mu} = k \tag{16}$$

K is a constant independent on particle size. Relating Eq. (4), (15) and (16), yields another relationship between collision frequency factor and Von Smoluchowski rate constant:

$$\beta = 2k_1 \tag{17}$$

also, $\beta = 2Ek_1$ (18)

and $E = \frac{\beta}{2K_1}$ (19)

The population balance Eq. (13) when compared with Eq. (16) becomes:

$$\frac{dC_k}{dt} = \frac{\mathrm{k}}{2}\sum\nolimits_{i=1;i+j=k}^{i=k-1} \mathrm{C_i C_j} - kC_k \sum\nolimits_{i=1}^{\infty} \mathrm{C_i} \tag{20}$$

Thus, the total concentration of particles per unit volume in a closed system at time, *t* is:

$$C_{tot}(t) = \sum\nolimits_{i=1}^{\infty} \mathrm{C_i} \tag{21}$$

Summing, overall particles $K = 1,2,3,.......,\infty$, obtains:

$$\frac{dC_{tot}}{dt} = \frac{K}{2}\sum_{k=1}^{\infty}\sum_{i=1;i+j=k}^{i=k-1} C_iC_j - KC_{tot}^2 \tag{22}$$

The first term on the right side of the above equation is given by $C_{tot} = C_o$, leading to:

$$\frac{dC_{tot}}{dt} = \frac{-\mathrm{k}}{2}C_{tot}^2 \tag{23}$$

The above Eq. (23) for Brownian coagulation is analogous to second-order reaction kinetics. The condition is given by $C_{tot} = C_o$ at $t = o$. Integrating Eq. (23) leads to

$$C_{tot}(t) = \frac{C_0}{1 + KC_0\frac{t}{2}} \tag{24}$$

Eq. (24) shows the decay in the total number of particles with time. Making use of Eq. (24) shows that:

$$C_k(t) = \frac{C_0\left(\frac{t}{T_{ag}}\right)^{K-1}}{\left(1 + \frac{t}{T_{ag}}\right)^{K+1}} \tag{25}$$

where

$$T_{ag} = \frac{2}{KC_0} = \frac{3\mu}{4C_0K_BT} \tag{26}$$

The characteristic time, T_{ag} is known as the coagulation-flocculation time and it is the time for the concentration to halve itself [19]. Flocculation in a later stage of the process involves the formation of triplet, quadruplet, quintuplet, etc., Number of k-mers, can be solved by means of Eq. (25). Therefore, For singlet formation:

$$C_1 = \frac{C_0}{\left(1 + \frac{t}{T_{ag}}\right)^2} \tag{27}$$

For doublet formation:

$$C_2 = \frac{C_0\left(\frac{t}{T_{ag}}\right)}{\left(1 + \frac{t}{T_{ag}}\right)^3} \tag{28}$$

For triplet formation:

$$C_3 = \frac{C_0\left(\frac{t}{T_{ag}}\right)^2}{\left(1 + \frac{t}{T_{ag}}\right)^4} \tag{29}$$

For quadruplet formation:

$$\frac{\left(\frac{\quad}{_{ag}}\right)}{\left(\quad\frac{\quad}{_{ag}}\right)} \tag{30}$$

2.6. Equation governing the mathematical modelling

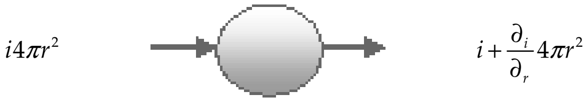
In this study, model equation investigated was used to describe the time-dependent behaviour of the particle transfer towards the adsorbing particles triggered by coagulation mechanisms [10]. The following assumptions were considered: model was governed and derived from Fick's law, that angular symmetry exist for the particles, homogeneous system was assumed, single-dimensional particle transfer occurs, the process is isothermal, external resistance to particle transport is neglected.

The coefficient of diffusion, D, is an important transport property of a colloidal particle and it represents the role of Brownian motion on particle movement. Diffusion coefficient is generally associated with Fick's law [20] as:

$$I = -D\frac{\partial C_i}{\partial_r} \tag{31}$$

where I is the particle diffusive flux, C_i is particle concentration and $(\partial C_i)/\partial_r$ is the particle concentration gradient. Diffusion is associated with particle transport from a high concentration region to a low concentration region due to Brownian motion. Fig. 2 demonstrates a spherical particle transfer considering a microscopic system.

The basic differential equation for mass transfer in a particle is obtained by taking a material balance (continuity equation) over a spherical shell as derived below:



Time rate of change of reference spherical particle = mass influx into the reference spherical particle – mass efflux from the references spherical particle (32)

Eq. (32) in mathematical terms, becomes

$$\frac{\partial(C_i)4\pi r^2}{\partial t} = i4\pi r^2 - \left(i + \frac{\partial_i}{\partial_r}\right)4\pi r^2 \tag{33}$$

Simplifying Eq. (33) gives

$$\frac{r^2\partial C_i}{\partial t} = -r^2\frac{\partial_i}{\partial_r} \tag{34}$$

Combining Eq. (34) with Fick's law of Eq. (31) and obtain

$$\frac{\partial C_i}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial_r}\left(r^2\frac{\partial C_i}{\partial_r}\right) \tag{35}$$

where C_i is the number of concentration of the spherical particle i and r is the radial coordinate of the sphere. Eq.

(35) becomes a partial differential equation that describes the rate of mass transfer of particle during the coagulation-flocculation process studied in this research. Eq. (35) is similar to mass transfer to a sphere in a homogeneous fluid by Coulson and Richardson [20]. Substituting $C_j r^2$ for C, Eq. (35) becomes

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial_r}D\frac{\partial C}{\partial_r} \tag{36}$$

Given the initial condition

$$C_i\left(t=0,r\right)C_{io} \tag{37}$$

The boundary conditions are

$$C_i\left(r=0,t\right)C_{io} \tag{38}$$

$$C_i\left(r=a,t\right)C_{eo} \tag{39}$$

where C_{eo} is the concentration of spherical particles in the system and is in equilibrium with the surface concentrations at both boundaries, and C_{io} is the initial particle concentration.

Proceeding to dimensionless and normalised dependent variables and boundary conditions. Then, using the following dimensionless parameters;

$$\text{Dimensionless position variable, } \eta=\frac{r}{R_o} \tag{40}$$

$$\text{Dimensionless time variable, } \tau=\frac{D_1 t}{R_o^2} \tag{41}$$

$$\text{Dimensionless concentration, } C=\frac{C_t-C_e}{C_0-C_e} \tag{42}$$

Changes in the initial and boundary conditions due to dimensionless function, gives

$$C\left(\tau=0,\eta\right)=1 \tag{43}$$

$$C\left(\tau,0\right)=0 \tag{44}$$

$$C\left(\tau,1\right)=0 \tag{45}$$

Substituting dimensionless variables into Eq. (36) gives:

$$\frac{\partial C}{\partial \tau}=\frac{\partial^2 C}{\partial \eta^2} \tag{46}$$

Eq. (46) is a dimensionless equation predicting rate of particle mass transfer at different operating process conditions. Similar result was gotten by [10].

The partial differential Eq. (46) was solved using separating of variables technique, which, entails seeking a solution in which the time variable (τ) is separated from space variable (η) [21,22]. The partial differential Eq. (46) is reduced to ordinary differential equation. Applying the necessary boundary conditions and substituting all dimensionless variables gives:

$$\frac{C_t-C_e}{C_0-C_e}=2\sum\nolimits_{n=0}^{\infty}\frac{1-\cos n\pi}{n\pi}\left(\mathrm{sinn}\pi\frac{\mathrm{r}}{\mathrm{R}_0}\right)\left(e^{-(n\pi)^2\frac{K_1 t}{16\pi r R_0^2}}\right) \tag{47}$$

Thus, expressing Eq. (47) as C_t, in order to determine the concentration of organic particles in the system at any process time *t*,

$$C_t=C_e+2\left(C_0-C_e\right)\sum_{n=0}^{\infty}\frac{1-\cos n\pi}{n\pi}\left(\mathrm{sinn}\pi\frac{\mathrm{r}}{\mathrm{R}_0}\right)\left(e^{-(n\pi)^2\frac{K_1 t}{16\pi r R_0^2}}\right) \tag{48}$$

Therefore, Eq. (48) is a mathematical model equation used in predicting the colour particles transfer in dye containing wastewater at any process time.

where, C_t = concentration of particles during process at time, t C_o = concentration of particles during process at time (t) = 0; C_e = concentration of particles at equilibrium time.

The resultant Eq. (48) from the numerical analysis was implemented and verified in MATLAB 9.3 by developing codes to obtain different concentrations of the contaminants during the coagulation-flocculation process at different operating time. MATLAB is a powerful code-based mathematical and engineering program [24,25]. The criterion used to check the accuracy of each model was the mean relative percentage deviation modulus (%*M)* which explains the mean divergence of the predicted data from measured data [26]. It is calculated by the expression in Eq. (49) below:

$$\%M=\left[\sum\nolimits_{n=1}^{n}\frac{\left|M_{\exp}-M_{pre}\right|}{M_{\exp}}\right]\times\frac{100}{N} \tag{49}$$

where M_{exp} = experimental value; M_{pre} = predicted value

Values of M% less than 5 show an extremely good fit; M% value between 5 and 10 represents a reasonably good fit, and (% *M)* value greater than 10 shows poor fit [27]. Furthermore, the relationship between the experimental data and predicted data was subjected to statistical tools such as: coefficient of determination (R^2), Chi-square (χ^2), F-test, and T-test using Microsoft Excel spread sheet.

2.7. Polymer coag-adsorption studies

Due to the polymer nature of the coagulant, adsorption mechanism plays an important role in the colour removal process. Determination of adsorption capacity, adsorption equilibrium, and adsorption kinetics studies were needed to discover the adsorption nature of the organic polymer used. The parameter extensively used in studying the capacity of adsorbent in the adsorption processes is the adsorption capacity (q). In this study, the contaminant removal by coagulation-flocculation occurs through various mechanisms. The first mechanism charge neutralization, there is destabilization of colloids which might be governed by chemical interactions between polymer molecules (cationic, positively charged) and the contaminant molecules (anionic, negatively charged). Then, once the polymer-contaminant complex is formed, flocs begin to grow by adsorption mechanisms. Previous study has found the adsorption capacity

(q) a suitable evaluation parameter [4]. Polymer adsorption capacity (q) at any contaminant concentration is determined according to Eq. (50):

$$q_t\left(\frac{mg}{g}\right)=\frac{\left(C_o-C_t\right)V}{M} \tag{50}$$

where C_o is the initial contaminant concentration (*mg/L*) C_t is the contaminant concentration at time t in the bulk solution (*mg/L*), V is the volume of solution (*L*), and M is the coagulants mass (*mg/L*)

2.8. Polymer coag-adsorption kinetics

To gain more insight on the rate of particle transfer, adsorption kinetics was studied. Adsorption kinetic provides knowledge into the controlling mechanism of adsorption processes which in turn governs mass transfer and the residence time [28]. The kinetic data was analysed using pseudo first-order, pseudo second-order and Elovich model.

Lagergren proposed pseudo first-order kinetic equation [29] in the form of:

$$\log\left(q_e-q_t\right)=\log q_e-\frac{\mathrm{K}_{\mathrm{F1}}}{2.303t} \tag{51}$$

where q_t is the amount of adsorbate adsorbed at time t (*mg/L*), q_e the adsorption capacity at equilibrium (*mg/L*), k_{F1} the pseudo first-order rate constant (*1/min*), and t is the time (*min*).

Pseudo second-order equation [30] predicts the behaviour over the whole range of adsorption with chemisorption being the rate controlling step and it is represented by:

$$\frac{t}{q_t}=\frac{1}{k_2q_e}+\frac{1}{q_e}t \tag{52}$$

where K_2 is the pseudo second-order rate constant *(gm/g min)* The initial adsorption rate *h (m/gmin)* at *t = 0* is defined as follows:

$$h=k_2q_e^2 \tag{53}$$

Elovich kinetic model equation, one of the most useful methods describing chemisorption processes [31], is defined as;

$$q_t=\frac{1}{\beta}\ln\left(\alpha\beta\right)+\frac{1}{\beta}\ln t \tag{54}$$

where α *(mg/gmin)* is the initial sorption rate and *β (mg/g)* is related to the extent of surface coverage and activation energy for chemisorption. The value of *(1/β)* is indicative of the available number of sites for adsorption while 1/β ln (αβ) is the adsorption quantity when $t = 0$.

The suitability of the kinetic model to describe the adsorption process was validated by the normalized standard deviation, *Δq (%)* given by:

$$\Delta q(\%)=100\sqrt{\frac{\sum\left[\frac{\left(q_{exp}-q_{cal}\right)}{q_{exp}}\right]^2}{d_f}} \tag{55}$$

where d_f is the degrees of freedom of the fitting equation. The number of degree of freedom as follows $N–n_p$, where N is the number of data points and n_p is the number of parameters. q_{exp}*(Mg/g)* and *(Mg/g)* are the experimental and calculated adsorption capacities, respectively.

3. Results and discussion

3.1. Characterization result

3.1.1. Proximate analysis

The proximate analysis of coagulant precursor was summarized in Table 2. The moisture content value shows water absorption ability of the coagulant which enhances particle flocculation. High crude protein contents recorded in the precursor indicates the presence of protein. This characteristic shows the main reason for using the precursor and it agrees with the literatures that the protein content of the precursor is cationic poly-peptides (long chains of amino acids held together by peptide bonds) [32,33]. Fibre content present established that the precursor is an organic polymer with repeating small molecules that could extend as tails and loops when dispersed in water [5]. The presence of protein, moisture and fibre in the precursor has led to the study of the coagulation and adsorption nature of the coagulant. These characteristics made adsorption a relevant mechanism in the coagulation-flocculation process.

3.1.2. FTIR (Fourier transformed infra-red) analysis

FTIR spectroscopy is very vital to ascertain the nature of the polymer coagulant as shown in Fig. 1. The figure shows that there is an absorption peak of 3656.92 1/cm which is

Table 2
Proximate compositions of the Moringa oleifera seed

S/No.	Parameters	Values
1.	Yield	32.68
2	Bulk density (g/mL)	0.425
3.	Moisture content (%)	5.02
4.	Ash content (%)	2.12
5.	Protein content (%)	39.34
6.	Fat content (%)	19.47
7.	Fibre content (%)	1.16
8.	Carbohydrate (%)	32.89

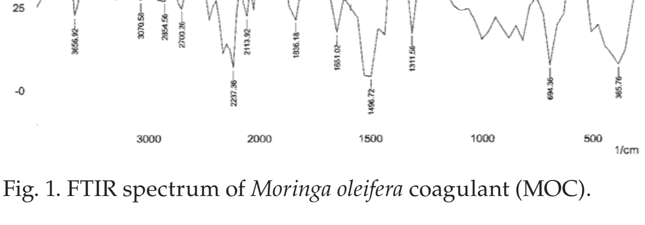


Fig. 1. FTIR spectrum of *Moringa oleifera* coagulant (MOC).

attributed to the stretching vibration of –OH groups and to the vibration of water absorbed, or complexes in the coagulant [34]. Free hydroxyl groups present in the spectral confirms the presence of carboxylic acids, alcohols and phenols on the coagulant. This band also corresponds to the O-H stretching vibrations of cellulose, pectin and lignin. The result from proximate analysis shown in Table 2 agrees with the –OH signalling of the presence of moisture (water), oil and carbohydrate (glycerides). The IR spectrum study revealed that the characteristics absorption peak for amines was evident in the range of 3656.92–3683.93 1/cm for aliphatic primary a mine (N-H stretch) and 2237.36 1/cm for primary a mine. The presence of N-H stretching signals in the peaks also detects the presence of amino compounds which confirms protein contents present in the coagulant as evident in Table 2. A major band present in the coagulants in the broad region of 1651.02–1496.72 1/cm usually indicates the presence of a C=O group (carbonyl compound). In addition, there was a strong adsorption peak at 1311.56 1/ cm and 694.36 1/cm for both, which is the characteristic frequency for C-H out of plane deformation groups. The C-H out-of plane bending is typically the most informative relative to the location and spatial geometry of the double bond [34]. The FTIR spectrum of *Moringa oleifera* and the proximate analysis presented in Table 2 suggest the presence of moisture, proteins and esters, which justify its use as source of coagulant in this present work.

3.1.3. Scanning electron microscopy (SEM) analysis

Fig. 2 shows the surface morphology of MOC in 600× magnifications. The SEM image reveals pores of different shapes and sizes. The pore sizes (micro-pores, macro-pores and meso-pores) are properties that are unique to organic polymers. Rough surfaces as observed show that the coagulant is coarse fibrous substance largely composed of cellulose and lignin which confirms its polymeric characteristics. Particles could be adsorbed or attached it selves on these polymer chains forming large settle able agglomerates through electrostatic interactions, inter-particle bridging or sweep flocculation mechanisms. The pores and rough surfaces observed on the coagulant morphology indicates that smaller colour particles could be adsorbed on the polymer surface thereby confirming adsorption as an important mechanism in coagulation-flocculation process. The morphology also possessed a compact-net structure which is more favourable to particle flocculation due to adsorption and bridge formation among flocs as compared to branched structure [35].

3.3. Effect of process variables on the colour removal efficiency using MOC.

pH plays an important role in the coagulation-flocculation process. An optimum pH must be established for an efficient operation. Flocs growth involves both interactions of coagulant hydroxide precipitate following hydrolyses reaction and particles contact. The highest removal efficiency of 92.10% was recorded at pH 2 as shown in Fig. 3, indicating influx of positively charged ions (H^+). Charge on the hydrolysis products of dye particles and precipitation of polymeric hydroxides are both controlled by pH variations [13]. As functional group of the acid dye is anionic, hydrolysis products of the organic polymers can neutralize the negative charges on dye molecules followed by flocculation. Charge neutralization and particle adsorption on to the polymer surfaces occurred mostly during this factor interaction. As pH value increases, natural organic compounds become more negatively charged (-ve) and polymer hydrolysis species become less positively charged, resulting in less adsorption tendency. At this point, charge reversal results in re-stabilization and flocs breaking which in turn reduces the removal efficiency.

Fig. 4 shows that the percentage removal of colour was enhanced by increasing the coagulant dosage (CD) up to 800 mgMOC/L. The high removal efficiencies of 92.20% for the 800 mgMOC/L confirms it as the right quantity of coagulants (+ve) which is required to destabilize the dye wastewater charge (-ve). Positive charge species of the bio-coagulant particles are responsible for removal of particles by charge neutralization and adsorption mechanisms. The use of cationic bio-polymers for coagulation-flocculation of negatively-charged colour particles is needed because strong adsorption affinity and neutralization of the particle charges could occur. With the increase of coagulant dosages, the removal efficiency steadily increased and no "re-stabilization zones" with negative dye removals were found even at the applied maximum dosage (800 mgMOC/L). The coagulant apparently served as condensation nuclei and the dye particles enmeshed as the precipitate were settled. The

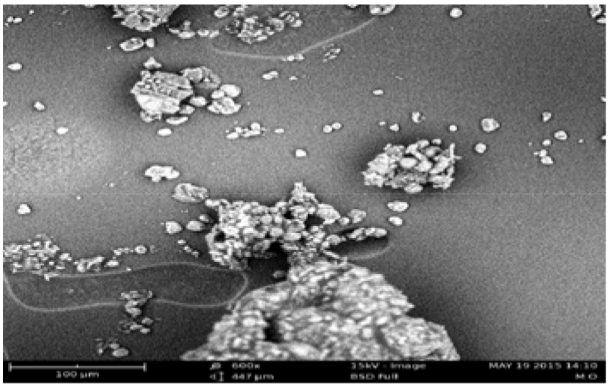


Fig. 2. SEM micrograph of MOC.

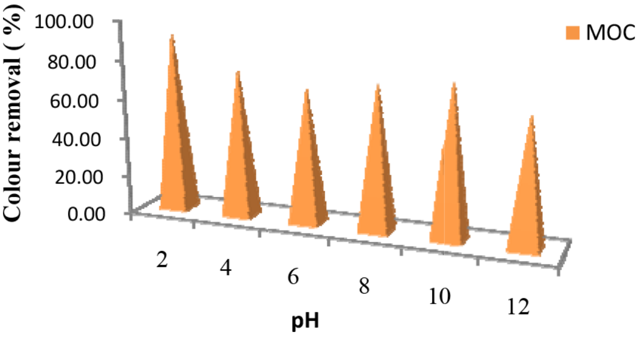


Fig. 3. Effect of pH on the colour removal (%) using polymer coagulants. CD = 800 mg/L, DC = 20 mg/L, ST = 420 min, Temperature = 303 K.

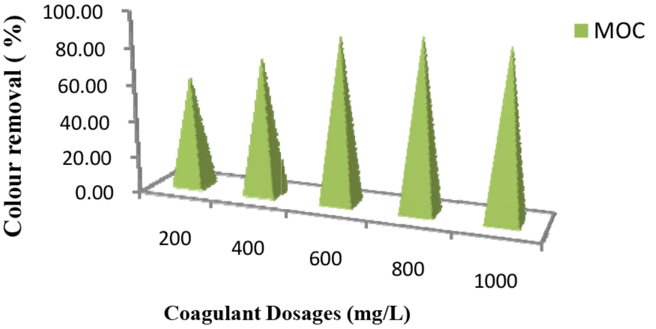


Fig. 4. Effect of coagulant dosage on the colour removal (%) using MOC. pH = 2, DC = 20 mg/L, ST = 420 min, Temperature = 303 K.

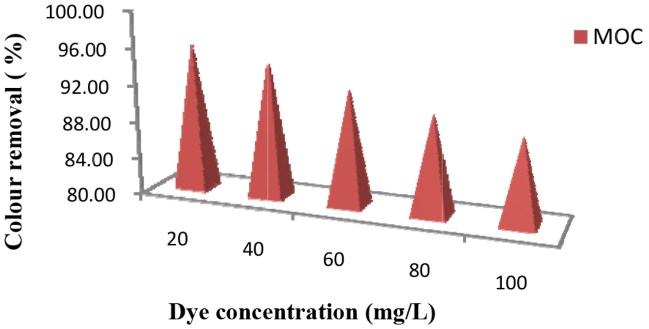


Fig. 5. Effect of dye concentration on the colour removal (%) using MOC. pH = 2, CD = 800 mg/L, ST = 420 min, Temperature = 303 K.

high dosages of the organic polymer could also give rise to chain bridging and adsorption mechanism [1]. Therefore, at high dosages of MOC, more polymer units are suspended in the solution causing bridging-adsorption to be imminent mechanism in the process. Furthermore, sudden decrease in the removal efficiency at 1000 mgMOC/L observed was as a result of re-stabilization which might have occurred due to polymer overdosing. Overdosing deteriorates supernatant quality which makes particles to lose their coagulation affinity.

Dye concentration determines the extent of particle transfer rate in the process. The dye concentration in the solution provides a driving force for all the mass transfer between the aqueous particles and solid polymer surfaces. As observed in Fig. 5, the colour removal efficiency was enhanced at dye concentration of 20 mg/L. Excessive dye loading rate is not required for effective particle transfer [13].

The removal efficiency decreases with increasing solution temperature as shown in Fig. 6. The optimum solution temperature was observed at 303K. This could be as a result of high solution temperature breaking polymer chains, thus, reducing the surface adsorption sites of the coagulants. Also, high temperature reduces the flocs growth which in turn retards coagulation-flocculation process.

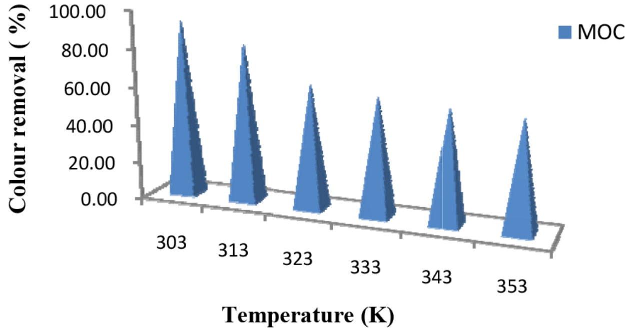


Fig. 6. Effect of temperature on the colour removal (%) using MOC. pH = 2, CD = 800 mg/L, DC = 20 mg/L, ST = 420 min, Temperature = 303 K.

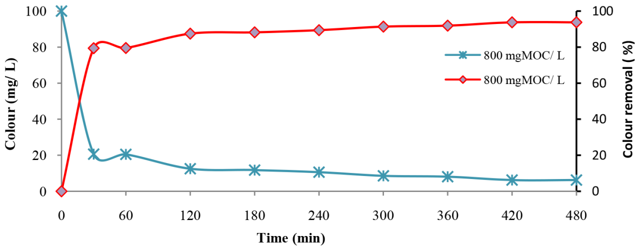


Fig. 7. Effect of settling time on colour removal removal (%) using MOC. pH = 2, CD = 800 mgMOC/L, DC = 20 mg/L, Temperature = 303 K.

The coagulation-flocculation performance generally was evaluated through time-dependent decrease in particle concentration which coincides with the growth of aggregates. Fig. 7 shows that the highest reduction in concentration is observed at settling time (ST) of 420 min with removal efficiency of 93.8%. The sudden reduction observed within 30 min indicates a rapid coagulation process revealing the possible coagulation time (T_{ag}). This rapid decrease in concentration observed between 0 and 30 min implies that as the reaction proceeds, the amount of particle available for coagulating activity decreases. It could be as a result of either charge neutralization or combination of charge neutralization-sweep flocculation mechanism [35]. The slow decrease in concentration with time after 30 min indicates the low availability of contaminants in the coagulation process. The process was fast at onset resulting to over 80% removal within 120 min and slowed down afterwards. The longer flocculation time could be due to the presence of adsorption mechanism which requires longer process time to be completed. The reduction in concentration did not vary significantly after 300 min showing that equilibrium sets up after that time. Aggregate destabilization could set in after this time due to saturation of the active adsorption sites which does not allow further adsorption and consequently, prolonging settling time.

3.4. Brownian coagulation kinetics result

3.4.1. Coagulation-flocculation rate and reaction order

Coagulation parameters obtained from the linear regression were presented in Table 3. Coagulation rate constant, K and order of reaction, α were obtained from the intercept and slope, respectively from the equation describing the kinetics of aggregation [Eq. (3)]. The value of coagulation

Table 3
Coagulation kinetics parameters

Coagulation parameters	800 mgMOC/L
K (L/mg min)	2.28E-04
α	2
R^2	0.948
Rate equation (–r)	2.28×10^{-4} C^2
T_{ag} (min)	87.72
K_1 (L/(min))	1.14E-04
β (L/(mgmin))	0.000228
E (m g^{-1})	1.00

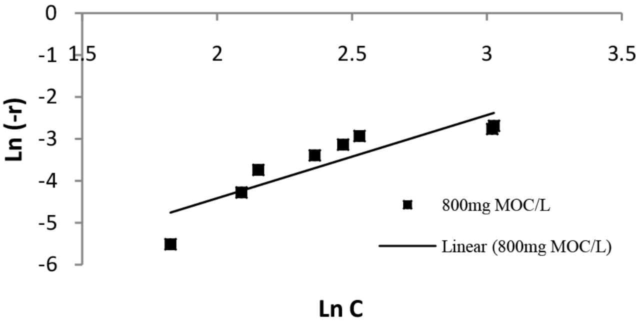


Fig. 8. Regression plot for colour removal at pH 2 and optimum coagulant dosages.

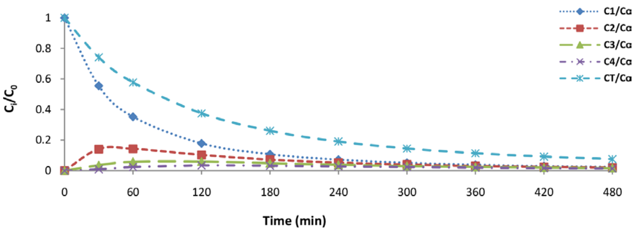


Fig. 9. Time dependency on particle removal in terms of total particles, singlets, doublets, triplets and quadruplets.

rate constant is the proportionality constant that relates the reaction rate to the concentration of the reacting substances. This signifies that each minute, 0.000228 mg/L of colour particles was adsorbed or attached to the polymer chain forming larger flocs. The value of order of reaction obtained shows that the reaction agrees with the conventional theory of coagulation-flocculation being a second-order process [15,16]. This confirms the accuracy of the regression method adopted. The correlation coefficient (R^2) value shows high agreement and the significance of the kinetic data studied. The value of T_{ag} is inversely related to initial concentration of colour particles. This implies that the more the particle concentration, the lesser coagulation time is required for their removal. The value of the collision efficiency (E) obtained explains the attainability assumption that particles collision between the contaminant and the coagulant for aggregate formation is 100% efficient. This means that almost all particles will stick together after the bimolecular collision and there is an even particle distribution or coagulation-complex distribution during the process [19]. The regression plot for MOC is shown in Fig. 8.

3.5. Particle variations behaviour as a function of time.

The variations in C_T, C_1, C_2, C_3 and C_4 with time calculated from Eqs. (25), (27)–(30) for initially mono-dispersed particles are shown in Fig. 9. Total colour concentration, C_t and concentration of singlet (C_i) both decreases monotonically with increasing time. From the plots, the concentrations of $C_2(t)$, $C_3(t)$ and $C_4(t)$ pass through a maximum. This is because they are not present at t = 0 and $C_0 = 0$ [9]. The number of singlet can be seen to decrease more rapidly than the total number of particles because of increasing number of particle concentration on aggregate formation with time. Thus, the total number of particles decreases according to a bi-molecular reaction. From the plots, we also observed that the lower the value of K, the higher the coagulation time T_{ag} with respect to its C_o. At low value of K, the rate process is very slow giving rise to more time for the coagulation-flocculation process. The rapid coagulation time as depicts in the plot is in agreement with the computed time obtained.

3.6. Adsorption kinetics results

Adsorption kinetic models were adopted to study the kinetic make-up of particle transfer as shown in Figs. 10–12. The kinetic parameters obtained were summarized in Table 4. The experimental data shows a good agreement with the pseudo second-order kinetic data, with a good normalized standard deviation, Δq (%) value of 0.96%. Fig. 11 shows a clear linear plot of a second-order process. The agreement of the kinetic data to pseudo-second order model with high coefficient of determination of R^2 0.999 further validates coagulation-flocculation (adsorption mechanism) process as a second-order process. Elovich model slight agreement gave a further insight to the adsorption-chemisorption process implying specific adsorption without site competition which is also common in organic ions. This also leads to the importance of Langmuir model in the adsorption process, suggesting that the overall rate of adsorption process was controlled more by chemisorption which involved valence forces through electrons sharing between the polymer-coagulant and contaminants.

3.5. Prediction of spherical particles transfer rate

Verification of particle transfer rate was based on the colour-concentration measurement. The experimental and predicted particles transfer rates during the coagulation process is shown in Fig. 12. The predicted results showed that concentration reduction was rapid at the beginning of the process resulting to rapid rate of mass transfer. A close relationship between the experimental and predicted concentration reduction was observed. The equilibrium point for the predicted was closer to that of the experimental.

The comparative statistical analysis between experimental data and predicted data was done using mean relative deviation modulus (M%), correlation coefficient (R^2), chi-square (χ^2), F-test and T-test as shown in Table 5. The value of M% less than 10% indicates good prediction of experimental data and the lower the percentage, the better the model prediction. Correlation coefficient result gave high correlation value of 0.986, indicating positive correlation. Chi-square value more than 0.05 are more significant than those less than 0.05. The F-test and T-test values are found to be significant at 95% confidence level. The trend of predicted particle reduction during the coagulation-flocculation process is also similar to the earlier works reported by Jimoda et al. [10] on modelling of mass transfer rate during bio coagulation-flocculation of coal-rich wastewater and also Bina et al. [37] on the effectiveness of *Moringa oleifera* coagulant protein as natural coagulant aid in the removal of turbidity and bacteria from turbid water.

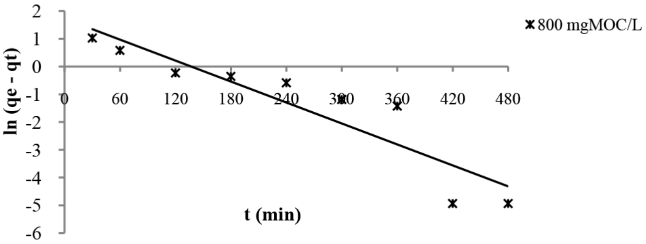


Fig. 10. Plot of pseudo first -order kinetics at optimum coagulant dosage.

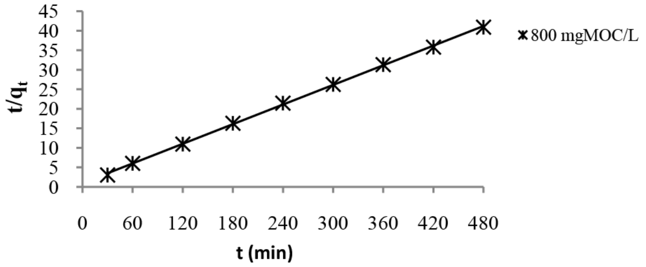


Fig. 11. Plot of pseudo second-order kinetics at optimum coagulant dosage.

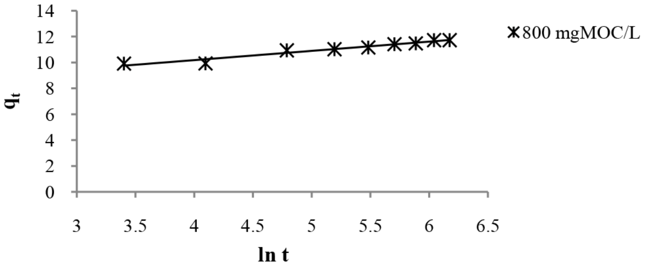


Fig. 12. Plot of Elovich kinetic model at optimum coagulant dosages.

Table 4
Adsorption kinetics parameters

	Pseudo first-order kinetics					Pseudo second-order kinetics					Elovich kinetics		
Coagulants dosages (mg)	q_e, exp (mg/g)	q_e, cal (mg/g)	K_{F1} (1/min)	R^2	Δq (%)	q_e, cal (mg/g)	K_2 (g/mg min)	R^2	h (mg/g min)	Δq (%)	a	b	R^2
800 mgMOC/L	11.73	4.78	0.012	0.824	20.95	12.05	0.0853	0.999	12.39	0.96	21368.2	1.404	0.953

4. Conclusion

The present study showed that the organic polymer coagulant used was effective for clarifying colour from AR 44 dye wastewater. The efficacy of MOC was due to its coagulation and adsorption characteristics. Proximate analysis showed that MOC has the features of a coagulant. FTIR analysis indicated that some chemical bonds such as -OH, N-H, C=H present aids the coagulation-flocculation process. SEM image revealed rough surfaces, different pores sizes, and compact-net structure. In general, the characterization results showed the ability of the coagulant; to destabilize contaminant particles due to its cationic nature, to enhance flocs formation due to its polymer characteristics, and to adsorb particles on its surfaces due to different pores and rough surfaces it possesses. Operational parameters studied (pH, coagulant dosage, dye concentration, settling time, and temperature) extremely influenced the colour removal process. Coagulation-flocculation study showed a time-dependent process and was incomplete without an adequate knowledge of the kinetics study. The values of *K* and α obtained from the kinetics study were in agreement with the conventional theory of coagulation being a sec-

Table 5
Cross validation testing of the modelling

Coagulants	MOC
M%	0.954
R^2	0.986
$\chi 2$	2.062
F-test	0.908
T-test	0.250

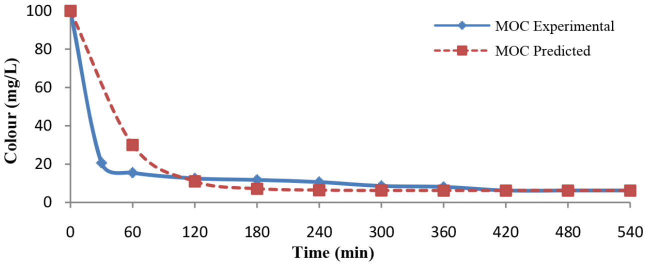


Fig. 13. Particle transfer rate during coagulation-flocculation process using MOC.

ond-order process. Coagulation-adsorption kinetics result showed a high agreement with the pseudo second-order kinetics with a positive R^2. Adsorption process occurred more as a second-order rate process, showing that the rate depends on the square of the particle concentration. In addition, the overall coagulation and adsorption process were second-order process and also controlled by chemisorption mechanism. Modelling study showed a close agreement between the experimental and predicted data. It demonstrated a satisfactory prediction with M% value of less than 10% with a positive R^2 value. The model studied could be used to monitor colour particles transfer at any given conditions and to predict the rate of particle transfer in a process without using experimental approach. It could be used also to extrapolate space and time not specified by the experimental result. This research has demonstrated the need for application of kinetics study in vast area of wastewater treatment and other mass-transfer processes.

References

[1] M.H. Zonoozi, M.R. AlaviMoghaddam, M. Arami, Removal of acid red 398 dye from aqueous solutions by coagulation/flocculation process, Environ. Eng. Manage. J., 7 (2008) 695–699.

[2] S.S. Moghaddam, M.R. AlaviMoghaddam, M. Arami, Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology, J. Hazard. Mater., 175 (2010) 651–657.

[3] C.Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, Process Biochem., 45 (2010) 1437–1444.

[4] J. Beltran-Heredia, J. Sanchez-Martin, M.A. Davila-Acedo, Optimization of the synthesis of a new coagulant from a tannin extract, J. Hazard. Mater., 186 (2011) 1704–1712.

[5] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Resour., 41 (2007) 2301–2324.

[6] I.A. Obiora-Okafo, O.D. Onukwuli, Optimization of coagulation-flocculation process for particle removal from dye using natural polymers: Response surface methodological approach, Der Pharma Chemica, 8 (2016) 1–12.

[7] J.H. Van Zanten, M. Elimelech, Determination of absolute coagulation rate constants by multi angle light scattering, J. Collid Interface Sci., 154 (1992) 1–15.

[8] H. Stechemesser, H. Sonntag, Coagulation and flocculation; coagulation kinetics, Taylor and Francis Group, LLC. Surfactant Science Series, 126, 2005, pp. 89–92.

[9] M. Von Smoluchowski, Versucheiner mathemtischen theorie der koagulations kinetic kolloider lousungen, Z. Phys. Chem., 92 (1917) 129–168.

[10] L.A. Jimoda, E.O. Oke, K.K. Salam, Modelling of mass transfer rate during bio coagulation-flocculation of coal-rich wastewater, J. Scient. Res. Report, 2 (2013) 376–390.

[11] A.O.A.C. "Official Methods of Analysis", 15th ed., Association of Official Analytical Chemists, Washington D.C, U.S.A., 1990.

[12] G.H. Jeffrey, J. Bassat, J. Mendham, R.C. Denney, Textbook of quantitative chemical analysis. 5th ed. Longman Scientific & Technical, 2001, pp. 649–720.

[13] I.A. Obiora-Okafo, O.D. Onukwuli, M. Omotioma, The relevance of adsorption mechanism on spectrometric colour removal: investigation of optimum operation parameters, Der Pharma Chemica., 10 (2018) 139–151.

[14] J.H. Masliyah, S. Bhattachayer, Electro kinetic and colloid transport phenomena, John Wiley and Sons, Inc., 2006, 433 pp.

[15] M.J. Schick, A.T. Hubbard, Coagulation and flocculation: experimental and modelling studies, Structure Formation in Dispersed Systems, Surfactant Science Series, Taylor & Francis Group, LLC, 126 (2005) 162–813.

[16] J.U. Ani, N.J.N. Nnaji, O.D. Onukwuli, C.O.B. Okoye, Nephelometric and functional parameters response of coagulation for the purification of industrial wastewater using Detarium micro carpum, J. Hazard. Mater., 243 (2012) 59–66.

[17] J.A. Mensah, Coagulation and flocculation; structure formation in dispersed systems, Taylor and Francis group, LLC. Surfactant Science Series, 126 (2005) 162.

[18] A.P. Philipse, Notes on brownian diffusion: Brownian encounters. Utrecht University, Debye Institute. Van't Hoff Laboratory, Physical and Colloid Chemistry, (2011) 7–63.

[19] R.F. Probstein, Physicochemical Hydrodynamics, An Introduction, 2nd ed., Wiley Inter-science, NewYork, (2003) 21–24.

[20] J.M. Coulson, J.F. Richardson, Fluid flow, Heat transfer and mass transfer, department of chemical and process engineering, University of New Castle-Upon Tyne. 6th ed., Elsevier Butter Worth Heinemann, (2008) 617–630.

[21] K.A. Stroud, J.B. Dexter, Advanced engineering mathematics: partial differential equations. 4th ed., Palgrave Macmillan, (2003) 415–434.

[22] R.H. Perry, D.W. Green, Perry's chemical engineers' Handbook. 8th ed., McGraw-Hill, New York, (2007) 5–45.

[23] J.W. Brown, R.V. Churchill, Fourier series and boundary value problems. 6th ed., New York, Mc Graw-Hill, (2001) 13–20.

[24] A.C. Carnell, MATLAB applications in chemical engineering, North Carolina State University, 2003.

[25] D. Mc Mahon, Matlab Demystified. Mc Graw Hill Companies, 2007.

[26] L. Greenspan, J. Research, National Bureau of Standard (US), Series A., 81 (1977) 89–96.

[27] M. Mundada, B.S. Hathan, S. Maske, Convective dehydration kinetics of osmotically pretreated promegranate arils, Poro. Syst. Eng., 107(4) (2010) 307–316.

[28] T. Zhang, Q. Li, Y. Liu, Y. Duan, W. Zhang, Equilibrium and kinetics studies of fluoride ions adsorption on FeO_2/Al_2O_3 composites pre-treated with non-thermal plasma, Chem. Eng. J., 168 (2011) 665–671.

[29] S.K. Lagergren, B.K. Svenska, About the theories of so-called adsorption of soluble substances, Kungsven Velenska-Psad. Hand., 24 (1898) 1–6.

[30] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[31] C. Aharoni, F.C. Tompkins, In: D.D. Eley, H. Pines and P.B. Weisz, Advance Catalysis, Related Subj., 21, Academic Press, New York, (1970) 98–102.

[32] M.S.S. Diz, A.O. Carvalho, V.M. Gomes, Purification and molecular mass determination of a lipid transfer protein exuded from *Vigna unguiculata* seeds, Braz. J. Plant Physiol., 15 (2003) 417–421.

[33] A. Kuku, U.J. Etti, I.S. Ibironke, Processing of fluted pumpkin seed, *Telfairia occidentalis* (Hook F) as it affects growth performance and nutrient metabolism in rats, Plant Physiol. Biochem., 39 (2014) 137–146.

[34] M.C. Bongiovani, F.P. Camacho, P.F. Coldebella, K.C. Valverde, L.N.R. Bergamasco, Removal of natural organic matter and trihalomethane minimization by coagulation/flocculation/filtration using a natural tannin, Desal. Water Treat., 57 (2015) 5406–5415.

[35] Y. Zheng, J. Park, Characterization and coagulation performance of a novel inorganic polymer coagulant: Poly-zinc-silicate-sulphate, Colloids Surfaces A: Physicochem. Eng. Aspects, 334 (2009) 147–154.

[36] Water Science technology (WST), About Coagulation and Flocculation. Information Bulletin, U.S.A, 2005.

[37] M. Yarahmadi, M. Hossieni, B. Bina, M.H. Mahmoudian, Application of moringa oleifera seed extract and polyaluminium chloride in water treatment, World Appl. Sci. J., 7(8) (2009) 962–967.